PHYSICOCHEMICAL DESCRIPTORS FOR ORGANIC COMPOUNDS OF ENVIRONMENTAL IMPORTANCE

A Thesis presented to the University of London in partial requirements for the degree of Doctor of Philosophy in the Faculty of Science

by

Amal J. M. Al-Hussaini

Chemistry Department
University College London

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Abstract

The work presented may be divided into three sections:

In the first section the solvation descriptors for the 209 polychlorobiphenyls (PCBs) have been determined, from data on gas-liquid chromatographic (GLC) experiments, together with more limited data from high-performance liquid chromatography (HPLC) experiments and on octanol-water partition coefficients (log Poct). The descriptors are the excess molar refraction (R_2), the dipolarity/polarizability (π^H_2), the overall hydrogen bond basicity ($\Sigma\beta^H_2$), the logarithm of gas- hexadecane partition coefficient (log L^{16}) and the McGowan volume (V_X). The calculated descriptors for the PCBs were linearly related to the number of chlorine atoms, with due regard to the position of the chlorine atoms. The effect for ortho-substitution was noted, so that the sets of the descriptors for the PCBs were divided into three groups. From the obtained equations, descriptors for any of the 209 PCBs could be calculated by fitting a given PCBs to a specific group. Using the calculated descriptors, values of log Poct were predicted for all the PCBs. Good agreement with experimentally obtained log Poct values was found where the latter were available. The aqueous solubility, as log Sw, was also calculated and compared with experimental values. As future work, more properties could be calculated using these descriptors, and possibly other descriptors related to solute shape.

In the second section, the same descriptors were determined for the 75 polchloronaphthalenes (PCNs) using literature data on various properties. Using these descriptors, it was possible to estimate for all 75 (PCNs) values of log Poct, log Sw, the gas-water partition coefficient, as log K^W, and the gas-dry octanol partition coefficient, as log K^{oct}.

In the third section literature data on various physicochemical properties of N-nitrosodialkylamines were similarly analyzed to yield descriptors for these compounds. From these descriptors, a number of important properties have been estimated, including the gas-water and water–octanol partition coefficients.

A List of Abbreviations

R_2-Excess molar refraction

π_2^H-Dipolarity/polarizability

$\Sigma\alpha_2^H$-Overall hydrogen bond acidity

$\Sigma\beta_2^H$-Overall hydrogen bond basicity

Vx-McGowan characteristic volume

Log L^{16}-Logarithm of gas-hexadecane partition coefficient

Log Poct- Logarithm of octanol-water partition coefficient

Log Sw-Logarithm of aqueous solubility

K^W-Gas-water partition coefficient

K^{oct}-Gas-dry octanol partition coefficient

P_{16}-Water-hexadecane partition coefficient

GLC-Gas-liquid chromatography

HPLC-High-performance liquid chromatography

IUPAC-International union of pure and applied chemistry

I-Retention indices

LFER-Linear free energy relationship

LSER-Linear solvation energy relationship

MR-Molar refraction

MLRA-Multiple linear regression analysis

PCBs-Polchlorobiphenyls

PCNs-Polychloronaphthalenes

QSAR-Quantitative structure-activity relationship

Sd-Standard deviation

SP-A set of solute properties

TSA-Total surface area

TEA-Thermal energy analyzer

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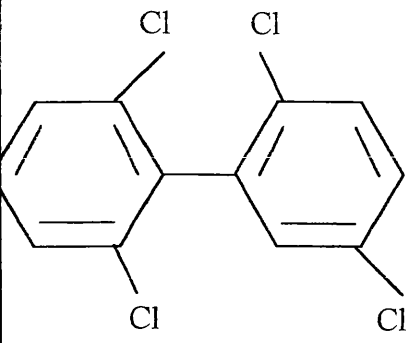
Introduction

There are currently about 70000 organic compounds in commercial production, with approximately 1000 being added every year. Roughly one third of all organic compounds produced end up in the environment due to misuse, carelessness and leaching, which in turn, can lead to environmental contamination. The presence of pollutants in human beings, animals and plants, is causing a great deal of global concern. Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), naphthalene, phenols and N-nitrosodialkylamines (NOCs) are among some of the most hazardous and toxic of organic pollutants to enter the environment.[1,2,3] Figure 1. shows the structures of some common pollutants.

PCBs 54



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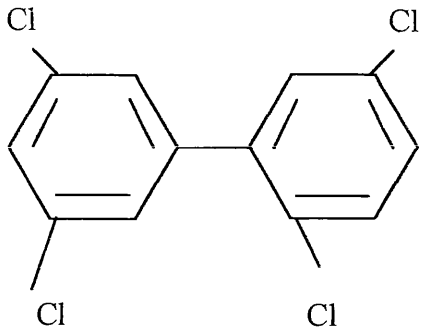

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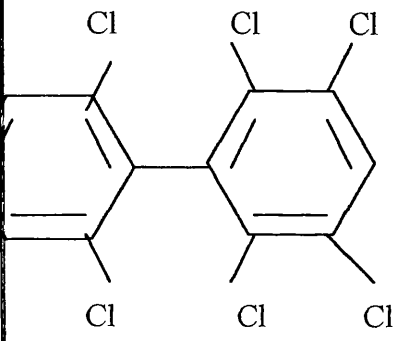

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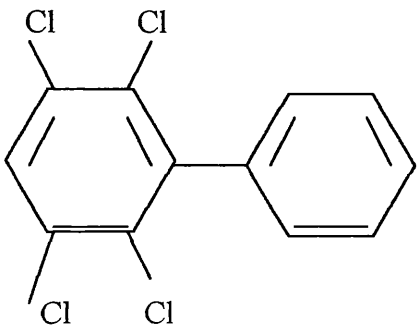
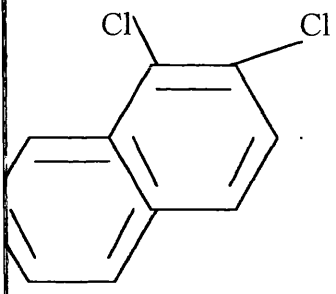


PCNs



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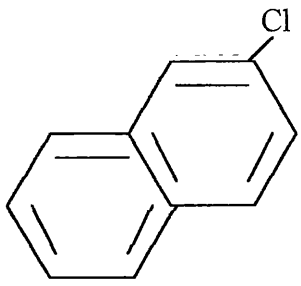
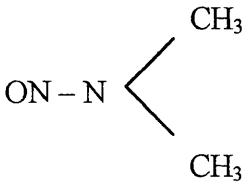
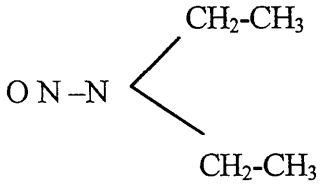




Dimethylnitrosoamine



Diethylnitrosoamine

Figure 1. The structure of some (PCBs), (PCNs) and (NOCs)

The polychlorinated biphenyls (PCBs) are a group of xenobiotic chemicals first manufactured commercially in about 1930 and which were widely used as transformer coolants, dielectric fluids, solvents, and flame retardants until restriction on their use were introduced in the early 1970s. [4] Some of the PCBs were thought to be mobile in the environment and some were in landfill or equipment dumps. There are 209 possible chlorinated biphenyls ranging from the monochlorobiphenyls to decachlorobiphenyl. It is only recently that all 209 congeners have been individually synthesized and characterized. [5]

The polychloronaphthalenes (PCNs), of which most are toxic,[6,7,8] have been manufactured in the USA and in several other countries since the 1920s for use as dielectric fluids and insulators. [6,7] In addition, they are formed during the combustion process in waste incineration. [9,10] The characteristic properties of PCBs and PCNs are hydrophobicity or low aqueous solubility, relatively low vapour pressure and resistance to chemical reaction.[2,11,12,13] These properties result in persistence in the environment and accumulation in soil, sediments, plankton, marine animals and all the way through the food chain to humans.

The third type of toxic compound to be studied is the N-nitrosodialkylamines which form a large class of genotoxic chemical carcinogens which occur in the human diet and in foods and consumer products such as meat,[14] beer,[15] cosmetics,[16] infant pacifiers,[17] and drug formulation.[18] They can also formed endogenously in the human body, especially tragastrically. Much interest is therefore directed toward quantitation of various N-nitroso organic compounds (NOC) that occur in different matrices. Their widespread prevalence can be attributed to the relative ease of formation and to the abundance of their amine precursors in the environment. The occurrence of N-nitroso

compounds in the above products is of great concern, owing to the carcinogenic properties that many of them exhibit.[19]

In order to evaluate the potential environmental behavior of the PCBs and other compounds, a knowledge of their physicochemical characteristics is essential. A key parameter in assessing the potential environmental behavior of such lipophilic chemicals is the octanol–water partition coefficient, Poct.[20] The determination of Poct is recommended in the OECD chemical hazard evaluation program[21] and it has been used with considerable success in estimating bioconcentration factors, soil and sediment uptake, toxicities and aqueous solubilities.[22-28] A number of techniques have been used to measure Poct values. The first was the shake-flask method. The second were the measurements and estimates based upon reverse-phase high–performance liquid chromatography (RP-HPLC) and thin–layer chromatography (RP-TLC). These have achieved moderate success for various groups of lipophilic compounds but require the use of empirical correction factors in the case of PCBs.[29-34] Also reliable and consistent Poct values for a number of PCB congeners have been obtained by the generator column technique.[35-36] Some success has been recently achieved in relating log Poct to calculated molar volumes.[38] The total surface area (TSA), which is a function of molar volume, has been found to have linear relationship with log Poct for compounds such as polyaromatic hydrocarbons, alkyl and halobenzenes.[37-40]

For a number of polychloronaphthalenes (PCNs) a few physicochemical properties have been reported, including normal phase HPLC capacity factors,[41] RP-HPLC capacity factors[42] and gas liquid chromatographic (GLC) retention data.[6,10,43,44,45] Water-octanol partition coefficients, as log Poct , have been determined for a number of PCNs [42,46] and values of log Poct can be estimated for all the 75 PNCs through the CLOG P program.[47]

For the detection of N-nitroso compounds the majority of the analytical methods had employed gas chromatography (GC) or liquid chromatography (LG) in conjunction with a thermal energy analyzer (TEA),[48] which relies on the pyrolytic breakdown of N-NO moieties to release the nitrosyl radical. The disadvantage of these techniques, however, is that a subsequent confirmation is needed to ensure that the method does not give rise to a false-positive response.[48] A combination of LC and mass spectrometry (LC-MS) offers significant analytical advantages over the aforementioned techniques. The two most common ionization techniques available to LC-MS, thermo spray (TSP) and electro spray ionization (ESI), yield primarily molecular weight information, that is little fragmentation is observed to confirm the structure of the analyze. Alternatively, on–line photolysis can be used to induce photolytic dissociation of varying types of compounds.[49-51] These techniques, however, are often unreliable and can suffer from a significant loss in sensitivity,[52] and also there are many practical difficulties in the experimental determination of these quantities for very lipophilic compounds. So resort is often had to some form of estimation. It is the aim of this work to obtain from the available physicochemical data, solvation descriptors for the PCBs, the PCNs and the NOCS that can then be used to estimate all kinds of other physicochemical data and which will be of considerable use in environmental analyses.

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Chapter 1 Introduction to Linear Free Energy Relationships

1.0 Introduction

Around 1900, Overton[1] put forward his lipoid theory of aqueous anesthesia and showed that the potency of compounds was related to their partition between water and lipid-like phases such as olive oil. Overton and Meyer[1-3] also showed for numerous series of compound that the narcotic concentration, C, of aqueous solutes toward the tadpole was related to their water- olive oil partition coefficient (P) with the latter defined as

$$P = (\text{concentration in organic phase}) / (\text{concentration in water}) \qquad (1.1)$$

In 1920, K. H. Meyer and Gottlieb-Billroth [4] expressed the Overton relationship in the quantitative form,

$$C \,.\, P = \text{constant} \qquad (1.2)$$

This work [4] represents the first quantitative structure-activity relationship ever reported. Some years later, Meyer and Hemmi[5] showed that water-oleyl alcohol partition coefficients could be used in equation (1.2), again with narcotic concentrations of aqueous solutes towards the tadpole. It is useful to examine equation (1.2) more closely. The chemical potential of a species can be expressed as:

$$\mu = \mu_o + R\,T \ln a \qquad (1.3)$$

Where μ_o is the chemical potential under a standard set of conditions and a is the activity of the solute in solution; a is taken as C.f, where C is the concentration and f is the activity coefficient. The latter approaches unity as C approaches zero. Thus through equation (1.3), the concentration can be seen to be a free energy (in this context a Gibbs free energy) quantity. A partition coefficient defined as in equation (1.1) is simply an equilibrium constant, related to the standard Gibbs free energy change through,

$$\Delta G^{o} = -R\,T \ln P^{o} \qquad (1.4)$$

Hence equation (1.2) is an example of a linear free energy relationship, or LFER, and the work of Meyer in the 1920s' and 1930s' represents some of the first examples of such a relationship. Equation (1.2) can be expressed in logarithmic form as equation (1.5) or more generally as equation (1.6) where SP can be a biological property such as 1/C for tadpole narcosis, or can be a physicochemical property, such as another partition coefficient.

$$\text{Log}\,(1/C) = \log P + \text{constant} \qquad (1.5)$$

$$\text{Log SP} = a.\,\log P + c \qquad (1.6)$$

Equation (1.6) was applied by Collander [6] to the correlation of different types of partition coefficients,

$$\text{Log } P_2 = a. \log P_1 + c \qquad (1.7)$$

He was very careful to point out that equation (1.7) applied only to partitions in similar solvent systems, otherwise equation (1.7) was restricted to homologous series.

Equation (1.6) has been applied to numerous series of biological activities in aqueous solution and is now referred to as the Overton-Meyer relationship, or sometimes the Overton rule. Also the first quantitative analysis of gaseous narcosis was carried out by K.H. Meyer [4] in the same paper in which aqueous narcosis was discussed. A similar relationship to equation (1.2) was found,

$$C . L = \text{constant} \qquad (1.8)$$

Here C, is the gaseous concentration of the narcotic, and L is the Ostwald solubility coefficient of the narcotic in some particular solvent,

$$L = (\text{concentration in solvent}) / (\text{concentration in gas phase}) \qquad (1.9)$$

This type of analysis is nowadays referred to as the Ferguson rule or relationship. It should be pointed out that the Overton rule and the Ferguson rule apply only to non-

reactive compounds. Another set of quantitative structure-activity relationships (QSARs) has been constructed using the Hansch[7] equation,

$$\text{Log RBR} = -a(\log P_{oct})^2 + b \log P_{oct} + cE + dS + e \qquad (1.10)$$

Here RBR is a relative biological response of a series of substrates, or solutes, in a given system. The descriptors are log P_{oct} where P_{oct} is the water /1-octanol partition coefficient, E is an electronic parameter such as Hammets' σ value, and S is a steric term. Even today equation (1.10) is still used to interpret and predict biological activities[8] especially for a series of structurally related compounds. There is however an insuperable difficulty in the application of equation (1.10) when the substrate series includes quite different structures, for example, aliphatic ketones, esters and alcohols, yet there are numerous very important areas in which substrates of all kinds of structure are involved. This problem can only be solved by the construction of other types of LFERs and QSARs.

1.1 The Solvation Process

To obtain other types of LFERs and QSARs, it seemed essential to start by devising new solute descriptors. Since processes such as partitions, above, involve the solvation of a compound in two phases, some model of the solvation process itself is needed. A simple solvation model was used by Abraham, Kamlet and Taft (AKT).[9,10] The solvation of a gaseous molecule was broken down into stages as follows.

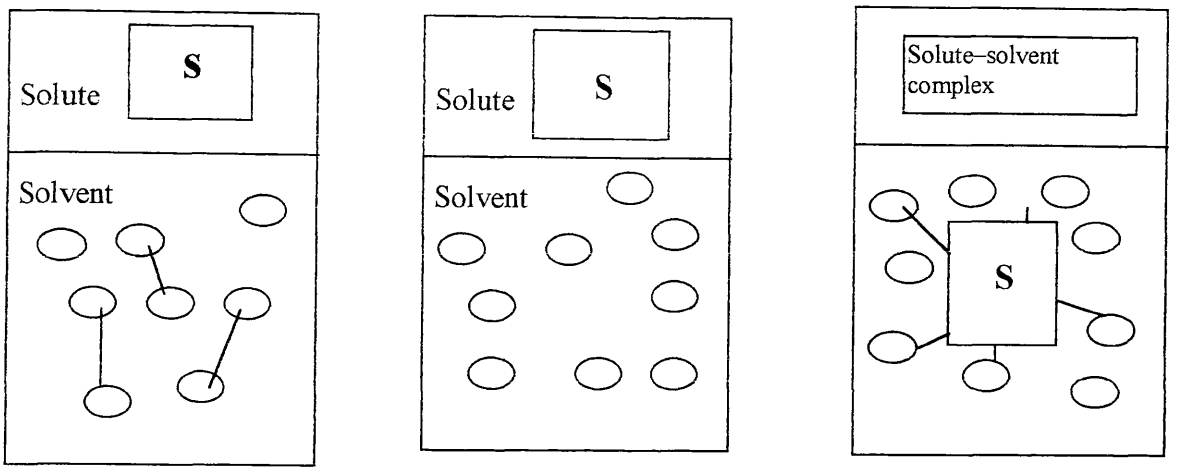


Figure 1.1 The cavity model of solvation

1- The creation of a cavity of a suitable size in the solvent, this involves the endoergic breaking of the solvent-solvent bonds.

2- The solvent molecules are reorganized into their equilibrium position round the solute.

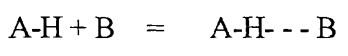
3- The solute is inserted into the cavity and various solute-solvent interactions are set up all of which are exoergic.

The creation of a cavity requires work, and is an endoergic process. If the solvent is constant, and cavities of various sizes are created, the Gibbs energy of cavity formation can be taken as proportional to the solute volume or to the solute surface area. Finally there will be a number of solute-solvent interaction terms, all of which will be energetically favorable, that is, exoergic. What are now required are solute parameters or descriptors that can be identified with these interaction terms, again for the case in which the solvent is constant and the solute is varied. One type of solute-solvent interaction

which is very important involves hydrogen-bonding of the type solute acid-solvent base, and solute base-solvent acid.

1.2 The solute 1:1 hydrogen-bond scales, α_2^H and β_2^H

The original solute hydrogen - bond acidity scale, α_2, and basicity scale, β_2, of AKT were not very rigorously defined,[11-12] and other such scales were therefore constructed. The 1:1 hydrogen bond acidity scale of Abraham[13] was formulated from log K where K is the equilibrium constant for 1:1 complexion of a series of monomeric acids against a given reference base in an inert solvent, tetrachloromethane. Both the acid and the base must be present at low concentration in order for both to be in solution as monomeric and unassociated forms.



A-H + B = A-H- - - B

A scale of hydrogen-bond acidity was set up by plotting a series of log K values (against a given reference base) vs log K values (against another reference base). The various plots could be generalized through equation 1.11, where log K_A^H is an 'average' hydrogen-bond acidity constant. Plots according to equation 1.11 yielded straight lines, with an intersection point at log K = -1.1 when K, is expressed on the molar concentration scale.

$$\text{Log K (series of acids against base B)} = L_B \,.\log K_A^H + D_B \qquad (1.11)$$

In a similar way, a scale of 1:1 hydrogen-bond basicity, β_2, was established by Abraham et al., [14] with equation 1.12 taking the place of equation 1.11,

$$\text{Log K (series of bases against acid A)} = L_A \,.\log K_B^H + D_A \qquad (1.12)$$

The 1:1 hydrogen-bond basicity scale was set up by plotting log K values of a series of bases (against a given reference acid) versus a series of bases (against another reference acid). These plots gave straight lines passing through the same magic point, log K = -1.1, and enabled the average hydrogen-bond basicity, log K_B^H for solutes in CCl_4 to be obtained.

The log K_A^H and log K_B^H scales were transformed into more useful scales through the simple equations,

$$\alpha_2^H = (\log K_A^H + 1.1)\,/4.636 \qquad (1.13)$$

$$\beta_2^H = (\log K_B^H + 1.1)\,/4.636 \qquad (1.14)$$

The factor 4.636 has no physical significance other than to serve as a convenient working range of β_2^H and α_2^H values.

1.3 The polarisabilty

The polarisability-correction parameter, δ_2, in the LFERs of AKT is only an empirical factor, limited to one of three values; 1.0 for aromatic compounds, 0.5 for halogenated aliphatic and 0.0 for all other compounds. A number of possible replacements for δ_2, were considered. The molar refraction (MR)[15] was a possibility because it is often used to measure polarisability; it can be defined in terms of the McGowan volume as;

$$MR_x = 10 \left[(n^2 - 1) / (n^2 + 2) \right] V_x \qquad (1.15)$$

Where n is the refractive index taken at 293 K with the sodium-D line, and V_x is the McGowan characteristic volume [16] in ($cm^3 mol^{-1}$) /100 . Because of the volume term in the molar refraction, equation (1.15), there is a strong connection between MR_x and V_x, so that it is not possible to incorporate MR_x into a linear equation together with V_x. The refractive index function itself is an indication of the polarisable electrons in a molecule that is either aromatic or a halogenated aliphatic compounds, and so some sort of molar refraction would be a useful parameter. Abraham et al. therefore defined an 'excess molar refraction, as molar refraction in excess of the molar refraction[17] of an alkane of the same characteristic volume as the solute in question,

$$R_2 = MR_x \text{ (observed)} - MR_x \text{ (for alkane of the same } V_x) \qquad (1.16)$$

By definition $R_2 = 0$, for all alkanes, and by calculation R_2 is also zero for branched chain alkanes and for the rare gases as well. Like MR_2, R_2 , is almost an additive quantity, and can reasonably easily be estimated for solid compounds.

1.4 Solute dipolarity / polarisability scale, π_2^H

In the AKT system, π^*_2 was taken to be identical to the Kamlet and Taft [18,19] solvatochromic parameter π^*_1, for non-associated liquids. As π^*_1, can only be experimentally obtained for compounds that are liquid at 298.15 K, values of π^*_2, had to be estimated for all associated compounds (including acids, alcohol, phenols and amides) as well as solids and gases. So, once again, it was necessary to set up a new scale instead of the old AKT scale of solute dipolarity-polarisability. Abraham et al. constructed the new dipolarity-polarisability parameter, π_2^H for use in LSER from the extensive sets of retention GLC data of McReynolds [20] and Patte et al.[21]

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Chapter 2 Calculation of Descriptors by the Method of Abraham

2.0 Introduction

Many studies have been carried out on relationships between chemical equilibrium and rate constants for chemical reactions. Studies show that if a series of changes in conditions or reactant structure affects the rate or equilibrium of the second reaction in exactly the way it affected the first, there exists a linear free - energy relationship (LFER) between the two set of data. These relationships are called linear free - energy because at constant temperature the rate of reaction is related to the free energy of activation and the equilibrium is related to the standard free energy change. If such relationships exist they can be very useful in explaining the mechanism, and in the prediction of reaction rates and chemical equilibria.[1]

As was noted in Chapter 1 the Hansch [2] equation is one of the best known examples of a LFER, and his work has formed a sound basis for many other studies to be carried out involving LFERs. When applied to solvation processes, LFERs are sometimes denoted as linear solvation energy relationships (LSERs).

2.1 The Abraham solvation equation

The Abraham solvation equation is based on a simple solvation model used by Abraham, Kamlet and Taft,[3-6] (see Figure 1.1). As was outlined in the previous chapter, both the cavity term and the solute-solvent interaction term will depend on the properties

of the solute and the solvent under consideration. Hence to describe these effects for the general case of a number of solutes in a number of solvents, it is necessary to construct an equation that includes the relevant properties of both the solutes and the solvents.

In the first case, a single solute undergoes dissolution into a series of solvents. In this case the solute properties remain constant, and only the varying properties of the solvents need to be considered. Abraham, Kamlet and Taft [3-6] suggested that the solvent property that could be related to the cavity effect was Hildebrands cohesive energy density δ_H.[2,7,8] The solvent properties that describe the interaction term were polarisability, π^*_1, the solvent hydrogen-bond acidity,a_1 and the solvent hydrogen-bond basicty, β_1, where subscript 1 denotes a solvent property. The various solvent properties or descriptors were combined into a solvatochromatic equation;

$$SP = SP_0 + d.\ \delta_1 + s.\ \pi_1 + a.\ \alpha_1 + b.\ \beta_1 + h.(\delta_H{}^2)_1 \qquad (2.1)$$

Where SP is some property of a given solute in a series of solvents, and SP_0 is a constant. The term d. δ_1 was introduced as a polarisability correction term.

In the second case, a series of solutes is investigated in a given solvent (or solvent system) so that the solvent properties are constant, and it is now the solute properties that vary. Abraham, Kamlet and Taft found that a similar equation to equation (2.1) could be used,

$$SP = SP_0 + d.\ \delta_2 + s.\pi^*_2 + a.\ \alpha_2 + b.\ \beta_2 + m.\ V_2 \qquad (2.2)$$

Now SP is a property of a series of solutes in a given solvent system and the descriptors are solute properties as follows; π^*_2 is the dipolarity/polarisability of the solute and α_2 and β_2 are the solute acidity and basicity; now subscript 2 denotes a solute property. The cavity term V_2 was taken as the intrinsic volume of Leahy, V_1.[9] The determination of the solute descriptors for equation (2.2) proved to be a problem for many solutes. It therefore seemed necessary to develop a method that would allow the determination of a dipolarity/polarisability scale,π_2^H, that would include all types of solute molecule. Downfalls also existed for the hydrogen-bond acidity and basicity scales set out by Abraham, Kamlet and Taft.[5,6] In an attempt to overcome some of these downfalls of the Abraham, Kamlet and Taft method, Abraham introduced a new solvation equation taking on a similar form to equation (2.2) and is given as equation (2.3). The $d.\delta_2$, term is replaced with $r.R_2$, where R_2, is the solute excess polarisability.[10] This provides a quantitative measure of the ability of a solute to interact with the solvent through n and π, electrons. Abraham et al. also improved on the other solute descriptors so that now the solute dipolarity/polarisability is given as π_2^H [11-13] and the solute effective hydrogen-bonding acidity[14-16] and basicity[15-17] as $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$. Finally, V_2 is replaced by the McGowan characteristic volume, Vx;[18-19] the reasons for doing so will be given later in this chapter. The superscript H it denotes the descriptor is that determined by Abraham and co-workers. The Abraham solvation equation is now written in the recognisable form given in equation 2.3;

$$\text{Log SP} = c + r.\,R_2 + s.\,\pi_2^H + a.\,\Sigma\alpha_2^H + b.\,\Sigma\beta_2^H + v.\,Vx \qquad (2.3)$$

This equation can be applied to the transport of solutes from one phase in to another, where the equation coefficients c, r, s, a, b, and v describe the two-phase system. The new solute descriptors were determined by Abraham et al., using various experimental and empirical methods. Details of how they were obtained are given below.

2.1.1 The McGowan characteristic volume, Vx

Leahy's[9] computer calculated intrinsic volume, V_1, was rather complicated to evaluate, and so Abraham chose a more straight forward measure Vx (in cm^3 mol^{-1}/ 100).[18, 19] In the calculation of Vx, atom contributions are summed, and a 'bond' term is then subtracted. All bonds are considered equal, so that a double bond such as C=C or C= O or triple bond such as C $\overline{=}$ C is regarded as one bond. An algorithm proposed by Abraham, allows the number of bonds in a molecule to be obtained simply.[18,19]

$$B = N - 1 + R \tag{2.4}$$

Here B is the number of bonds, N is the total number of atoms and R is the total number of ring structures. Therefore;

$$Vx = (\Sigma \text{ atom contributions} - (6.56 * B)) /100 \tag{2.5}$$

Some typical values for atom contributions required for the calculation of Vx are given in Table (2.1). The Vx descriptor models the (endoergic) cavity effect that arises through

the disruption of solvent-solvent interactions to form a cavity, together with the (exoergic) solute-solvent general dispersion interaction.

Table (2.1) Atom contributions for calculation of Vx (in cm^3 mol^{-1}).

C = 16.35	P = 24.78	Sc = 27.81
N = 14.39	S = 22.91	Br = 26.21
O = 12.43	Cl = 20.95	Sn = 39.35
F = 10.48	B = 18.32	Sb = 37.74
H = 8.71	Ge = 31.02	Te = 36.14
Si = 26.83	As = 29.42	I = 34.35

2.1.2 The excess molar refraction, R_2

The polarisability-correction descriptor, δ_2, used in equation (2.2) is only an empirical factor and had limited values. Abraham [20] considered a number of possible alternatives for δ_2. The molar refraction (MRx) equation (1.15) was of little use because the volume term in the molar refraction means that molar refraction is very nearly linear with this Vx. Abraham et al. therefore defined excess molar refraction equation (1.16); R_2 , can be easily estimated for structures using fragment or substructure values.[16,18]

2.1.3 The solute dipolarity/polarisability, π_2^H

In order to obtain the new π_2^H parameter, use was made of gas chromatographic specific retention volumes, V_G , that had been measured for several hundred solutes on 75 stationary phases.[21] The 75 phases contained no hydrogen bonding acidic groups, so a simplified [11] set of LFERs was used;

$$\text{Log } V_G = c + r.R_2 + s.\ \pi_2^* + a.\ \Sigma\ \alpha_2^H + l.\ \log L^{16} \qquad (2.6)$$

Here L^{16} is the Oswald solubility coefficient, L on n-hexadecane at 298 K.[22] Log L^{16} is used instead of Vx as a cavity size descriptor for the dissolution of a gaseous solute into a solvent. The solute parameters R_2, $\Sigma\alpha_2^H$, log L^{16} and π_2^* were used in correlations to give equation coefficients c, r, s, a and l, for the 75 phases. The equation took the generalised form;

$$\text{Log } V_G = c_n + r_n.\ R_2 + s_n.\ \pi_2^* + a_n.\ \Sigma\alpha_2^H + l_n.\ \log L^{16} \qquad (2.7)$$

The constant c was then subsumed into the dependent variable to give 75 equations;

$$V_{n-1} = r_{n-1}.R_2 + s_{n-1}.\pi_2^* + a_{n-1}.\Sigma\alpha_2^H + l_{n-1}.\log L^{16} \qquad (2.8)$$

$$\vdots$$

$$V_{n-75} = r_{n-75}.R_2 + s_{n-75}.\pi_2^* + a_{n-75}.\Sigma\alpha_2^H + l_{n-75}.\log L^{16} \qquad (2.9)$$

Where

$$V_n = \log V_{Gn} - c_n \qquad (2.10)$$

The matrix defined by equation (2.10) was used in a vertical format, taking R_2, π_2^H, $\Sigma\alpha_2^H$, and log L^{16} as the unknown coefficients that were then evaluated by MLR analysis. π_2* was replaced by the descriptor π_2^H since all the data in the analysis related purely to properties of the solute, and R_2 can be calculated for any solute, so equation (2.11) was achieved;

$$V_{Gn} - c_n - r_n.R_2 = \pi_2^H.s_n + \Sigma\alpha_2^H.\ s_n + \log L^{16}.\ I_n \qquad (2.11)$$

When the constant, c, was left to float, the best values of π_2^H, $\Sigma\alpha_2^H$ and log L^{16} were given (the best values of the descriptor were decided as those that reproduced the LFER equations with minimum standard deviation). These new π_2^H, $\Sigma\alpha_2^H$ and log L^{16} values are 'average' values for each solute on a range of stationary phases, and represent three new scales of solute properties.

Patte et al.[23] determined values for more solutes in a similar way using retention data on five stationary, non-acidic phase. This time, five values of π_2^H were determined by back calculation, using known values of π_2^H, α_2^H and log L^{16}, which were then averaged. Although the combination of solutes in the McReynolds[21] and Patte et al.[23] sets amounted to several hundred solutes, such as substituted aromatics, polyhalogenated aliphatic compounds, etc., many other solutes were missed out. These included functionally substituted aromatic solutes, nitroalkanes and nitriles. Hence π_2^H for many aromatic compounds were then determined by back calculation using the general solvation equation with Fellous et al. retention data on 17 stationary phases.[24] For halogenated and

polyhalogenated aromatic solutes, π_2^H values were obtained by Abraham et al.[12,13] using the same method.

Abraham et al. then devised two simple rules governing π_2^H values for aliphatic solutes.

1. In any homologous series of functionally substituted aliphatic compounds, π_2^H is constant except for the first one or two members.
2. In any given series of functionally substituted aliphatic compounds, π_2^H decreases by 0.03 unit for each branch in a carbon chain.

2.1.4 The solute overall hydrogen-bond scales, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$

There is no certainty that α_2^H and β_2^H are the appropriate scales to use when a solute is surrounded by a number of solvent molecules. For example, propanone is largely mono-hydrogen-bonded in methanol but is di-hydrogen-bonded in water and triphenylphosphine oxide is mono-and di-hydrogen-bonded in methanol but tri-hydrogen-bonded in water. In the case of acidic solutes, the problem is not so difficult, because even when surrounded by solvent molecules a hydrogen-bond acid will usually associate with one solvent molecule.

However, Abraham et al.[14] decided to set out two new hydrogen-bond scales that referred to 'overall' or 'effective' hydrogen-bond capability, and which would be appropriate to use in an LFER or QSAR situation where the solute is surrounded by

solvent molecules. These overall scales were labeled $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$. They were both derived from various equilibrium processes such as gas liquid chromatography and water-solvent partition. To obtain $\Sigma\alpha_2^H$ values a preliminary version of equation (2.3) was set up using α_2^H as the hydrogen-bond acid descriptor and was applied to various water-solvent partitions (SP in log SP is then the water-solvent partition coefficient).[15,16] The α_2^H descriptor was then modified where necessary, in order to obtain the effective value, $\Sigma\alpha_2^H$. A new set of equations was then constructed, and the same process repeated until a self-consistent set of equations and $\Sigma\alpha_2^H$ values was given. Since the solutes in the water-solvent partitions are surrounded by solvent molecules, the overall hydrogen-bond acidity scale is the actual scale required. It was observed that values of $\Sigma\alpha_2^H$ were constant along any homologous series, except perhaps for the first one or two members, so once a few values are established, values for the rest of the homologous series can be deduced. Multiple hydrogen bonding of a solute with several solvent molecules gives a higher $\Sigma\alpha_2^H$ values than α_2^H, as shown in Table (2.2) for the case of solute water.

Table (2.2) A comparison of α_2^H and $\Sigma\alpha_2^H$ for some solutes.

Solute	α_2^H	$\Sigma\alpha_2^H$
Butanone	0.00	0.00
Ethanol	0.33	0.37
Pyrrole	0.41	0.41
Water	0.35	0.85
Acetic acid	0.55	0.61
Phenol	0.60	0.60

The β_2^H descriptor can be used as the overall or effective hydrogen bond basicity descriptor, $\Sigma\beta_2^H$, with mono–bases, but with poly-bases, again there seems to be no alternative than to calculate $\Sigma\beta_2^H$. Table (2.3) shows a comparison of β_2^H and $\Sigma\beta_2^H$ values for some solutes.

Table (2.3) a comparison of β_2^H and $\Sigma\beta_2^H$ values

Solute	β_2^H	$\Sigma\beta_2^H$
n-Heptane	0.00	0.00
Diethylether	0.45	0.45
Butanone	0.45	0.51
Acetonitrile	0.44	0.32
Ethanol	0.44	0.48
Benzene	0.15	0.14
Pyridine	0.62	0.52
Dimethylsulfoxide	0.78	0.88
Phenol	0.22	0.30
4-Methoxyaniline	0.45	0.65
1,4-Doxane	0.47	0.64

A large number of $\Sigma\beta_2^H$ values were determined in a similar way as $\Sigma\alpha_2^H$.[15,16,17,25] A preliminary version of equation (2.3) was set up using β_2^H as hydrogen-bond base descriptor and was applied to various water-solvent partitions. The β_2^H descriptor was then modified where necessary, in order to obtain $\Sigma\beta_2^H$ values. A new set of equations was then constructed, and the same process repeated until a self consistent set of equations and $\Sigma\beta_2^H$ values was given. Again, values of $\Sigma\beta_2^H$ were constant along any homologous series, allowing values for other members in the series to be deduced. One can note that the work carried out to obtain an overall $\Sigma\alpha_2^H$ scale from the 1:1 α_2^H scale proceeded side by side with the calculation of $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ that took place during

the π_2^H calculation, as seen in 2.1 3. Therefore a constant check had to be made on the self-consistency of the derived $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ values.

A summary of the Abraham solute descriptors and the processes involved in obtaining them is given in Figure (2.1).

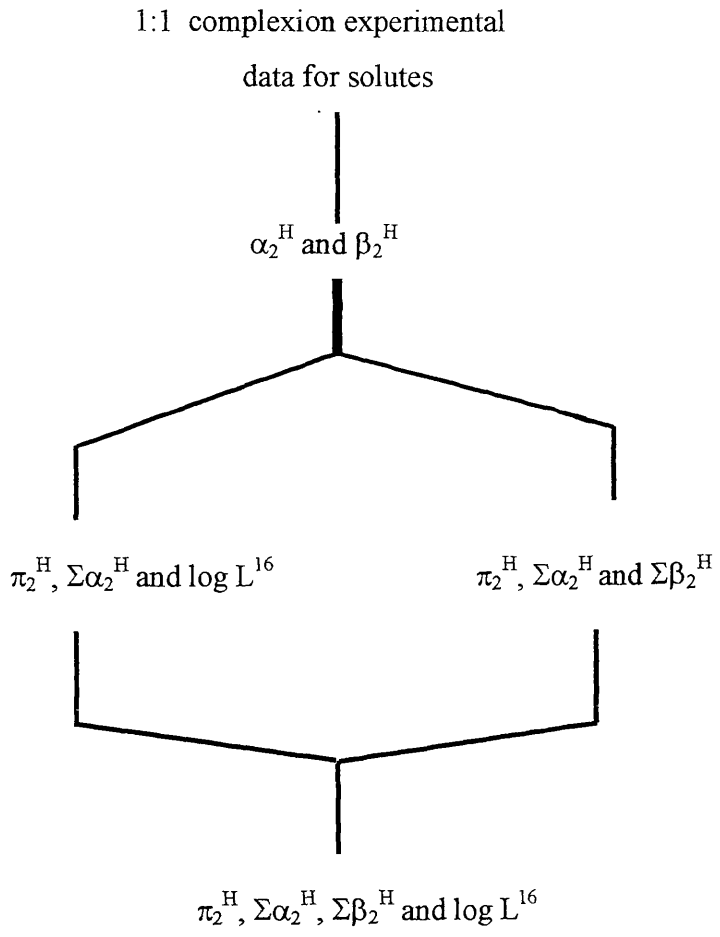

Figure (2.1) A summary of the processes involved in obtaining the Abraham solute descriptors.

Step 1 Equilibrium constants for 1:1 complexation of a series of acids (against a reference base) and a series of bases (against a reference acid) used to set up new hydrogen-bond acidity and basicity scales.

Step 2 Gas-liquid chromatography data used to develop a new dipolarity/polarisability scale, log L^{16} values and overall hydrogen-bond acidity scales, developed adjacently with work carried out in step 3.

Step 3 Effective hydrogen-bond acidity and basicity scales developed form water-solvent partition solvation equation; these values were constantly checked for consistency with those obtained in step 2.

Step 4 The π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and log L^{16} scales for solute are all checked for self-consistency to confirm that solute descriptors can be obtained using either method (step 2 and 3).

2.2 Applications of Abraham Solvation Equation

The Abraham general solvation equation is summarized as follows;

$$\text{Log SP} = c + r.\ R_2 + s.\ \pi_2^H + a.\ \Sigma\alpha_2^H + b.\ \Sigma\beta_2^H + v.\ V_x \qquad (2.12)$$

Here SP is a property of a series of solutes in a given system, and the independent variables are solute descriptors as follows: R_2, is an excess molar refraction, π_2^H, is the dipolarity/polarizability, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ are the solute overall hydrogen-bond acidity and basicity, V_x is the McGowan characteristic volume.[15,16] One example of LFER is the

Abraham solvation equation which correlates a physical, chemical or biological property (log SP) for a set of solutes with a corresponding set of solute physico-chemical property descriptors (R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and V_x). The equation coefficients (c, r, s, a, b and v) obtained are dependent on the two-phase system under investigation and can be used to predict or estimate further values of the independent variable for a completely new solute providing the descriptors are known. In addition, the equation coefficients provide information on the phase system. In case of the partition between two phases, they will refer to differences in physico-chemical properties of the two phases. The r-coefficient is a measure of difference in phase polarisability and the s-coefficient is a measure of phase dipolarity/polarisability difference. The a-coefficient measures the difference in the two phases hydrogen-bond basicity (because an acidic solute will interact with a basic phase) and the b-coefficient is a measure of how the phases differ in hydrogen-bond acidity. The v-coefficient is a measure of how the hydrophobicity of the two phases differs.

The generality of the solvation equation is highlighted by the fact that it has been applied to a very diverse range of processes. This equation has been employed for processes that take place in condensed phases, such as water-solvent partition,[26] water-micelle partition,[27] high performance liquid chromatography (HPLC),[28] normal phase liquid chromatography,[29] microemulsion[30] and micellar[31] electro-kinetic chromatography, thin-layer chromatography,[32] solid phase extraction,[33] blood-brain distribution,[34,35] brain perfusion, [36] water -skin permeation [35,37] and tadpole narcosis.[38] A modified form of the Abraham solvation equation can be used to calculate and predict the solubility of solids and liquids in water.[39] Because the solvation equation is going to be used through this

work so it was necessary to discuss the general method behind the development of the Abraham solvation equation in detail.

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Chapter 3 Correlation Method

3.0 Correlation and regression analysis

The correlation method used in this work is that of multiple linear regression analysis, MLRA. This is a common technique in statistics, and is an extension of the simple regression of y against x. A set of y-values, the dependent variable, may be linearly related to the independent variable x. A relationship between two variables is shown, and if it is linear when y values are plotted against x values, then a straight line can be drawn through the points, and the equation can be written as,

$$y = mx + c \tag{3.1}$$

Here c - is the intercept on the y -axis and m - is the slope of the line. The x-variable is the explanatory or independent variable. If there are scattered points in the plot, then drawing a straight line may not be too obvious, and any line chosen will affect the prediction of y values. In such a case, a method called least squares is often used to decide the best straight line to choose. This is done by taking into account all the deviations between observed and estimated values of the variable from the line, squaring them and adding them up.[1] The criterion of least squares is that the best line is the one with the least sum of squared deviations. This can be drawn when one variable is present, but starts to be complicated when the number of variables increases, as in the case of the general solvation equation. In this case the calculation is done by the use of computer.[2]

Correlation gives the association between the variables, but it is the regression that uses the variables to help explain the variation in the dependent variable and thus estimates the parameters of the model, provides a test of the validity of the model, and the calculation of the confidence limits of the parameter. Since the correlation alone can not measure the success of the relationship between the variables, other statistical methods can be used, such as the standard deviation of the estimate, sd, the correlation coefficient, r, and the F-statistic. Standard deviation is the square root of the quantity (sum of squares of deviations of individual results from the mean, divided by one less than the number of results in the set) and is given by:

$$Sd = [\Sigma (x_i - \bar{x})^2 / (n - 1)]^{1/2} \qquad (3.2)$$

Standard deviation has the same units as the property being measured. It becomes a more reliable expression of precision as (n) gets larger, so sd is a means of assessing the reliability of an equation, and is also used in considering the significance of deviant points. The sd measures the spread of a distribution around the mean. A low sd value indicates a low spread, i.e. a good relationship, and a high sd value indicates that the data set contains a high distribution of points from the mean, which is unfavourable in MLRA. The correlation coefficient gives the measure of success of the correlation of the dependent variable (y) against the independent variable (x). The equation for the correlation coefficient which take into account the standard deviation is:

$$r = [1 - sd^2 (n - 2) / \sigma^2_y n]^{1/2} \qquad (3.3)$$

Here $\sigma^2_y = \Sigma (y - \bar{y})^2 /n$ and $\bar{y}$ is the mean, Σ y /n. The quantity σ^2_y is the variance of the sample values of y. From this equation it can seen that as the sd$\rightarrow$ 0, r $\rightarrow$ 1, ie. The correlation get nearer to perfection, r is a measure of how closely the data set fits the relationship given by the MLRA and can range from -1 through to 1. A value of -1 or 1 indicates that the data set is explained by the correlation equation perfectly, while a value of zero means there is no relationship between the data set and the MLRA. A negative value of r - may be interpreted as a poor correlation by an inexperienced eye so more often than not it is r^2 - that is quoted in relation to multiple linear regression, r^2 has values of zero through to one and is basically an indicator of how well the regression analysis explains the relationship among the variables. Now though the correlation r, is often used, it is r^2, that is meaningful, because it gives the fraction of the variance of y which is explained by the regression equation. It is more convenient to convert it to a percentage. Thus when $r^2 = 0.90$ the regression equation explains about 90 % of the variance. It is very important that the correlation coefficient should be considered in relation to the number of data sets correlated. Students' t-test can be used to investigate the significance of the coefficient, and assumes normal distribution of the errors. The t-test is set as a confidence limit, usually at 90 % but can go up to 99 % depending on the accuracy of the test required. In MLR analysis, the t-test is performed on each individual variable to test their significance. Sometimes not all the variables are necessary and this would be indicated by the level of significance. Another significant test, which is used in MLRA is the F-statistic or the Fisher statistic. This test accounts for the number of variables, v , present and the number of data point (n). The value of the F-statistic gives an indication of the quality of the regression, to determine whether the observed

relationship between the dependent and independent variables occurs by chance the higher the value of F, the better is the regression.

$$F = r^2 (n - v - 1) / (1 - r^2) v \qquad (3.4)$$

Here r, is the correlation coefficient, n, is the number of data points and v is the degrees of freedom, which is (v -1), where v, is the number of variables. From the equation, it can be seen that the main factors that contribute to the improvement of the regression are n, and r, because as these two parameters increase, F increases. Once a MLRA output has been obtained it is essential to measure how reliable the relationship is, i.e. it is necessary to validate the model so any predicted values can be obtained with accuracy and confidence. The main problem with MLR is its sensitivity to collinearities among the independent variables. Collinearities occur when there is a high degree of linear correlation between two or more of the independent variables. It is therefore very important to make sure the variables used in MLR, i.e. the solute descriptors in the case of the Abraham Solvation Equation, are well defined and independent. To use MLRA the number of data points is important, as this improves the reliability of the correlation. It has been suggested that at least five data points are required per variable, but this seems to be the very minimum that should be used.

3.1 Information provided by the regression output

The significance of an interaction term can be identified by the magnitude of the coefficients and also by the Students' t-test at 95%. As an example is given the output for the solvation equation of water-tributylphosphate which was obtained from the

value of the partition coefficient for a series of compounds. Log P values for a series of 50 solutes were obtained from the Med Chem data base (Table 3.1)

Table (3.1) The regression output for the water-tributylphosphate system

Correlation coefficients between variables

1)VAR:	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	Vx
π_2^H	0.802				
$\Sigma\alpha_2^H$	0.559	0.859			
$\Sigma\beta_2^H$	0.187	0.474	0.474		
Vx	0.681	0.620	0.518	0.404	
Yobs	0.623	0.351	0.280	-0.335	0.70

2)VAR:	R_2	π^H_2	$\Sigma\alpha^H_2$	$\Sigma\beta^H_2$	Vx	Yobs
MEAN	0.43	0.59	0.40	0.40	0.75	1.63
ST.DEV	0.34	0.34	0.25	0.22	0.29	1.38

3)VAR:	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	Vx	const
COEFFS	0.804	-0.862	1.389	-4.647	4.129	0.015
ST.DEV	0.191	0.273	0.248	0.169	0.147	0.085
T	4.200	3.155	5.593	27.492	28.005	0.175
TTEST	0.9998	0.9971	1.0000	1.0000	1.0000	1.0000

4)OVERALL.COR.COEFF	0.9906
ST.DEV.YOBS-YCALC	0.200
DEGREES-FREEDOM	44.00
F-STATISTIC	460.5

The information can be divided in to four sections.

1- The first information given is the correlation coefficient between variables, this shows how the variable is correlated due to the importance of multicollinearity. If there is a high correlation then a high coefficient between the variables is shown. The correlation of Yobs against each solute descriptors is also shown.

2 - The next section gives information of the set of solute descriptor itself, in terms of the mean of the parameter coefficients and the spread of the parameters. For a set of solutes a large standard deviation is favourable as this shows a diversity of the descriptor, thus a more general equation is obtained.

3 - Section 3 shows the coefficients of the solvent system, the constants c, r, s, a, b and v . Also the standard deviation of these coefficients are given, this is important when back calculation of the descriptors are called for. If the values of the t-tests are above 0.95 this means that the coefficients are statistically significant.

4 - The last section gives the overall view of the regression output. The quality of the regression is indicated by the correlation coefficient, r; this depends somewhat on the type of the system studied, (for example in solid adsorbent, r = 0.95 is generally accepted). The best regression is indicated by the smallest value of the standard deviation (Yobs -Ycalc). The F-statistic indicates the quality of the correlation and thus shows a goodness of fit, F-statistic improves as the number of the data set increases and the sd decreases.

3.2 Conclusion

According to the information in these two chapters (2, 3), one could say it has been possible to devise a set of solute descriptors. These descriptors, particularly the effective or overall hydrogen-bond acidity and basicity, can be used to construct LFERs and QSARs. Also two general equations have been formulated, one that is more useful for gas-condensed phase processes, and one that is better for processes within condensed phases. Comparing the two equations the descriptors in both are the same, except for the size parameter log L^{16} and V_x. The two equations (LFERs and QSARs) have been applied to a wide variety of solubility-related processes, and generally give good results. The r-coefficient shows the tendency of the phase to interact with solutes through π- and n-electron pairs. Usually the r-constant is positive, but for phases that contain fluorine atoms, the r-constant can be negative. The s-coefficient gives the tendency of the phase to interact with dipolar/polarizable solutes, the a-coefficient denotes the hydrogen-bond basicity of the phase (because acidic solutes will interact with a basic phase), and the b-coefficient is a measure of the hydrogen-bond acidity of the phase (because basic solutes will interact with acidic phase). It is important to note that for gas - phase processes, the s, a, and b-constants must always be positive (or zero), because interaction between the phase and a solute will increase the solubility of a gaseous solute. Equation (2.12) provides a new method for the characterization of GLC stationary phases. There is a need for much more work to be done to improve and increase the applicability of the two general equations because in both equations there is no descriptor related to solute shape.

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Chapter 4 Introduction to Polychlorobiphenyls (PCBs) and to Gas Liquid Chromatography

4.0 Introduction

Technical polychlorobiphenyls (PCBs) constitute a group of chlorin-substituted biphenyl compounds; each commercial product is assigned a code number indicating the chlorine content or number of substituted chlorine atoms of the predominant PCBs present. Moreover, highly toxic by products (such as polychlorinated dibenzofurans) coexist in technical products and the content of such byproducts may vary according to the mode of synthesis.

The polychlorinated biphenyls, or PCBs, are a group of xenobiotic chemicals first manufactured commercially in the 1930's and which were widely used as transformer coolants, dielectric fluids, solvents, and flame retardant until restrictions on their use were introduced in the early 1970's.[1] Of the approximately 570 000 000 Kg sold in the U. S as of 1975, some 68 000 000 Kg were estimated to be mobile in the environment and some 130 000 000 Kg were in landfills or some equipment dumps. There are 209 possible chlorinated biphenyls ranging from the three monochlorobiphenyls to decachlorobiphenyl. It is only recently[2] that all 209 congers have been individually synthesized and characterized. The characteristic properties of the PCBs are hydrophobicity or lipophilicity (i e. large octanol-water partition coefficient and low aqueous solubility), relatively low vapour pressure, and extreme resistance to chemical

reactions.[3] These properties result in persistence in the environment, a tendency to accumulate in biota and in sediments, and the ability to be transported through the atmosphere to regions remote from source discharges;[4] for example, appreciable concentrations are found in the soils, sediments, waters, biota atmosphere, and precipitation in the Great Lakes Basin.[5, 6] The biological and human health effects of PCBs, have been reviewed recently.[7] PCBs, and various chlorinated organic pesticides are known to induce drug- metabolizing enzymes in the liver, and potent inducers such as DDT, dieldrin heptachlor, etc. are known to act additively with PCBs. Present levels of these compounds in human adipose tissues vary widely from locality to locality, and at worst surpass the 20 ppm level. The possibility exists therefore that such levels could lead to abnormal enzyme introduction in the liver resulting in accelerated breakdown of essential hormones and other important biological substances. Indeed, the reduction in population of certain fish-eating species has been attributed to this cause.

However, in man, it has yet to be established that such effects could result from present environmental contamination. Another possible effect of environmental PCBs, is liver damage. In certain parts of Japan, U.S.A. and W. Germany, mothers' milk has been shown to contain more than 0.06 ppm PCBs,[8] which gives rise to considerable concern. PCBs have similar structural functionalities, and so gas- liquid chromatography (GLC) is often be used to separated them. The π_2^H parameter could possibly be obtained from gas-liquid chromatographic measurements, so it was useful to give some detail about chromatography, in this chapter.

In Table (4.1) are listed all 209 PCBs together with their CAS numbers, their IUPAC number (the individual polychlorinated are identified by numbers according to the

International Union of Pure and Applied Chemistry (IUPAC)),[9] and the substitution in the two rings. These are referred to as ring A and ring B.

Table (4.1) Names of PCBs and alkanes, CAS No., IUPAC No. and the PCB No.

CAS	Name	IUPAC	Ring A	Ring B	PCB
92-52-4	Biphenyl	-		NONE	1
2051-60-7	2-Monochloro	1	2	NONE	2
13029-08-8	2,2'-Dichloro	4	2	2	3
2051-61-8	3-Monochloro	2	3	NONE	4
25569-80-6	2,3'-Dichloro	6	3	2	5
2050-67-1	3,3'-Dichloro	11	3	3	6
2051-62-9	4-Monochloro	3	4	NONE	7
34883-43-7	2,4'-Dichloro	8	4	2	8
2974-90-5	3,4'-Dichloro	13	4	3	9
2050-68-2	4,4'-Dichloro	15	4	4	10
33146-45-1	2,6-Dichloro	10	2,6	NONE	11
38444-73-4	2,2',6-Trichloro	19	2,6	2	12
38444-76-7	2,3'6-Trichloro	27	2,6	3	13
38444-77-8	2,4',6-Trichloro	32	2,6	4	14
15968-05-5	2,2',6,6'-Tetrachloro	54	2,6	2,6	15
34883-39-1	2,5-Dichloro	9	2,5	NONE	16
37680-65-2	2,2',5-Trichloro	18	2,5	2	17
38444-81-4	2,3',5-Trichloro	26	2,5	3	18
16606-02-3	2,4',5-Trichloro	31	2,5	4	19
41454-41-9	2,2',5,6'-Tetrachloro	53	2,5	2,6	20
35693-99-3	2,2',5,5'-Tetrachloro	52	2,5	2,5	21
33284-50-3	2,4-Dichloro	7	2,4	NONE	22

Table 4.1 cont.

37680-66-3	2,2',4-Trichloro	17	2,4	2	23
55712-37-3	2,3',4-Trichloro	25	2,4	3	24
7012-37-5	2,4,4'-Trichloro	28	2,4	4	25
65194-04-7	2,2',4,6'-Tetrachloro	51	2,4	4	26
41464-40-8	2,2'4,5',-Tetrachloro	49	2,4	2,5	27
2437-79-8	2,2',4,4'-Tetrachloro	47	2,4	2,4	28
16605-91-7	2,3-Dichloro	5	2,3	NONE	29
38444-78-9	2,2',3-Trichloro	16	2,3	2	30
38444-84-7	2,3,3'-Trichloro	20	2,3	3	31
38444-85-8	2,3,4'-Trichloro	22	2,3	4	32
41464-47-5	2,2',3,6'-Tetrachloro	46	2,3	2,6	33
41464-39-5	2,2',3,5'-Tetrachloro	44	2,3	2,5	34
36559-22-5	2,2',3,4'-Tetrachloro	42	2,3	2,4	35
38444-93-8	2.2',3,3'-Tetrachloro	40	2,3	2,3	36
34883-41-5	3,5-Dichloro	14	3,5	NONE	37
37680-68-5	2',3,5-Trichloro	34	3,5	2	38
38444-87-0	3,3',5-Trichloro	36	3,5	3	39
38444-88-1	3,4',5-Trichloro	39	3,5	4	40
74338-23-1	2,3',5',6-Tetrachloro	73	3,5	2,6	41
41464-42-0	2,3',5,5'-Tetrachloro	72	3,5	2.5	42
73575-52-7	2,3',4,5'-Tetrachloro	68	3,5	2,4	43
41454-49-7	2,3,3',5'-Tetrachloro	58	3,5	2,3	44
33284-52-5	3,3',5,5'-Tetrachloro	80	3,5	3,5	45
2974-92-7	3,4-Dichloro	12	3,4	NONE	46
38444-86-9	2',3,4-Trichloro	33	3,4	2	47
37680-69-6	3,3',4-Trichloro	35	3,4	3	48
41464-46-4	2,3',4',6-Tetrachloro	71	3,4	2,6	50
32598-11-1	2,3',4',5-Tetrachloro	70	3,4	2,5	51
32598-10-0	2,3',4,4'-Tetrachloro	66	3,4	2,4	52
41464-43-1	2,3,3',4'-Tetrachloro	56	3,4	2,3	53
41464-48-6	3,3',4,5'-Tetrachloro	79	3,4	3,5	54

Table 4.1 cont.

32598-13-3	3,3',4,4'-Tetrachloro	77	3,4	3,4	55
35693-92-6	2,4,6-Trichloro	30	2,4,6	NONE	56
62796-65-8	2,2',4,6-Tetrachloro	50	2,4,6	2	57
60233-24-1	2,3',4,6-Tetrachloro	69	2,4,6	3	58
32598-12-2	2,4,4',6-Tetrachloro	75	2,4,6	4	59
56558-16-8	2,2',4,6,6'-Pentachloro	104	2,4,6	2,6	60
60145-21-3	2,2'.4,5',6-Pentachloro	103	2,4,6	2,5	61
39485-83-1	2,2',4,4',6-Pentachloro	100	2,4,6	2,4	62
60233-25-2	2,2',3',4,6-Pentachloro	98	2,4,6	2,3	63
56558-18-0	2,3',4,5',6-Pentachloro	121	2,4,6	3,5	64
56558-17-9	2,3',4,4',6-Pentachloro	119	2,4,6	3,4	65
33979-03-2	2,2',4,4',6,6'Hexachloro	155	2,4,6	2,4,6	66
58702-45-9	2,3,6-Trichloro	24	2,3,6	NONE	67
70362-45-7	2,2',3,6-Tetrachloro	45	2,3,6	2	68
74472-33-6	2,3,3',6-Tetrachloro	59	2,3,6	3	69
60233-24-1	2,3,4',6-Tetrachloro	64	2,3,6	4	70
73575-54-9	2,2',3,6,6'-Pentachloro	96	2,3,6	2,6	71
38379-99-6	2,2',3,5',6-Pentachloro	95	2,3,6	2,5	72
58194-05-8	2,2'3,4',6-Pentachloro	91	2,3,6	2,4	73
73575-57-2	2,2'3,3',6-Pentachloro	84	2,3,6	2,3	74
68194-10-5	2,3,3',5',6-Pentachloro	113	2,3,6	3,5	75
38380-03-9	2,3,3',4',6-Pentachloro	110	2,3,6	3,4	76
68194-08-1	2,2',3,4',6,6'-Hexachloro	150	2,3,6	2,4,6	77
38411-22-2	2,2',3,3',6,6'-Hexachloro	136	2,3,6	2,3,6	78
55720-44-0	2,3,5-Trichloro	23	2,3,5	NONE	79
70362-46-8	2,2',3,5-Tetrachloro	43	2,3,5	2	80
70424-67-8	2,3,3',5-Tetrachloro	57	2,3,5	3	81
74472-35-8	2,3,4',5-Tetrachloro	63	2,3,5	4	82
73575-55-0	2,2',3,5,6'-Pentachloro	94	2,3,5	2,6	83
52663-61-3	2,2',3,5,5'-Pentachloro	92	2,3,5	2,5	84
68194-07-0	2,2',3,4',5-Pentachloro	90	2,3,5	2,4	85

Table 4.1 cont.

60145-20-2	2,2',3,3',5-Pentachloro	83	2,3,5	2,3	86
39635-32-0	2,3,3',5,5'-Pentachloro	111	2,3,5	3,5	87
70424-68-9	2,3,3',4',5-Pentachloro	107	2,3,5	3,4	88
74472-42-7	2,2',3,4',5,6'-Hexachloro	148	2,3,5	2,4,6	89
52744-13-5	2,2',3,3',5,6'-Hexachloro	135	2,3,5	2,3,6	90
35694-04-3	2,2',3,3',5,5',-Hexachoro	133	2,3,5	2,3,5	91
15862-07-4	2,4,5,-Trichloro	29	2,4,5	NONE	92
70362-47-9	2,2',4,5-Tetrachloro	48	2,4,5	2	93
73575-53-8	2,3',4,5-Tetrachloro	67	2,4,5	3	94
32690-93-0	2,4,4',5-Tetrachloro	74	2,4,5	4	95
68194-06-9	2,2',4,5,6'-Pentachloro	102	2,4,5	2,6	96
37680-73-2	2,2',4,5,5'-Pentachloro	101	2,4,5	2,5	97
38380-01-7	2,2',4,4',5-Pentachloro	99	2,4,5	2,4	98
41464-51-1	2,2',3',4,5-Pentachloro	97	2,4,5	2,3	99
68194-12-7	2,3',4,5,5'-Pentachloro	120	2,4,5	3,5	100
31508-00-6	2,3',4,4',5-Pentachloro	118	2,4,5	3,4	101
60145-22-4	2,2',4,4',5,6'-Hexachloro	154	2,4,5	2,4,6	102
038380-04-0	2,2',3,4',5',6-Hexachloro	149	2,4,5	2,3,6	103
51908-16-8	2,2',3,4'.5,5'-Hexachloro	146	2,4,5	2,3,5	104
35065-27-1	2,2',4,4',5,5-Hexachloro	153	2,4,5	2,4,5	105
52663-59-9	2,2',3,4-Tetrachloro	41	2,3,4	2	107
74338-24-2	2,3,3',4-Tetrachloro	55	2,3,4	3	108
33025-41-1	2,3,4,4'-Tetrachloro	60	2,3,4	4	109
73575-57-2	2,2',3,4,6'-Pentachloro	89	2,3,4	2,6	110
38380-02-8	2,2',3,4,5'-Pentachloro	87	2,3,4	2,5	111
65510-45-4	2,2'3,4,4'-Pentachloro	85	2,3,4	2,4	112
52663-62-4	2,2',3,3',4-Pentachloro	82	2,3,4	2,3	113
70362-41-3	2,3,3',4,5'-Pentachloro	108	2,3,4	3,5	114
32598-14-4	2,3,3',4,4'-Pentachloro	105	2,3,4	3,4	115
59291-64-4	2,2',3,4,4',6'-Hexachloro	140	2,3,4	2,4,6	116

Table 4.1 cont.

38380-05-1	2,2',3,4,4',6'-Hexachloro	132	2,3,4	2,3,6	117
52663-66-8	2,2',3,3',4,5'-Hexachloro	130	2,3,4	2,3,5	118
35065-28-2	2,2',3,4,4',5'-Hexachloro	138	2,3,4	2,4,5	119
38380-07-3	2,2',3,3',4,4'-Hexachloro	128	2,3,4	2,3,4	120
53555-66-1	3,4,5-Trichloro	38	3,4,5	NONE	121
70362-48-0	2',3,4,5-Tetrachloro	76	3,4,5	2	122
70362-49-1	3,3',4,5-Tetrachloro	78	3,4,5	3	123
70362-50-4	3,4,4',5-Tetrachloro	81	3,4,5	4	124
74472-39-2	2',3,4,5,6'-Pentachloro	125	3,4,5	2,6	125
70424-70-3	2',3,4,5,5'-Pentachloro	124	3,4,5	2,5	126
65510-44-3	2',3,4,4',5-Pentachloro	123	3,4,5	2,4	127
76842-07-4	2',3,3',4,5-Pentachloro	122	3,4,5	2,3	128
39635-33-1	3,3',4,5,5'-Pentachloro	127	3,4,5	3,5	129
31508-00-6	2,3',4,4',5-Pentachloro	118	3,4,5	3,4	130
59291-65-5	2,3',4,4',5',6-Hexachloro	168	3,4,5	2,4,6	131
74472-45-0	2,3,3',4',5',6-Hexachloro	164	3,4,5	2,3,6	132
39635-34-2	2,3,3',4',5,5'-Hexachloro	162	3,4,5	2,3,5	133
52663-72-6	2,3',4,4',5,5'-Hexachloro	167	3,4,5	2,4,5	134
69782-90-7	2,3,3',4,4',5'-Hexachloro	157	3,4,5	2,3,4	135
32774-16-6	3,3',4,4',5,5'-Hexachloro	169	3,4,5	3,4,5	136
33284-54-7	2,3,5,6-Tetrachloro	65	2,3,5,6	NONE	137
73575-56-1	2,2',3,5,6-Pentachloro	93	2,3,5,6	2	138
74472-36-9	2,3,3',5,6-Pentachloro	112	2,3,5,6	3	139
68194-11-6	2,3,4',5,6-Pentachloro	117	2,3,5,6	4	140
68194-09-2	2,2',3,5,6,6'-Hexachloro	152	2,3,5,6	2,6	141
52663-63-5	2,2',3,5,5',6-Hexachloro	151	2,3,5,6	2,5	142
68194-13-8	2,2'.3,4',5,6-Hexachloro	147	2,3,5,6	2,4	143
52704-70-8	2,2',3,3',5,6-Hexachloro	134	2,3,5,6	2,3	144
74472-46-1	2,3,3',5,5',6-Hexachloro	165	2,3,5,6	3,5	145
74472-44-9	2,3,3',4',5,6-Hexachloro	163	2,3,5,6	3,4	146

Table 4.1 cont.

74487-85-7	2,2',3,4',5,6,6'-Heptachloro	188	2,3,56	2,4,6	147
52663-64-6	2,2',3,3',5,6,6'-Heptachloro	179	2,3,5,6	2,3,6	148
52663-67-9	2,2',3,3',5,5',6-Heptachloro	178	2,3,5,6	2,3,5	149
52663-68-0	2,2',3,4',5,5',6-Heptachloro	187	2,3,5,6	2,4,5	150
52663-70-4	2,2',3,3',4',5,6-Heptachloro	177	2,3,5,6	2,3,4	151
69782-91-8	2,3,3',4',5,5',6-Heptachloro	193	2,3,5,6	3,4,5	152
2136-99-4	2,2',3,3',5,5',6,6'-Octachloro	202	2,3,5,6	2,3,5,6	153
54230-23-7	2,3,4,6-Tetrachloro	62	2,3,4,6	NONE	154
55215-17-3	2,2',3,4.6-Pentachloro	88	2,3,4,6	2	155
74472-35-8	2,3,3',4,6-Pentachloro	109	2,3,4,6	3	156
74472-38-1	2,3,4,4'.6-Pentachloro	115	2,3,4,6	4	157
74472-40-5	2,2',3,4,6,6'-Hexachloro	145	2,3,4,6	2,6	158
68194-14-9	2,2',3,4,5',6-Hexachloro	144	2,3,4,6	2,5	159
56030-56-9	2,2',3,4,4',6-Hexachloro	139	2,3,4,6	2,4	160
74472-43-8	2,3,3',4,5',6-Hexachloro	161	2,3,4,6	3,5	162
61798-70-7	2,2',3,3',4,6-Hexachloro	131	2,3,4,6	2,3	161
74472-48-3	2,2',3,4,4',6,6'-Heptachloro	184	2,3,4,6	2,4,6	164
52663-65-7	2,2',3,3',4,6,6'-Heptachloro	176	2,3,4,6	2,3,6	165
40186-70-7	2,2',3,3',4,5',6-Heptachloro	175	2,3,4,6	2,3,5	166
52663-69-1	2,2',3,4,4',5',6-Heptachloro	183	2,3,4,6	2,4,6	167
52663-71-5	2,2',3,3',4,4',6-Heptachloro	171	2,3,4,6	2,3,4	168
74472-50-7	2,3,3',4,4',5',6-Heptachloro	191	2,3,4,6	3,4,5	169
40186-71-8	2,2',3,3',4,5',6,6'-Octachloro	201	2,3,4,6	2,3,5,6	170
33091-17-7	2,2',3,3',4,4',6,6'-Octachloro	197	2,3,4,6	2,3,4,6	171
33284-53-6	2,3,4,5-Tetrachloro	61	2,3,4,5	NONE	172
55312-69-1	2,2'3,4,5-Pentachloro	86	2,3,4,5	2	173
70424-69-0	2,3,3',4,5-Pentachloro	106	2,3,4,5	3	174
74472-37-0	2,3,4,4',5-Pentachloro	114	2,3,4,5	4	175
68194-15-0	2,2',3,4,5,6'-Hexachloro	143	2,3,4,5	2,6	176
52712-04-6	2,2',3,4,5,5'-Hexachloro	141	2,3,4,5	2,5	177
35694-06-5	2,2',3,4,4',5-Hexachloro	137	2,3,4,5	2,4	178

Table 4.1 cont.

55215-18-14	2,2',3,3',4,5,-Hexachloro	129	2,3,4,5,	2,3	179
39635-35-3	2,3,3',4,5,5'-Hexachloro	159	2,3,4,5	3,5	180
38380-08-4	2,3,3',4,4',5-Hexachloro	156	2,3,4,5	3,4	181
60145-23-5	2,2',3,4,4',5,6'-Heptachloro	182	2,3,4,5	2,4,6	182
38411-25-5	2,2',3,3',4,5,6'-Heptachloro	174	2,3,4,5	2,3,6	183
52663-74-8	2,2',3,3',4,5,5'-Heptachloro	172	2,3,4,5	2,3,5	184
35065-29-3	2,2',3,4,4',5,5'-Heptachloro	180	2,3,4,5	2,4,5	185
35065-30-6	2,2',3,3',4,4',5-Heptachloro	170	2,3,4,5	2,3,4	186
39635-31-9	2,3,3',4,4',5,5'-Heptachloro	189	2,3,4,5	3,4,5	187
52663-75-9	2,2',3,3',4,5,5',6'-Octachloro	199	2,3,4,5	2,3,5,6	188
42740-50-1	2,2',3,3',4,4',5,6'-Octachloro	196	2,3,4,5	2,3,4,6	189
35694-08-7	2,2',3,3',4,4',5,5'-Octachloro	194	2,3,4,5	2,3,4,5	190
18259-05-7	2,3,4,5,6-Pentachloro	116	2,3,4,5,6	NONE	191
41411-61-4	2,2',3,4,5,6-Hexachloro	142	2,3,4,5,6	2	192
41411-62-5	2,3,3',4,5,6-Hexachloro	160	2,3,4,5,6	3	193
41411-63-6	2,3,4,4',5,6-Hexachloro	166	2,3,4,5,6	4	194
74472-49-4	2,2',3,4,5,6,6'-Heptachloro	186	2,3,4,5,6	2,6	195
52712-05-7	2,2',3,4,5,5',6-Heptachloro	185	2,3,4,5,6	2,5	196
74472-47-2	2,2',3,4,4',5,6-Heptachloro	181	2,3,4,5,6	2,4	197
68194-16-1	2,2',3,3',4,5,6-Heptachloro	173	2,3,4,5,6	2,3	198
74472-51-8	2,3,3',4,5,5',6-Heptachloro	192	2,3,4,5,6	3,5	199
41411-64-7	2,3,3',4,4',5,6-Heptachloro	190	2,3,4,5,6	3,4	200
74472-52-9	2,2',3,4,4',5,6,6'-Octachloro	204	2,3,4,5,6	2,4,6	201
52663-73-7	2,2',3,3',4,5,6,6'-Octachloro	200	2,3,4,5,6	2,3,6	202
68194-17-2	2,2',3,3',4,5,5',6-Octachloro	198	2,3,4,5,6	2,3,5	203
52663-76-0	2,2',3,4,4',5,5',6-Octachloro	203	2,3,4,5,6	2,4,5	204
52663-78-2	2,2',3,3',4,4',5,6-Octachloro	195	2,3,4,5,6	2,3,4	205
74472-53-0	2,3,3',4,4',5,5',6-Octachloro	205	2,3,4,5,6	3,4,5	206
52663-77-1	2,2',3,3',4,5,5',6,6'-Nonachloro	208	2,3,4,5,6	2,3,5,6	207
52663-79-3	2,2',3,3',4,4',5,6,6'-Nonachloro	207	2,3,4,5,6	2,3,4,6	208
40186-72-9	2,2',3,3',4,4',5,5',6-Nonachloro	206	2,3,4,5,6	2,3,4,5	209

Table 4.1 cont.

2051-24-3	2,2',3,3',4,4',5,5',6,6'-Decachloro	209	2,3,4,5,6,	2,3,4,5,6	210
	Dodecane	266			
	Teradecane	268			
	Hexadecane	270			
	Octadecane	272			
	Eicosane	274			
	Docosane	276			
	Tetracosane	278			
	Hexacosane	280			
	Octacosane	282			
	Triacosane	284			
	Dotriacontane	286			
	Pentatriacontane	289			

4.1 Chromatography

4.1.1 Introduction

One of the notable scientific achievements of this century is the discovery and application of chromatography. Chromatography was discovered around the turn of the century by a Russian botanist named Mikhall S. Tswett [10] who separated green leaf pigments, namely the chlorophylls into a series of coloured bands using powdered calcium carbonate tamped firmly into a glass tube. The coloured bands shown on the column of the adsorbent bed evoked the term chromatography for this kind of separation. Although colour has little to do with modern chromatography the name has persisted and despite its irrelevance is still used for all separation techniques that involve a mobile and a stationary phase.

The theory of partition chromatography were developed by Martin and Synge;[11] they used mathematics to describe the separation process which result from the use of a liquid - coated solid phase and a moving liquid phase. Although the historical start of liquid chromatography (LC) was earlier than gas chromatography (GC), GC grew more rapidly. As a result, many fundamental studies worked toward the optimization of high- speed gas separations, and the speed of LC was increased. All these advances contributed to advent of high performance liquid chromatography (HPLC).

There are three types of chromatographic development:

i. Elution development. This is best described as a series of absorption-extraction processes which are continuous from the time a small volume of the sample is

injected into the chromatographic system, until the various sample components exit the column in the form of concentration bands separated in time.

ii. Frontal analysis. In frontal analysis the sample is fed continuously into the column, either as a pure sample or as a solution in the mobile phase. Only part of the first compound is eluted in a relatively pure state, each subsequent component being mixed with those previously eluted.

iii. Displacement development. This is a version of elution chromatography, which depends on the competition between solutes for the active sites of the absorbent and is applicable to strongly retained solutes, which cannot be eluted by the mobile phase alone. It is assumed that the sample components distribute themselves on the column in zones according to their adsorption strength. To develop the separation, a substance (the displacer) that is even more strongly held on the stationary phase than any of the solutes is introduced into the mobile phase.

4.1.2 Concepts of reversed-phase HPLC

Liquid chromatography is a separation method in which a mixture of components is resolved into its constituent parts by passage through a chromatographic column. It is carried out by passing the mobile phase, containing the mixture of the components, through the stationary phase, which consists of a column packed with solid particles. Physical and chemical forces acting between the solutes and the two phases are responsible for the retention of solutes on the chromatographic column. It is the differences in the magnitude of these forces that determine the resolution and hence

separation of the individual solutes. The term reversed-phase liquid chromatography derived from the fact that the mobile phase is more polar than the stationary phase, which is the opposite of normal-phase chromatography. The reversed phase method is popular because of numerous advantages it has for the potential chromatographer. The inertness of the stationary phase allows the exploitation of a wide range of solvent effects through variation of the mobile phase composition. Analyses with a wide range of polarity can be separated by this technique. Also, the fact that it requires aqueous mobile phases means that reversed-phase liquid chromatography is generally compatible with most aqueous samples which can be directly injected onto the column without the need for pre-treatment.

When a sample is injected onto a column, the compounds that do not interact with the stationary phase will be eluted at time t_0 in the void volume V_0. The retention time of the sample (t_r) is the time from injection to the time of maximum concentration in the eluted peak. Quite simply, in order for any two solutes to be separated, they must be retained to a different extent during their passage through the column so that different volumes of solvent are required to elute each solute Figure (4.1).

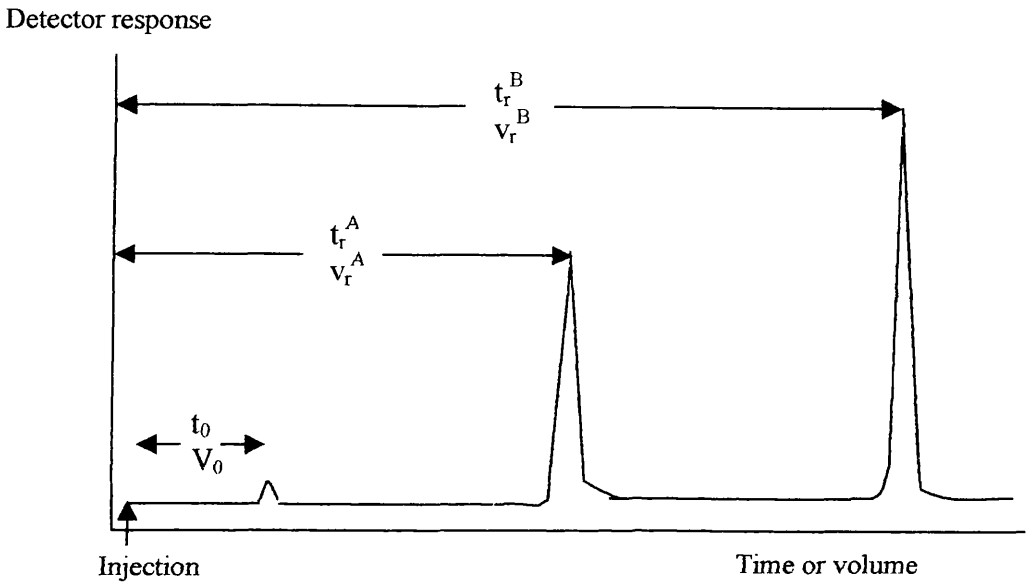

Figure (4.1) Chromatographic separation of solutes

Here components A and B are separated, whilst a non-retained compound would be eluted in the void volume.

4.1.3 Retention volume

The retention volume V_r is the volume of solvent required to elute the solute as measured from the centre of the chromatographic band. V_r and t_r can be related by:

$$V_r = t_r \times f \qquad (4.1)$$

Where f represents the flow rate.

In chromatographic separations, the ratio of the time spent by the solute in the stationary phase to the time it spends in the mobile phase must be optimised. This ratio is called the solute capacity factor and is given by:

$$k' = (t_r - t_0)/t_0 = (V_r - V_0)/V_0 \qquad (4.2)$$

where k' is the number of column volumes required to elute a particular solute, t_r is the time taken for a specific solute to reach the detector (retention time) and t_0 is the time taken for a non-retained species to reach the detector (hold up time). The same value of k' is obtained if volumes are used instead of times. The capacity factor of a column is mostly a function of the packing material but can be manipulated to a degree by varying the solvent strength. Often, only a rough estimation of k' is required, in which case k' can be determined by simple inspection of the chromatogram without exact calculation. From its capacity factor, the retention time of any solute can be calculated from equation (4.3)

$$t_r = t_m(1+k') = (L/u)\,(1+k') \qquad (4.3)$$

where L is the column length and u the average mobile phase velocity.

It is generally assumed that, initially, injection volumes will spread to give a Poisson distribution and then to a Gaussian distribution. A typical Gaussian peak is shown in Figure (4.2)

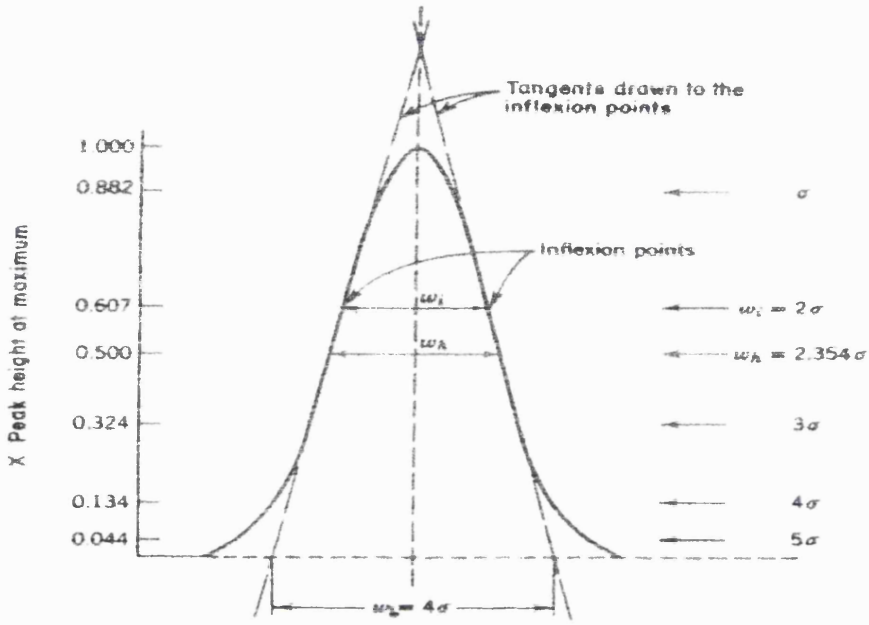

Figure (4.2) Characteristic properties of a Gaussian peak

The efficiency of a chromatographic column is measured by the number of theoretical plates (N) to which the column is equivalent. The term was originally used to describe the process of distillation and can be visualised as a series of hypothetical layers in which the solute concentrations in the relevant phases are assumed to be in equilibrium. The number of theoretical plates is also a measure of the amount of band broadening caused by a column. It can be calculated from the formula:

$$N = (t_r / \sigma)^2 \qquad (4.4)$$

where σ is the mathematical term representing the standard deviation of a Gaussian peak.

Assuming that peak shapes are Gaussian, various peak width measurements can be employed to calculate N. The most commonly used method is the tangent method where tangents to the curve at the point of inflexion intercept the baseline at a distance of 4σ apart. Equation (4. 4) can then be written as:

$$N = 16 \times (t_r / wb)^2 \qquad (4.5)$$

Alternatively, the peak width can be measured at the inflexion point (w_I) or at half height (w_h), giving rise to equations (4.6) and (4.7) respectively.

$$N = 4 \times (t_r / w_i)^2 \qquad (4.6)$$

$$N = 5.54 \text{ x } (t_r / w_h) \qquad (4.7)$$

N is often quoted as a measure of the column performance and the larger the number, the better the column. In general, N increases for smaller stationary phase particle diameters, low mobile phase flow rates, higher separation temperatures, less viscous solvents, and smaller solute molecules. The value of N is independent of the retention time of a solute but is proportional to column length. To enable a direct comparison to be made between different columns, it is more useful to use the height equivalent to a theoretical plate, H (also referred to as the plate height), which is given by the ratio of the column length (L) to the column plate number, equation (4.8)

$$H = L/N \qquad (4.8)$$

The selectivity of the chromatographic system is a measure of the difference in retention times (or volumes) between two given peaks and describes how effectively a chromatographic system can separate two compounds. Selectivity is defined in terms of α, which is simply the ratio of capacity factors:

$$\alpha = k'_2 / k'_1 \qquad (4.9)$$

The value for α can range from unity when the retention times of the two components are identical, to infinity if the first component of interest is eluted in the void volume.

Resolution is defined as the degree of separation between two peaks and is related to the chromatographic variables of selectivity, efficiency and time.

$$Rs = [N^{1/2}/2][(\alpha-1)(/\alpha+1)[k'_{AV}/(1+k'_{AV})] \qquad (4.10)$$

where $k'_{AV} = (k'_1 + k'_2)/2$; k_1 and k_2 are the capacity factors of the two peaks. The retention volume may be related to a physicochemical property of the solute-solvent system, the partition coefficient, K. This is defined as;

$$K \text{ or } L = \frac{\text{Concentration of the solute in stationary phase}}{\text{Concentration of the solute in mobile phase}}$$

The gas-liquid partition coefficient is related to the capacity factor by equation (4.11)

$$K = \beta k' \qquad (4.11)$$

Where β is the phase ratio and is equal to the ratio of the volume of the gas (V_g) and liquid (V_l) phase in the column. For gas-solid chromatography the phase ratio is given by the volume of the gas phase divided by the surface area of the stationary phase. The partition coefficient, K or L, is dimensionless. The gas-liquid partition coefficient is evaluated from the specific retention volume using the equation below.

$$K = V_G / \rho_l \qquad (4.12)$$

$$V_G = t_r [F_c * J^2 / W_l]$$

or $$V_G = t_r * [F_w (P_0 - P_w) T_C * J^2 / P_0 T_w W_l] \qquad (4.13)$$

The variable F_w is the gas flow rate at the column outlet, P_0 is the outlet pressure, P_i is the pressure inlet, P_w is the vapour of the water at the temperature of the soap-bubble flow, T_w, Tc is the column, temperature, W_l, is the weight of the stationary phase on the column, and t_r is the retention time. And substituting equation 4.13 into equation 4.12

$$K \text{ or } L = t_r * [F_w (P_0 - P_w) T_c * J^2 / P_0 T_w W_l \rho_l] \qquad (4.14)$$

Where ρ_l is the liquid phase density at the column temperature, and K is the gas-liquid partition coefficient.

4.2 Method for the calculation of the descriptors for PCBs

The original work of Kamlet and Taft, and co-workers [12,13] showed that it was indeed possible to define a rather small set of descriptors that could be combined in a linear way for the correlation of solute properties. After considerable preliminary work,[14,15] Abraham and co-workers eventually succeeded in constructing a new and more rigorous set of five solute descriptors,[16-20] as shown in Chapter 2.

Various experimental methods such as HPLC or GLC are used regularly to determine the descriptors. For volatile compounds they could be obtained [22] from a combination of experimental data including gas chromatographic and HPLC retention data, water-solvent partitions, and Ostwald solubility coefficients (Henry's constants). For compounds that are solid at room temperature, use can be made of solubilities in water and organic solvents, especially if the vapour pressures are known.[23] In some cases it was possible to select the most self-consistent vapour pressure for a particular compound from a possibly variable set of literature data, or in extreme cases, such as that of Bukminsterfullerene,[24] to predict the vapour pressure. But all these methods can be time consuming and very difficult to produce reliable data.

Recently it has been shown that the descriptors can be calculated just from the structure of a compound, using a group contribution approach, very rapidly indeed (about 700 compounds per min).[25] This then opens the way for combinatorial libraries or virtual libraries to be scanned or screened for relevant transport-related properties. However, the reliability of such calculations depends on a knowledge of the descriptors for a wide range of compounds that include different functional groups and different heterocyclic

moieties.[25,26] No PCBs were used in the training set for the calculation of descriptors, [23] and so it is necessary to determine these from experiment.

The solvation equations to be used are those described in Chapter 2,

$$\text{Log SP} = c + r.\ R_2 + s.\ \pi_2^{\ H} + a.\ \Sigma\ \alpha_2^{\ H} + b.\ \Sigma\ \beta_2^{\ H} + v.\ V_x \qquad (4.15)$$

or

$$\text{Log SP} = c + r.\ R_2 + s\pi_2^{\ H} + a.\ \Sigma\ \alpha_2^{\ H} + b.\ \Sigma\ \beta_2^{\ H} + \log L^{16} \qquad (4.16)$$

4.3 The determination of descriptors

The determination of descriptors is based on equation (4.15) and equation (4.16). Consider a property of a given compound for a process that is correlated by equation (4.15), such as water-solvent partition. If the values of log SP (where log SP is now log P) for several water-solvent systems are known, a series of equations for which we know the coefficients and the values of log P can be set up, and where the descriptors for the compound in equation (4.15) are the unknowns. Now the McGowan characteristic volume Vx (10^{-2} cm^3 mol^{-1}) can be calculated simply from a table of atomic constants and the number of bonds,[21] especially if the algorithm of Abraham et al[27] for the number of bonds in any molecule is used. For compounds that are liquid at 293 K, the R_2 descriptor (10^{-1} cm^3 mol^{-1}) can be obtained from the refractive index.[28] In case of solids, either the hypothetical refractive index can be calculated, or R_2 can be obtained through the addition of values for fragments or sub-structures. This leaves only three descriptors (π_2^H, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$) as the unknowns in the set of partition equation. Values of the

descriptors can be assigned as those that yield the calculated values of log P that best reproduce the observed log P values. It is not necessary to restrict the set of equations to partition equations. Any property can be introduced, such as an equation for a characterized HPLC system.

If the log L^{16} descriptor is required, then processes correlated through equation (4.16) have to be considered. One such process is that of the solubility of gases and vapours in organic solvents, expressed as log L (equivalent to the gas solvent partition coefficient). If values of log L are known for the given compound in several solvents, the corresponding equations can be solved for the four unknown descriptors (π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and log L^{16}). However, it is then more convenient to combine the log P and log L sets into one entire set of equations that can be solved for the four unknown descriptors.

4.4 Techniques use to calculated partition coefficients

A number of techniques have been used to measure partition coefficients, P, especially water-octanol partition coefficients, (Poct). The original method was the shake-flask method in which the concentrations of the compound are measured in octanol and water, shaken together until equilibrium is attained. However, the water concentrations may be inaccurate due to formation of molecular aggregates and there are analytical difficulties inherent in the measurement of extremely low aqueous equilibrium concentrations.[29]

Measurement and estimates based upon reverse-phase HPLC and thin–layer chromatography have achieved moderate success for other groups of lipophilic compounds but require the use of empirical correction factors in the case of PCBs.[29-34] Some success has been recently achieved in relating log Poct to calculated molar volumes.[35] Also total surface area (TSA), which is a function of molar volume, has been found to have a linear relationship with log Poct for compounds such as polyaromatic hydrocarbons and halobenzenes.[36-37] Reliable and consistent (P) values for a number of PCBs congeners have been obtained by the generator column technique, which obviates problem such as colloidal suspensions, absorption, and volatilization of the solute.[38,39]

4.5 References

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Chapter 5 The First Calculation of the descriptors for PCBs

5.0 Introduction

The solvation equations have been described previously (in chapters 1and 2). Both equations have terms in five descriptors. However the PCBs have no hydrogen bond acidity and hence the term $a.\Sigma\alpha^{H}_{2}$ will be redundant. The modified solvation equations are therefore,

$$\text{Log SP} = c + r.\ R_2 + s.\ \pi^{H}_{2} + b.\ \Sigma\ \beta^{H}_{2} + v.\ V_x \qquad (5.1)$$

$$\text{Log SP} = c + r.\ R_2 + s.\ \pi^{H}_{2} + b.\ \Sigma\ \beta^{H}_{2} + \log L^{16} \qquad (5.2)$$

Hence a total of five descriptors (over the two equations) are needed to characterise any PCB. Now the McGowan characteristic volume, V_x, can be calculated simply from the structure of the molecule, using a table of atomic and bond contributions. A simple computer program was available for the calculation. Therefore only four descriptors remained to be determined for each PCB, that is, R_2, π^{H}_{2}, $\Sigma\ \beta^{H}_{2}$, and $\log L^{16}$.

One of the main sets of physicochemical data on PCBs is that of GLC retention indices, I , defined by equation 5.3

$$I = 100\left[\frac{\log x - \log(z)}{\log x(z+1) - \log x(z)} + z\right] \qquad (5.3)$$

Here x is a retention parameter such as adjusted retention time or retention volume, and x (z+1) and x (z) are the corresponding quantities for an alkane with z+1 and z carbon atoms; the retention parameter for the compound in equation (5.3) should be between x (z+1) and x (z) .

Fortunately, the retention indices of PCBs on various liquid-phases in packed columns have been measured before and values were kindly supplied by Dr. Albro (personal communication) These values were scanned on to a disc, then put in a spreadsheet in twelve columns starting from non-polar and going on to polar stationary phases, as shown in Table 5.1.

Table 5.1. IUPAC No. with retention indices of PCBs, on various liquid-phases in packed columns, at 200^0 C

IUPAC	OV-101	F-50	APLEZON	OV-210	OV-3	OV-17	OV-25	AN-600	OV-225	CHOM	HK- 325	POLMPE
-	1396	1408	1494	1660	1466	1656	1754	1740	1832	2000	1466	1954
1	1509	1518	1578	1780	1585	1792	1901	1869	1971	2127	1589	2072
4	1622	1628	1662	1900	1704	1928	2048	2010	2110	2254	1712	2190
2	1575	1592	1679	1997	1654	1954	1960	1965	2062	2252	1603	2198
6	1688	1702	1763	2017	1773	1990	2107	2103	2201	2379	1806	2316
11	1754	1776	1964	2134	1842	2052	2166	2205	2292	2504	1900	2442
3	1585	1600	1692	1914	1661	1875	1973	1986	2085	2273	1695	2222
8	1698	1710	1776	2034	1780	2011	2120	2117	2224	2400	1818	2340
13	1764	1784	1877	2151	1849	2073	2179	2220	2315	2525	1912	2466
15	1774	1792	1890	2168	1856	2094	2192	2248	2338	2546	1924	2490
10	1619	1627	1678	1902	1700	1913	2041	1994	2104	2254	1697	2197
19	1732	1737	1762	2022	1819	2049	2188	2135	2243	2381	1820	2315
27	1798	1811	1863	2139	1888	2111	2247	2228	2334	2506	1914	2441
32	1808	1819	1876	2156	1895	2132	2260	2248	2357	2527	1926	2465
54	1842	1846	1862	2144	1934	2170	2328	2263	2376	2508	1928	2440
9	1658	1674	1744	1969	1736	1944	2052	2044	2136	2319	1758	2262
18	1771	1784	1828	2089	1855	2080	2199	2172	2275	2446	1881	2380
26	1837	1858	1929	2206	1924	2142	2258	2274	2366	2571	1975	2506
31	1847	1966	1942	2223	1931	2163	2271	2287	2399	2592	1987	2530
53	1881	1893	1928	2211	1970	2201	2339	2302	2408	2573	1989	2505
52	1920	1940	1994	2278	2006	2232	2350	2352	2440	2638	2050	2570
7	1668	1679	1758	1965	1747	1943	2061	2042	2145	2322	1770	2280
17	1781	1788	1842	2085	1866	2079	2209	2176	2284	2449	1893	2398
25	1847	1862	1943	2202	1935	2141	2267	2273	2375	2574	1987	2524
28	1857	1870	1956	2219	1942	2162	2280	2290	2398	2595	1999	2548
51	1891	1897	1942	2207	1991	2200	2348	2301	2417	2576	2001	2523
49	1930	1944	2008	2274	2017	2231	2359	2347	2449	2641	2062	2598
47	1940	1948	2022	2270	2028	2230	2368	2349	2458	2644	2074	2606
5	1696	1703	1773	2010	1779	1995	2130	2101	2215	2370	1802	2328
16	1809	1813	1857	2130	1898	2131	2277	2235	2354	2497	1925	2446
20	1875	1887	1958	2247	1967	2193	2336	2332	2445	2622	2019	2572
22	1885	1895	1971	2264	1974	2214	2349	2352	2468	2643	2031	2596

Table 5.1 cont.

46	1919	1922	1957	2252	2013	2252	2417	2360	2487	2624	2033	2571
44	1958	1969	2023	2319	2049	2283	2428	2406	2519	2689	2094	2636
42	1968	1973	2037	2315	2060	2282	2437	2405	2528	2692	2106	2654
40	1996	1998	2052	2360	2092	2334	2506	2465	2598	2740	2138	2702
14	1721	1730	1843	2053	1793	1982	2081	2119	2208	2424	1842	2381
34	1834	1840	1927	2173	1912	2118	2228	2252	2347	2551	1965	2499
36	1900	1914	2028	2290	1981	2180	2287	2349	2438	2676	2059	2625
39	1910	1922	2041	2307	1988	2201	2300	2369	2461	2697	2071	2649
73	1944	1949	2027	2295	2027	2239	2368	2377	2490	2678	2073	2624
72	1983	1996	2093	2362	2063	2270	2379	2423	2512	2743	2134	2689
68	1993	2000	2107	2358	2074	2269	2388	2422	2521	2746	2746	2707
58	2021	2025	2122	2403	2106	2321	2475	2481	2591	2749	2178	2755
80	2046	2052	2192	2446	2120	2308	2408	2498	2584	2848	2218	2808
12	1770	1779	1985	2139	1859	2081	2187	2214	2317	2525	1902	2471
33	1883	1889	1969	2259	1978	2217	2334	2347	2456	2652	2025	2589
35	1949	1963	2070	2376	2047	2279	2393	2444	2547	2777	2119	2715
37	1959	1971	2083	2393	2054	2300	2406	2464	2570	2798	2131	2739
71	1993	1998	2069	2381	2093	2338	2474	2472	2589	2779	2133	2714
70	2032	2045	2135	2448	2129	2369	2458	2518	2621	2844	2194	2779
66	2042	2049	2149	2444	2140	2368	2494	2517	2630	2487	2206	2797
56	2070	2074	2164	2489	2172	2420	2563	2576	2700	2895	2238	2845
79	2095	2101	2234	2532	2186	2407	2514	2593	2693	2949	2278	2898
77	2144	2150	2276	2618	2252	2506	2620	2699	2802	3050	2338	2988
30	1734	1741	1823	2009	1803	2004	2127	2075	2175	2363	1842	2328
50	1847	1851	1907	2129	1922	2140	2744	2208	2314	2490	1965	2446
69	1913	1925	2008	2246	1991	2202	2333	2305	2305	2405	2059	2572
75	1923	1933	2021	2263	1998	2223	2346	2325	2428	2636	2071	2596
104	1961	1960	2007	2251	2037	2261	2414	2333	2447	2617	2073	2571
103	1996	2007	2073	2318	2073	2292	2425	2379	2479	2682	2134	2636
100	2006	2011	2087	2314	2084	2291	2434	2378	2488	2685	2146	2654
98	2034	2036	2102	2359	2116	2343	2503	2437	2558	2733	2178	2702
121	2060	2063	2172	2402	2130	2330	2454	2454	2551	2787	2218	2755
119	2108	2112	2214	2488	2196	2429	2560	2549	2660	2888	2278	2845
155	2072	2074	2152	2358	2140	2352	2500	2410	2518	2726	2218	2702
24	1786	1772	1832	2087	1845	2074	2204	2179	2276	2438	1873	2378
45	1899	1882	1916	2207	1964	2210	2351	2312	2415	2565	1996	2496
59	1965	1956	2017	2324	2033	2272	2410	2409	2506	2690	2090	2622

Table 5.1 cont.

64	1975	1964	2030	2341	2040	2293	2423	2429	2529	2711	2102	2646
96	2009	1991	2016	2329	2079	2331	2491	2437	2549	2692	2104	2621
95	2048	2038	2082	2396	2115	2362	2502	2483	2580	2757	2165	2686
91	2058	2042	2096	2392	2126	2361	2511	2482	2589	2670	2177	2704
84	2086	2067	2111	2437	2158	2413	2580	2451	2569	2808	2209	2752
113	2111	2094	2181	2480	2172	2400	2531	2558	2562	2862	2249	2805
110	2160	2143	2223	2566	2238	2499	2637	2653	2761	2963	2969	2895
150	2124	2105	2161	2436	2182	2422	2577	2514	2619	2901	2249	2752
136	2176	2136	2170	2514	2224	2492	2654	2618	2720	2876	2290	2802
23	1818	1817	1915	2100	1892	2100	2212	2210	2307	2490	1933	2463
43	1931	1927	1999	2220	2011	2236	2359	2337	2446	2617	2056	2581
57	1997	2001	2100	2337	2080	2298	2418	2434	2537	2742	2150	2707
63	2007	2009	2113	2354	2097	2319	2431	2454	2560	2763	2162	2731
94	2041	2036	2099	2342	2126	2357	2499	2462	2579	2744	2164	2706
92	2090	2083	2165	2409	2162	2388	2510	2508	2611	2809	2225	2771
90	2090	2097	2179	2405	2173	2387	2519	2507	2620	2812	2237	2789
83	2118	2112	2194	2450	2205	2439	2598	2566	2690	2860	2269	2837
111	2143	2139	2264	2493	2219	2426	2539	2583	2683	2914	2309	2890
107	2192	2188	2306	2579	2295	2525	2645	2678	2792	3015	2369	2980
148	2156	2150	2244	2449	2229	2448	2585	2539	2650	2853	2309	2837
135	2208	2181	2253	2527	2271	2518	2662	2643	2751	2928	2340	2887
133	2240	2226	2336	2540	2318	2544	2670	2667	2782	2980	2400	2972
29	1827	1830	1925	2161	1898	2106	2217	2224	2312	2514	1949	2474
48	1940	1940	2009	2281	2017	2242	2364	2354	2451	2641	2072	2592
67	2006	2014	2110	2398	2086	2304	2423	2451	2452	2766	2166	2718
74	2016	2022	2123	2415	2093	2325	2436	2471	2565	2787	2178	2742
102	2050	2049	2109	2403	2132	2363	2504	2479	2584	2760	2180	2717
101	2090	2096	2175	2470	2394	2524	2515	2524	2616	2933	2241	2782
99	2100	2100	2199	2466	2179	2393	2524	2523	2625	2836	2253	2800
97	2127	2125	2204	2511	2211	2445	2593	2283	2695	2884	2285	2848
120	2152	2152	2274	2554	2225	2432	2544	2600	2688	2938	2325	2901
118	2201	2201	2316	2640	2291	2531	2650	2695	2797	3039	2389	2991
118	2201	2201	2316	2640	2291	2531	2650	2695	2797	3039	2389	2991
154	2165	2163	2254	2510	2235	2454	2590	2556	2655	2877	2325	2848
149	2217	2194	2263	2588	2277	2524	2667	2660	2756	2952	2356	2898
146	2250	2239	2346	2601	2324	2550	2675	2685	2787	3004	2416	2983
153	2258	2252	2356	2662	2330	2556	2680	2702	2792	3028	2432	2994
21	1961	1870	1958	2235	1945	2182	2317	2303	2396	2605	2432	2455

Table 5.1 cont.

41	1974	1990	2042	2355	2064	2318	2464	2436	2535	2732	2125	2663
55	2040	2054	2143	2472	2133	2380	2523	2533	2626	2857	2219	2789
60	2050	2062	2156	2489	2140	2401	2536	2553	2649	2879	2231	2813
89	2084	2089	2142	2477	2179	2439	2604	2561	2668	2859	2233	2788
87	2123	2136	2208	2544	2215	2470	2615	2602	2700	2924	2294	2853
85	2133	2140	2222	2540	2226	2469	2624	2606	2709	2927	2306	2871
82	2161	2165	2237	2585	2258	2521	2693	2665	2779	2975	2338	2919
108	2186	2192	2307	2628	2272	2508	2644	2682	2772	3029	2378	2972
105	2235	2241	2349	2714	2338	2607	2750	2777	2881	3130	2438	3062
140	2199	2203	2287	2584	2282	2530	2690	2638	2739	2968	2378	2919
132	2251	2234	2296	2662	2324	2600	2767	2742	2840	3043	2409	2969
130	2283	2279	2379	2675	2371	2626	2775	2767	2871	3095	2469	3054
138	2292	2292	2389	2736	2377	2632	2780	2784	2876	3119	2485	3065
128	2326	2332	2422	2810	2424	2708	2880	2880	2960	3210	2530	3136
38	1923	1942	2060	2330	2008	2232	2347	2406	2500	2710	2093	2686
76	2036	2052	2144	2450	2127	2368	2494	2539	2639	2837	2216	2804
78	2102	2126	2245	2567	2196	2430	2553	2636	2730	2962	2310	2930
81	2112	2134	2258	2584	2203	2451	2566	2656	2753	2983	2322	2954
125	2146	2161	2244	2572	2242	2489	2634	2664	2772	2964	2324	2929
124	2185	2208	2310	2639	2278	2520	2645	2710	2904	3029	2385	2994
123	2195	2212	2324	2635	2289	2519	2654	2709	2813	3032	2397	3012
122	2223	2237	2339	2680	2321	2571	2723	2768	2883	3080	2429	3060
127	2248	2264	2409	2723	2335	2558	2674	2785	2876	3134	2469	3113
118	2297	2313	2451	2809	2401	2657	2780	2880	2985	3235	2529	3203
168	2261	2275	2389	2679	2345	2580	2720	2741	3843	3073	2469	3060
164	2313	2306	2398	2757	2387	2650	2797	2845	2944	3148	2500	3110
162	2345	2351	2481	2770	2434	2676	2805	2870	2975	3200	2560	3195
167	2354	2364	2491	2831	2440	2682	2810	2887	2980	3224	2576	3206
157	2388	2404	2524	2905	2487	2758	2910	2969	3064	3315	2629	3277
169	2450	2476	2626	3000	2550	2808	2940	3072	3168	3420	2720	3418
65	1955	1960	2020	2274	2047	2221	2358	2341	2452	2612	2009	2614
93	2014	2011	2020	2333	2092	2319	2454	2394	2475	2627	2066	2625
112	2080	2085	2121	2450	2161	2381	2513	2500	2566	2752	2160	2751
117	2090	2093	2134	2467	2168	2402	2526	2520	2589	2773	2172	2775
152	2124	2120	2120	2455	2207	2440	2594	2519	2608	2754	2174	2750
151	2163	2167	2186	2522	2243	2471	2605	2565	2640	2819	2235	2815
147	2173	2171	2200	2518	2254	2470	2614	2564	2649	2822	2247	2833
134	2201	2196	2215	2563	2286	2522	2683	2623	2719	2870	2279	2801

Table 5.1 cont.

165	2226	2223	2285	2606	2300	2509	2634	2640	2712	2924	2319	2934
163	2275	2272	2327	2692	2366	2608	2740	2735	2821	3025	2379	3024
188	2239	2234	2265	2562	2310	2531	2680	2596	2679	2863	2319	2881
179	2291	2265	2274	2640	2352	2601	2757	2700	2780	2938	2350	2931
178	2323	2310	2357	2653	2399	2627	2765	2725	2811	2990	2410	3016
187	2332	2323	2367	2714	2405	2633	2770	2742	2816	3014	2426	3027
177	2366	2636	2400	2788	2452	2709	2807	2824	2900	3105	2479	3098
193	2428	2435	2502	2883	2515	2759	2900	2927	3004	3210	2570	3239
202	2406	2394	2378	2766	2480	2710	2860	2783	2840	3000	2420	3060
62	1953	1938	2015	2280	2019	2247	2386	2343	2451	2592	2095	2621
88	2011	2004	2013	2340	2064	2324	2459	2403	2474	2607	2064	2599
109	2077	2078	2114	2457	2133	2386	2518	2500	2565	2732	2158	2725
115	2087	2086	2127	2474	2140	2407	2531	2520	2588	2753	2170	2749
145	2121	2113	2113	2462	2179	2445	2599	2601	2607	2734	2172	2724
144	2160	2160	2179	2529	2215	2476	2610	2647	2639	2799	2233	2789
139	2170	2164	2193	2525	2226	2475	2619	2646	2648	2902	2245	2907
131	2198	2189	2208	2570	2258	2527	2688	2705	2718	2850	2277	2855
161	2223	2216	2278	2613	2272	2514	2639	2722	2711	2904	2317	2908
158	2272	2265	2320	2699	2338	2613	2745	2817	2920	3005	2377	2998
184	2236	2227	2258	2569	2282	2536	2685	2605	2679	2843	2317	2855
176	2288	2258	2267	2647	2324	2606	2762	2709	2779	2918	2348	2905
175	2320	2303	2350	2660	2371	2632	2770	2734	2910	2970	2408	2990
183	2330	2316	2360	2721	2377	2638	2775	2751	2815	2994	2424	3001
171	2363	2356	2393	2795	2424	2714	2875	2833	2899	3085	2477	3072
191	2425	2428	2495	2990	2487	2764	2905	2936	3003	3190	2568	3213
201	2403	2387	2371	2773	2452	2715	2865	2791	2839	2980	2418	3034
197	2400	2380	2364	2780	2424	2720	2870	2800	2838	2960	2416	3008
61	2039	2043	2127	2306	2110	2330	2470	2451	2570	2750	2200	2749
86	2123	2118	2180	2483	2206	2439	2583	2574	2686	2906	2266	2065
106	2189	2189	2281	2600	2275	2501	2642	2671	2777	2931	2360	2991
114	2199	2200	2294	2617	2282	2522	2655	2691	2800	2952	2372	3015
143	2233	2227	2280	2605	2321	2560	2723	2699	2819	2933	2374	2990
141	2272	2274	2346	2672	2357	2591	2734	2745	2851	2998	2435	3055
137	2282	2278	2360	2668	2368	2590	2743	2744	2860	3001	2447	3073
129	2310	2303	2375	2713	2400	2642	2812	2803	2930	3049	2479	3121
159	2335	2330	2445	2756	2414	2629	2763	2820	2923	3103	2519	3174
156	2384	2379	2487	2842	2480	2728	2869	2915	3032	3204	2579	3264

Table 5.1 cont.

182	2349	2341	2425	2712	2424	2651	2809	2776	2890	3042	2519	3121
174	2401	2372	2434	2790	2466	2721	2886	2880	2991	3117	2550	3171
172	2432	2417	2517	2803	2513	2747	2894	2905	3022	3169	2610	3256
180	2440	2430	2527	2864	2519	2753	2899	2922	3027	3193	2626	3267
170	2475	2470	2560	2939	2566	2829	2999	3004	3111	3284	2679	3338
189	2537	2542	2662	3033	2629	2879	3029	3107	3215	3389	2770	3479
199	2515	2501	2538	2916	2594	2830	2989	2962	3051	3179	2620	3300
196	2512	2494	2531	2923	2566	2035	2994	2971	3050	3159	2610	3274
194	2620	2608	2698	3066	3066	2708	2950	2664	2782	2311	2890	3540
116	2105	2133	2180	2480	2205	2459	2600	2557	2664	2782	2311	2890
142	2190	2183	2223	2570	2269	2513	2664	2579	2703	2929	2336	2868
160	2257	2257	2324	2687	2338	2575	2703	2676	2794	2954	2430	2994
166	2268	2265	2337	2704	2345	2596	2716	2696	2917	2975	2442	3018
186	2301	2292	2323	2692	2348	2634	2784	2704	2836	2956	2444	2993
185	2340	2339	2389	2759	2420	2665	2795	2749	2868	3021	2505	3058
181	2350	2343	2403	2755	2431	2664	2804	2748	2877	3024	2517	3076
173	2378	2368	2418	2800	2463	2716	2973	2808	2947	3072	2549	3124
192	2404	2395	2488	2843	2477	2703	2924	2825	2940	3126	2589	3177
190	2452	2444	2530	2929	2543	2802	2930	2920	3049	3227	2649	3267
204	2416	2406	2468	2799	2487	2725	2870	2781	2907	3065	2589	3124
200	2460	2437	2477	2077	2529	2795	2947	2505	3000	3140	2620	3174
198	2500	2482	2560	2090	2576	2821	2955	2910	3039	3192	2680	3259
203	2509	2495	2570	2951	2582	2927	2960	2927	3044	3216	2696	3270
195	2543	2535	2603	3025	2629	2903	3060	3009	3128	3307	2749	3341
205	2605	2607	2705	3120	2692	2953	3090	3112	3232	3412	2840	3482
208	2583	2566	2501	3003	2657	2904	3050	2967	3068	3202	2690	3303
207	2580	2559	2574	3010	2629	2909	3055	2976	3067	3182	2688	3277
206	2692	2673	2741	3153	2771	3024	3179	3147	3279	3381	2890	3543
209	2760	2738	2784	3240	3834	3098	3240	3152	3296	3404	2960	3546

5.1 Estimation of the excess molar refraction, R_2

The excess molar refraction is a measure of the ability of a solute to undergo dispersion interactions. It differs from the molar refraction in that it is the excess part of molar refraction above the theoretical value for an alkane having the same volume. It has been estimated for chlorobiphenyls by comparison with other derivatives such as the methylbiphenyls. The estimated values are shown in Table 5.2.

Table 5.2. R_2 values for PCBs

Biphenyl	1.36
2-chloro	add 0.12
3-chloro	add 0.15
4-chloro	add 0.14

The following representative calculations can be carried out for R_2.

2-Chlorobiphenyl = 1.36 +0.12 = 1.48
2,3'-Dichlorobiphenyl = 1.36 + 0.12 +0.15 = 1.62
3,3'-Dichlorobiphenyl = 1.36 + 0.15 +0.15 = 1.66
Decachlorobiphenyl = 1.36 +4*0.12 +4* 0.15+2*0.14 = 2.72

For the rest of the PCBs, values were calculated as shown in Table 5.2, and are given in Table 5.3.

Table 5.3. IUPAC No. for PCBs, and alkanes, estimated values of R_2 and $\Sigma\beta^H_2$, calculated values of V_x and some estimated (a) values of π^H_2 and log L^{16}.

IUPAC	R_2	π^H_2	β^H_2	V_x	Log L^{16}
-	1.36	0.990	0.26	1.324	6.014
1	1.48	1.120	0.19	1.447	6.650
2	1.51		0.20	1.447	
3	1.50	1.090	0.20	1.447	6.480
4	1.60		0.14	1.569	
5	1.63		0.16	1.569	
6	1.63		0.14	1.569	
7	1.62		0.16	1.569	
8	1.62		0.14	1.569	
9	1.63		0.16	1.569	
10	1.66		0.16	1.569	
11	1.66		0.14	1.569	
12	1.65		0.16	1.569	
13	1.65		0.14	1.569	
14	1.65		0.16	1.569	
15	1.64	1.200	0.13	1.569	7.920
16	1.75		0.10	1.691	
17	1.74		0.10	1.691	
18	1.75		0.10	1.691	
19	1.72		0.10	1.691	
20	1.78		0.10	1.691	
21	1.77		0.13	1.691	
22	1.77		0.10	1.691	
23	1.78		0.13	1.691	
24	1.75		0.13	1.691	
25	1.77		0.10	1.691	
26	1.78		0.10	1.691	
27	1.76		0.10	1.691	
28	1.76		0.10	1.691	
29	1.77		0.13	1.691	
30	1.74		0.13	1.691	
31	1.77		0.10	1.691	
32	1.74		0.10	1.691	
33	1.77		0.01	1.691	
34	1.78		0.01	1.691	
35	1.80		0.01	1.691	
36	1.79		0.01	1.691	
37	1.79		0.01	1.691	
38	1.80		0.13	1.691	
39	1.80		0.01	1.691	
40	1.90		0.06	1.814	
41	1.89		0.07	1.814	
42	1.89		0.07	1.814	

Table 5.3 continue

43	1.90		0.07	1.814	
44	1.90		0.07	1.814	
45	1.87		0.07	1.814	
46	1.87		0.07	1.814	
47	1.88		0.07	1.814	
48	1.89		0.07	1.814	
49	1.89	1.450	0.05	1.814	8.800
50	1.86		0.07	1.814	
51	1.86		0.06	1.814	
52	1.90		0.06	1.814	
53	1.87		0.06	1.814	
54	1.84		0.07	1.814	
55	1.92		0.07	1.814	
56	1.92		0.06	1.814	
57	1.93		0.07	1.814	
58	1.93		0.06	1.814	
59	1.91		0.07	1.814	
60	1.91		0.07	1.814	
61	1.92		0.13	1.814	
62	1.89		0.13	1.814	
63	1.92		0.07	1.814	
64	1.89		0.07	1.814	
65	1.89		0.13	1.814	
66	1.91		0.06	1.814	
67	1.92		0.07	1.814	
68	1.92		0.06	1.814	
69	1.89		0.07	1.814	
70	1.89		0.06	1.814	
71	1.89		0.06	1.814	
72	1.93		0.06	1.814	
73	1.90		0.06	1.814	
74	1.91		0.07	1.814	
75	1.88		0.07	1.814	
76	1.91		0.07	1.814	
77	1.94		0.06	1.814	
78	1.95		0.07	1.814	
79	1.95		0.06	1.814	
80	1.96		0.06	1.814	
81	1.94		0.07	1.814	
82	2.04		0.03	1.936	
83	2.05		0.03	1.936	
84	2.02		0.03	1.936	
85	2.03		0.03	1.936	
86	2.04		0.07	1.936	
87	2.04		0.03	1.936	
88	2.01		0.07	1.936	
89	2.01		0.03	1.936	
90	2.04		0.03	1.936	

Table 5.3 continue

91	2.01		0.03	1.936	
92	2.05		0.03	1.936	
93	2.02		0.07	1.936	
94	2.02		0.03	1.936	
95	2.02		0.03	1.936	
96	1.99		0.03	1.936	
97	2.04		0.03	1.936	
98	2.01		0.03	1.936	
99	2.03		0.03	1.936	
100	2.00		0.03	1.936	
101	2.04	1.600	0.02	1.936	9.230
102	2.01		0.03	1.936	
103	2.01		0.03	1.936	
104	1.98		0.03	1.936	
105	2.04		0.03	1.936	
106	2.07		0.07	1.936	
107	2.07		0.03	1.936	
108	2.04		0.03	1.936	
109	2.04		0.07	1.936	
110	2.04		0.03	1.936	
111	2.08		0.03	1.936	
112	2.05		0.07	1.936	
113	2.05		0.03	1.936	
114	2.06		0.07	1.936	
115	2.03		0.07	1.936	
116	2.04		0.13	1.936	
117	2.04		0.07	1.936	
118	2.06		0.03	1.936	
118	2.06		0.03	1.936	
119	2.03		0.03	1.936	
120	2.07		0.03	1.936	
121	2.04		0.03	1.936	
122	2.07		0.03	1.936	
123	2.09		0.03	1.936	
124	2.07		0.03	1.936	
125	2.04		0.03	1.936	
127	2.10		0.03	1.936	
128	2.18		0.00	2.059	
129	2.19		0.03	2.059	
130	2.19		0.00	2.059	
131	2.16		0.03	2.059	
132	2.16		0.03	2.059	
133	2.20		0.00	2.059	
134	2.17		0.03	2.059	
135	2.17		0.00	2.059	
136	2.14		0.00	2.059	
137	2.18		0.03	2.059	
138	2.18		0.00	2.059	

Table 5.3 continue

139	2.15		0.03	2.059	
140	2.18		0.00	2.059	
141	2.19		0.03	2.059	
142	2.16		0.07	2.059	
143	2.16		0.03	2.059	
144	2.16		0.03	2.059	
145	2.13		0.03	2.059	
146	2.19		0.00	2.059	
147	2.16		0.03	2.059	
148	2.16		0.00	2.059	
149	2.16		0.00	2.059	
150	2.13		0.03	2.059	
151	2.17		0.03	2.059	
152	2.14		0.03	2.059	
153	2.18	1.630	0.00	2.059	9.890
154	2.15		0.00	2.059	
155	2.12		0.00	2.059	
156	2.21		0.03	2.059	
157	2.21		0.00	2.059	
158	2.18		0.03	2.059	
159	2.20		0.03	2.059	
160	2.19		0.07	2.059	
161	2.19		0.03	2.059	
162	2.20		0.00	2.059	
163	2.19		0.03	2.059	
164	2.19		0.00	2.059	
165	2.20		0.03	2.059	
166	2.18		0.07	2.059	
167	2.21		0.00	2.059	
168	2.18		0.00	2.059	
169	2.21		0.00	2.059	
170	2.33		0.00	2.181	
171	2.30		0.00	2.181	
172	2.34		0.00	2.181	
173	2.31		0.03	2.181	
174	2.31		0.00	2.181	
175	2.31		0.00	2.181	
176	2.31		0.00	2.181	
177	2.28		0.00	2.181	
178	2.31		0.00	2.181	
179	2.32		0.00	2.181	
180	2.29		0.00	2.181	
181	2.30		0.03	2.181	
182	2.30		0.00	2.181	
183	2.30		0.00	2.181	
184	2.27		0.00	2.181	
185	2.31		0.03	2.181	
186	2.28		0.03	2.181	

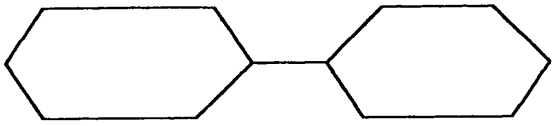
Table 5.3 continue

187	2.31		0.00	2.181	
188	2.28		0.00	2.181	
189	2.36		0.00	2.181	
190	2.33		0.03	2.181	
191	2.33		0.00	2.181	
192	2.34		0.03	2.181	
193	2.34		0.00	2.181	
194	2.48		0.00	2.303	
195	2.45		0.00	2.303	
196	2.45		0.00	2.303	
197	2.42		0.00	2.303	
198	2.46		0.00	2.303	
199	2.46		0.00	2.303	
200	2.43		0.00	2.303	
201	2.43		0.00	2.303	
202	2.44		0.00	2.303	
203	2.48		0.00	2.303	
204	2.52		0.00	2.303	
205	2.48		0.00	2.303	
206	2.75		0.00	2.426	
207	2.57		0.00	2.426	
208	2.58		0.00	2.426	
209	2.60		0.00	2.548	
266	0.00	0.000	0.00	1.799	5.696
268	0.00	0.000	0.00	2.081	6.705
270	0.00	0.000	0.00	2.363	7.714
272	0.00	0.000	0.00	2.645	8.722
274	0.00	0.000	0.00	2.927	9.731
276	0.00	0.000	0.00	3.208	10.740
278	0.00	0.000	0.00	3.490	11.758
280	0.00	0.000	0.00	3.772	12.770
282	0.00	0.000	0.00	4.054	13.782
284	0.00	0.000	0.00	4.336	14.794
286	0.00	0.000	0.00	4.617	15.785
289	0.00	0.000	0.00	5.040	17.320

a- Approximate estimated values by comparison to benzene and the polychlorobenzenes.

5.2 Estimation of overall hydrogen-bond basicity $\Sigma\beta^{H}_{2}$, for PCBs.

As a first step, a rough estimate of $\Sigma\beta^{H}_{2}$ was made by comparison to values for the polychlorobenzenes. Since only estimates were needed to start the analysis, it was felt that $\Sigma\beta^{H}_{2}$ values just based on the number of chlorine atoms in each PCBs ring would suffice. The values of $\Sigma\beta^{H}_{2}$ were calculated as shown in Table 5.4.



Ring A Ring B

Table 5.4. Estimated values of $\Sigma\beta^{H}_{2}$ for PCBs

No. of chlorine atoms in ring		**Total**	$\Sigma\beta^{H}_{2}$
A	B	A+B	
1	0	1	0.20
1	1	2	0.14
2	0	2	0.16
2	1	3	0.10
2	2	4	0.06
3	0	3	0.13
3	1	4	0.07
3	2	5	0.03
3	3	6	0.00
4	0	4	0.13

4	1	5	0.06
4	2	6	0.02
4	3	7	0.00
5	0	5	0.13
5	1	6	0.07
5	2	7	0.03
5	3	8	0.00
5	4	9	0.00
5	5	10	0.00

The values of $\Sigma\beta^H_2$ for all the PCBs have been calculated as shown in Table 5.4, and are listed in Table 5.3.

5.3 The calculation of $\log L^{16}$

Since retention indices are logarithmic, the solvation equation 5.2 becomes,

$$I = c + rR_2 + s\pi^H_2 + b\Sigma\beta^H_2 + l \log L^{16} \qquad (5.2)$$

Now GLC phases are almost all non-acidic so that the $\Sigma\beta^H_2$ term is also redundant, leading to,

$$I = c + rR_2 + s\pi^H_2 + l \log L^{16} \qquad (5.3)$$

For the non-polar phases such as OV-101, F-50 and Apiezon the $s\,\pi^H_2$ term will also be nearly zero, and hence,

$$I = c + r\,R_2 + l \log L^{16} \qquad (5.4)$$

In order to obtain a linear regression to get the values of log L^{16} for all PCBs using equation (5.2) or equation (5.3), a number of π^{H}_{2} and log L^{16} values for PCBs are necessary to start with (approximate estimated values by comparison to benzene and the polychlorobenzenes) note that π^{H}_{2} and log L^{16} are known for the alkanes, Table 5.3. The first step was to carry out linear regressions using the software system Smart for I-values on 12 stationary phases using equation (5.2). Details of the regressions are given in Table (5.5); results were not very satisfactory because many regression coefficients were negative, even though the equations are statistically good.

Table 5.5 Details of multiple linear regression for all the PCBs using equation 5.2.

Phase ----		**Coefficients**					**— Statistics —**		
Name	**No.**	**c**	**r**	**s**	**b**	**l**	**F**	**r^2**	**n**
OV-101	1	72.50	535.32	-583.12	119.93	197.98	2987	0.999	221
F-50	2	72.65	457.71	-480.40	198.45	197.96	3009	0.999	221
APIEZ	3	71.86	482.97	-459.72	304.29	198.04	1514	0.997	221
OV-210	4	71.12	282.68	-120.61	423.66	198.11	2276	0.996	221
OV-3	5	74.50	-97.48	340.32	-40.25	197.75	490	0.995	221
OV-17	6	73.26	-130.47	347.91	462.66	197.89	939	0.995	221
OV-25	7	72.40	333.82	-56.12	698.48	197.99	2971	0.998	221
AN-600	8	71.32	148.07	-193.83	696.64	198.09	1025	0.996	221
OV-225	9	71.53	156.76	239.62	-889.4	198.05	8114	0.999	221
CHOMS	10	71.63	-127.75	770.8	907.1	198.06	6664	0.997	221
3HK-325	11	71.70	444.92	-364.7	96.33	198.12	1477	0.997	221
POLMPE	12	70.75	224.62	-264.11	871.49	198.11	708	0.996	221

The regressions were therefore repeated by leaving out the term ($s\ \pi^{H}{}_{2}$) since most of the coefficients were negative. This time some of the b-coefficients were also negative. So, finally, regressions were done using the simple equation (5.4). The coefficients for these regressions were all positive as shown in Table (5.6). Now, not only are the equations statistically very good, but the coefficients all make chemical sense.

Table 5.6 Details of multiple linear regression for all PCBs using equation 5.4

Phase	**Coefficients**			**---- Statistics ---**		
Name	**c**	**r**	**I**	**F**	**r^2**	**n**
OV-101	83.92	93.30	197.03	4945	0.9984	221
F-50	89.90	97.07	196.55	4841	0.9983	221
APIEZO	100.56	142.47	195.75	2152	0.9969	221
OV-210	99.18	287.54	198.86	1258	0.9952	221
OV-3	69.01	162.33	198.21	1256	0.9937	221
OV-17	106.13	269.22	195.26	1687	0.9953	221
OV-25	128.76	316.17	193.45	1706	0.9955	221
AN-600	122.42	321.09	193.99	1263	0.9937	221
OV-225	138.88	371.90	192.67	973	0.9918	221
CHOMS	138.08	494.66	192.75	764	0.9896	221
3HK-325	74.35	168.35	197.83	3277	0.9976	221
POLMPE	138.15	458.15	192.75	825	0.9904	221

Since the regression coefficients in Table 5.6 were all positive it was possible to calculate log L^{16} for all 209 PCBs; values are given in Table 5.7. The nomenclature is as follows. Results of calculations of log L^{16} from the first phase are denoted as log c1 and from the second phase, log c2 , and so on up to, log c12 , for POLMPE. The values of logc for the first three non polar phases were in good agreement because the equation which had been used, that is equation 5.4, was suitable for non polar phases. But for the other phases the equations were not so good because the phases started to be polar.

Table 5.7 log L^{16} calculated for twelve phases for all PCBs based on equation 5.4.

IUPAC	Log c1 OV-101	Log c2 F-50	Log c3 APIEZON	Log c4 OV-210	Log c5 OV-3	Log c6 OV-17	Log c7 OV-25	Log c8 AN-600	Log c9 OV-225	Log c10 CHOM	Log c11 HK-325	Log c12 POLMPE
-	6.015	6.035	6.130	5.973	5.934	6.062	6.179	6.087	6.163	6.170	5.877	6.189
1	6.532	6.535	6.472	6.409	6.436	6.594	6.742	6.554	6.652	6.521	6.397	6.516
4	7.049	7.035	6.814	6.846	6.939	7.125	7.306	7.082	7.142	6.872	6.917	6.843
2	6.853	6.897	6.966	7.473	6.760	7.382	6.998	6.999	7.067	7.092	6.442	7.098
6	7.370	7.397	7.308	7.399	7.262	7.401	7.562	7.512	7.557	7.443	7.366	7.425
11	7.690	7.759	8.313	7.953	7.586	7.677	7.818	7.988	7.971	8.015	7.816	8.008
3	6.908	6.942	7.040	7.064	6.803	6.991	7.082	7.124	7.205	7.227	6.916	7.247
8	7.425	7.443	7.382	7.501	7.306	7.522	7.646	7.600	7.695	7.578	7.435	7.574
13	7.746	7.804	7.876	8.054	7.629	7.798	7.902	8.082	8.110	8.149	7.885	8.156
15	7.872	7.924	8.059	8.376	7.795	8.126	8.230	8.491	8.538	8.669	8.082	8.661
10	7.005	7.001	6.852	6.768	6.869	6.965	7.172	6.900	6.995	6.718	6.790	6.737
19	7.550	7.531	7.238	7.293	7.420	7.579	7.834	7.528	7.601	7.222	7.360	7.206
27	7.866	7.887	7.725	7.831	7.736	7.841	8.073	7.941	7.996	7.768	7.802	7.765
32	7.927	7.938	7.805	7.948	7.788	7.976	8.173	8.077	8.154	7.929	7.879	7.937
54	8.052	8.026	7.661	7.739	7.902	8.033	8.361	7.989	8.060	7.573	7.804	7.570
9	7.217	7.255	7.211	7.154	7.075	7.165	7.278	7.207	7.219	7.132	7.124	7.145
18	7.734	7.755	7.553	7.591	7.578	7.696	7.841	7.669	7.709	7.483	7.643	7.472
26	8.055	8.117	8.047	8.144	7.901	7.972	8.097	8.145	8.123	8.054	8.093	8.055
31	8.110	8.671	8.121	8.246	7.945	8.094	8.181	8.228	8.314	8.189	8.162	8.203
53	8.236	8.250	7.977	8.038	8.059	8.150	8.369	8.140	8.168	7.834	8.087	7.835
52	8.419	8.475	8.292	8.336	8.217	8.268	8.377	8.348	8.276	8.094	8.370	8.101
7	7.273	7.285	7.290	7.148	7.139	7.174	7.341	7.214	7.285	7.173	7.193	7.262
17	7.790	7.780	7.632	7.585	7.641	7.705	7.910	7.706	7.775	7.524	7.712	7.589
25	8.110	8.142	8.126	8.138	7.965	7.981	8.160	8.156	8.189	8.095	8.162	8.172
28	8.166	8.188	8.200	8.240	8.008	8.102	8.244	8.260	8.328	8.230	8.231	8.320
51	8.291	8.276	8.055	8.032	8.174	8.159	8.432	8.152	8.234	7.875	8.156	7.953
49	8.475	8.500	8.371	8.330	8.280	8.276	8.440	8.339	8.342	8.135	8.439	8.270
47	8.530	8.525	8.450	8.324	8.344	8.285	8.503	8.366	8.408	8.176	8.508	8.336
5	7.410	7.402	7.359	7.364	7.292	7.426	7.681	7.501	7.629	7.396	7.346	7.488
16	7.927	7.903	7.701	7.800	7.794	7.957	8.245	7.993	8.119	7.747	7.866	7.815
20	8.248	8.264	8.195	8.353	8.118	8.234	8.501	8.444	8.533	8.319	8.315	8.397
22	8.303	8.310	8.269	8.455	8.162	8.355	8.584	8.563	8.672	8.453	8.384	8.545
46	8.428	8.398	8.125	8.247	8.276	8.412	8.772	8.439	8.578	8.098	8.309	8.178
44	8.612	8.622	8.440	8.545	8.433	8.529	8.780	8.627	8.686	8.359	8.592	8.444
42	8.668	8.647	8.519	8.539	8.497	8.538	8.843	8.638	8.752	8.400	8.661	8.561
40	8.805	8.770	8.588	8.754	8.650	8.790	9.183	8.931	9.096	8.623	8.815	8.786
14	7.528	7.530	7.702	7.554	7.347	7.332	7.395	7.561	7.554	7.625	7.531	7.715
34	8.040	8.025	8.037	7.976	7.841	7.849	7.942	8.031	8.025	7.951	8.042	8.018
36	8.370	8.397	8.546	8.558	8.180	8.153	8.231	8.515	8.478	8.573	8.509	8.648
39	8.416	8.432	8.605	8.630	8.208	8.247	8.282	8.601	8.578	8.657	8.561	8.749

Table 5.7 Cont.

73	8.541	8.520	8.461	8.422	8.322	8.304	8.470	8.477	8.535	8.301	8.486	8.382
72	8.725	8.745	8.776	8.720	8.480	8.421	8.478	8.665	8.592	8.562	8.769	8.647
68	8.780	8.770	8.855	8.715	8.543	8.430	8.541	8.676	8.658	8.603	11.871	8.765
58	8.918	8.892	8.924	8.930	8.696	8.682	8.974	8.964	9.002	8.593	8.991	8.990
80	9.030	9.015	9.260	9.105	8.743	8.574	8.579	9.001	8.907	9.029	9.168	9.194
12	7.776	7.779	8.428	7.993	7.680	7.839	7.943	8.051	8.120	8.149	7.834	8.182
33	8.293	8.279	8.259	8.429	8.182	8.370	8.507	8.538	8.610	8.500	8.354	8.509
35	8.614	8.641	8.753	8.983	8.505	8.646	8.763	8.988	9.024	9.072	8.804	9.091
37	8.669	8.687	8.827	9.084	8.549	8.768	8.846	9.108	9.163	9.206	8.873	9.240
71	8.795	8.775	8.682	8.876	8.664	8.824	9.034	8.983	9.069	8.851	8.798	8.872
70	8.992	9.014	9.020	9.218	8.845	8.983	8.952	9.220	9.235	9.188	9.106	9.209
66	9.034	9.024	9.077	9.168	8.884	8.951	9.105	9.182	9.243	7.285	9.150	9.255
56	9.171	9.146	9.146	9.384	9.038	9.203	9.445	9.470	9.587	9.376	9.303	9.481
79	9.284	9.269	9.482	9.559	9.084	9.095	9.143	9.508	9.493	9.579	9.480	9.684
77	9.537	9.523	9.704	10.013	9.425	9.616	9.707	10.071	10.078	10.129	9.792	10.175
30	7.551	7.541	7.535	7.197	7.323	7.321	7.486	7.185	7.209	7.078	7.455	7.226
50	8.068	8.042	7.877	7.634	7.825	7.852	10.479	7.672	7.699	7.429	7.974	7.553
64	8.388	8.403	8.371	8.187	8.149	8.128	8.305	8.122	7.595	6.911	8.424	8.136
75	8.444	8.449	8.444	8.288	8.193	8.249	8.389	8.242	8.252	8.135	8.493	8.284
104	8.589	8.537	8.300	8.080	8.307	8.306	8.577	8.118	8.158	7.780	8.418	7.916
103	8.753	8.761	8.616	8.378	8.464	8.423	8.585	8.305	8.266	8.040	8.701	8.182
100	8.808	8.786	8.694	8.373	8.528	8.432	8.648	8.317	8.332	8.081	8.770	8.300
98	8.946	8.909	8.764	8.588	8.681	8.685	8.988	8.604	8.676	8.304	8.923	8.525
121	9.064	9.031	9.100	8.763	8.727	8.577	8.686	8.642	8.582	8.508	9.100	8.728
119	9.312	9.285	9.321	9.217	9.069	9.097	9.250	9.149	9.167	9.057	9.412	9.219
155	9.087	9.048	8.939	8.421	8.712	8.579	8.793	8.283	8.256	7.986	9.032	8.263
24	7.810	7.694	7.573	7.581	7.527	7.665	7.867	7.705	7.714	7.441	7.603	7.462
45	8.327	8.194	7.915	8.017	8.029	8.197	8.431	8.192	8.204	7.792	8.122	7.789
59	8.643	8.551	8.402	8.556	8.345	8.459	8.671	8.625	8.599	8.338	8.564	8.347
69	8.703	8.602	8.483	8.672	8.396	8.594	8.771	8.762	8.757	8.498	8.641	8.519
96	8.828	8.690	8.339	8.464	8.511	8.651	8.959	8.637	8.668	8.143	8.566	8.152
95	9.012	8.914	8.654	8.762	8.668	8.768	8.967	8.825	8.771	8.403	8.849	8.418
91	9.068	8.939	8.733	8.756	8.732	8.777	9.029	8.836	8.837	7.978	8.918	8.535
84	9.205	9.061	8.802	8.971	8.885	9.029	9.370	8.660	8.714	8.668	9.071	8.760
113	9.318	9.184	9.138	9.147	8.931	8.921	9.067	9.162	8.620	8.871	9.248	8.964
110	9.571	9.438	9.360	9.601	9.272	9.442	9.632	9.668	9.672	9.421	12.896	9.455
150	9.346	9.200	8.978	8.805	8.916	8.924	9.174	8.803	8.761	8.868	9.180	8.499
136	9.605	9.353	9.017	9.188	9.120	9.268	9.556	9.322	9.266	8.713	9.379	8.735
23	7.958	7.908	7.976	7.603	7.740	7.757	7.860	7.815	7.817	7.634	7.881	7.831
43	8.475	8.408	8.318	8.039	8.242	8.288	8.423	8.271	8.307	7.985	8.400	8.158
57	8.796	8.770	8.812	8.593	8.565	8.564	8.679	8.721	8.721	8.556	8.850	8.741
63	8.851	8.816	8.885	8.694	8.659	8.686	8.763	8.841	8.860	8.691	8.919	8.889
94	8.977	8.904	8.741	8.486	8.724	8.743	8.951	8.717	8.766	8.336	8.844	8.522
92	9.211	9.128	9.057	8.784	8.881	8.860	8.959	8.904	8.874	8.596	9.127	8.788
90	9.216	9.204	9.135	8.779	8.944	8.869	9.022	8.915	8.940	8.637	9.196	8.905
83	9.353	9.276	9.205	8.994	9.098	9.121	9.414	9.203	9.284	8.861	9.349	9.130
111	9.466	9.398	9.541	9.169	9.144	9.013	9.060	9.241	9.190	9.064	9.526	9.334
107	9.719	9.652	9.762	9.623	9.535	9.534	9.624	9.747	9.775	9.614	9.838	9.824
148	9.494	9.415	9.380	8.827	9.129	9.016	9.167	8.882	8.864	8.542	9.458	8.869
135	9.753	9.567	9.419	9.211	9.332	9.360	9.548	9.401	9.369	8.906	9.606	9.104
133	9.901	9.782	9.821	9.233	9.545	9.452	9.541	9.475	9.472	9.098	9.884	9.474
29	8.009	7.979	8.034	7.929	7.778	7.802	7.902	7.904	7.862	7.784	7.970	7.912
48	8.526	8.480	8.376	8.366	8.280	8.333	8.466	8.375	8.352	8.135	8.490	8.239

Table 5.7 Cont.

67	8.846	8.841	8.870	8.919	8.604	8.609	8.722	8.825	8.300	8.707	8.939	8.822
74	8.902	8.887	8.944	9.020	8.647	8.730	8.805	8.945	8.905	8.841	9.008	8.970
102	9.027	8.975	8.800	8.812	8.762	8.787	8.993	8.821	8.811	8.445	8.933	8.603
101	9.216	9.199	9.115	9.110	10.059	9.570	9.001	9.003	8.919	9.265	9.216	8.869
99	9.271	9.224	9.245	9.105	8.983	8.913	9.064	9.015	8.985	8.788	9.285	8.986
97	9.404	9.347	9.263	9.320	9.136	9.166	9.404	7.761	9.329	9.011	9.439	9.211
120	9.516	9.469	9.599	9.495	9.182	9.058	9.102	9.345	9.235	9.214	9.615	9.415
118	9.770	9.723	9.821	9.949	9.523	9.579	9.666	9.851	9.820	9.764	9.947	9.905
154	9.544	9.486	9.439	9.153	9.167	9.060	9.209	8.986	8.909	8.692	9.547	8.950
149	9.804	9.638	9.477	9.537	9.371	9.405	9.591	9.506	9.414	8.039	9.695	9.465
146	9.957	9.853	9.880	9.559	9.583	9.497	9.583	9.585	9.517	9.249	9.973	9.555
153	10.002	9.924	9.938	9.885	9.622	9.541	9.625	9.689	9.562	9.399	10.063	9.636
21	8.689	8.183	8.203	8.307	8.015	8.191	8.419	8.311	8.298	8.256	10.411	7.814
41	8.698	8.734	8.545	8.743	8.517	8.722	8.983	8.798	8.788	8.607	8.757	8.608
55	9.019	9.045	9.039	9.297	8.841	8.998	9.238	9.248	9.203	9.179	9.207	9.190
60	9.074	9.090	9.112	9.398	8.884	9.120	9.322	9.368	9.341	9.319	9.276	9.338
89	9.200	9.178	8.968	9.190	8.999	9.176	9.510	9.243	9.247	8.958	9.201	8.971
87	9.383	9.403	9.284	9.488	9.156	9.294	9.518	9.405	9.355	9.218	9.484	9.237
85	9.439	9.428	9.362	9.482	9.220	9.302	9.581	9.442	9.421	9.260	9.553	9.354
82	9.576	9.550	9.432	9.698	9.373	9.555	9.921	9.730	9.765	9.483	9.707	9.579
108	9.703	9.688	9.789	9.917	9.444	9.488	9.668	9.818	9.729	9.763	9.909	9.854
105	9.952	9.937	10.004	10.356	9.777	9.995	10.216	10.307	10.295	10.287	10.212	10.321
140	9.703	9.674	9.585	9.487	9.380	9.408	9.677	9.359	9.287	9.087	9.790	9.247
132	9.976	9.842	9.646	9.915	9.608	9.794	10.108	9.928	9.850	9.528	9.963	9.554
130	10.124	10.056	10.048	9.937	9.821	9.886	10.100	10.007	9.953	9.721	10.241	9.923
138	10.175	10.127	10.107	10.263	9.859	9.930	10.142	10.112	9.998	9.871	10.330	10.004
128	10.347	10.331	10.275	10.641	10.096	10.320	10.659	10.606	10.434	10.343	10.558	10.372
38	8.482	8.534	8.702	8.748	8.308	8.406	8.525	8.792	8.780	8.724	8.672	8.941
76	9.003	9.039	9.051	9.199	8.819	8.951	9.105	9.296	9.289	9.101	9.200	9.292
78	9.319	9.396	9.538	9.738	9.134	9.213	9.345	9.729	9.685	9.647	9.642	9.850
81	9.375	9.442	9.612	9.839	9.178	9.334	9.428	9.849	9.823	9.781	9.711	9.999
125	9.500	9.530	9.468	9.631	9.293	9.391	9.616	9.725	9.729	9.426	9.636	9.631
124	9.684	9.754	9.783	9.929	9.450	9.508	9.624	9.912	10.356	9.686	9.919	9.897
123	9.725	9.765	9.840	9.879	9.489	9.476	9.638	9.874	9.845	9.650	9.962	9.943
122	9.877	9.902	9.931	10.139	9.667	9.770	10.027	10.211	10.247	9.951	10.141	10.240
127	9.989	10.024	10.267	10.314	9.713	9.662	9.725	10.249	10.153	10.154	10.318	10.443
118	10.257	10.293	10.511	10.812	10.078	10.224	10.338	10.805	10.796	10.781	10.655	11.005
168	10.017	10.041	10.107	9.972	9.698	9.664	9.832	9.890	15.017	9.632	10.250	9.978
164	10.277	10.193	10.145	10.356	9.901	10.009	10.214	10.410	10.332	9.996	10.398	10.214
162	10.434	10.417	10.562	10.407	10.130	10.128	10.239	10.522	10.474	10.240	10.693	10.631
167	10.475	10.479	10.606	10.704	10.152	10.145	10.248	10.593	10.480	10.339	10.765	10.664
157	10.648	10.682	10.775	11.082	10.389	10.534	10.765	11.016	10.916	10.811	11.033	11.033
169	10.962	11.049	11.296	11.567	10.707	10.790	10.920	11.547	11.456	11.355	11.493	11.764
65	8.602	8.581	8.432	8.330	8.432	8.225	8.435	8.308	8.357	7.985	8.171	8.353
93	8.840	8.777	8.337	8.440	8.552	8.548	8.718	8.366	8.226	7.729	8.349	8.102
112	9.160	9.138	8.832	8.994	8.876	8.824	8.974	8.863	8.640	8.300	8.798	8.684
117	9.216	9.184	8.905	9.095	8.919	8.945	9.058	8.982	8.779	8.435	8.867	8.832
152	9.341	9.272	8.761	8.887	9.034	9.002	9.246	8.812	8.685	8.080	8.792	8.465
151	9.596	9.570	9.186	9.405	9.314	9.326	9.499	9.248	9.082	8.725	9.203	9.087
147	9.580	9.521	9.155	9.179	9.255	9.128	9.317	9.011	8.859	8.381	9.144	8.848
134	9.718	9.644	9.225	9.394	9.408	9.381	9.657	9.298	9.203	8.605	9.298	8.658
165	9.830	9.766	9.561	9.570	9.454	9.273	9.355	9.336	9.109	8.808	9.474	9.277
163	10.084	10.020	9.782	10.024	9.795	9.794	9.919	9.842	9.694	9.357	9.786	9.768

Table 5.7 Cont.

188	9.858	9.783	9.400	9.228	9.439	9.275	9.462	8.977	8.783	8.286	9.406	8.812
179	10.103	9.921	9.417	9.567	9.618	9.579	9.794	9.447	9.230	8.572	9.529	8.976
178	10.271	10.155	9.848	9.648	9.864	9.725	9.852	9.592	9.410	8.868	9.841	9.441
187	10.316	10.221	9.899	9.960	9.894	9.756	9.878	9.680	9.436	8.992	9.922	9.498
177	10.503	11.828	10.090	10.382	10.155	10.187	10.444	10.152	9.930	9.542	10.215	9.938
193	10.789	10.776	10.567	10.779	10.424	10.360	10.501	10.584	10.354	9.932	10.624	10.527
202	10.630	10.518	9.861	10.035	10.166	9.971	10.131	9.676	9.310	8.586	9.781	9.360
62	8.591	8.469	8.407	8.360	8.290	8.358	8.579	8.318	8.352	7.881	8.606	8.390
88	8.829	8.746	8.309	8.491	8.419	8.587	8.761	8.429	8.240	7.651	8.347	7.990
109	9.150	9.108	8.803	9.044	8.743	8.863	9.017	8.879	8.654	8.222	8.797	8.573
115	9.205	9.153	8.877	9.145	8.786	8.985	9.100	8.999	8.793	8.357	8.866	8.721
145	9.331	9.241	8.733	8.937	8.901	9.042	9.288	9.251	8.699	8.002	8.791	8.354
144	9.514	9.465	9.048	9.235	9.058	9.159	9.296	9.439	8.807	8.262	9.074	8.620
139	9.570	9.491	9.127	9.230	9.122	9.168	9.359	9.450	8.873	8.822	9.143	9.256
131	9.707	9.613	9.196	9.445	9.275	9.420	9.699	9.738	9.217	8.527	9.296	8.962
161	9.820	9.736	9.532	9.620	9.321	9.312	9.397	9.775	9.123	8.730	9.473	9.166
158	10.073	9.990	9.754	10.074	9.662	9.833	9.961	10.282	10.227	9.279	9.785	9.656
184	9.848	9.752	9.372	9.278	9.306	9.315	9.504	9.040	8.802	8.208	9.405	8.701
176	10.093	9.890	9.388	9.618	9.485	9.618	9.837	9.510	9.244	8.494	9.527	8.865
175	10.255	10.119	9.813	9.684	9.722	9.751	9.878	9.639	9.924	8.764	9.831	9.306
183	10.311	10.190	9.871	10.010	9.761	9.796	9.920	9.743	9.450	8.914	9.920	9.387
171	10.478	10.394	10.040	10.388	9.998	10.185	10.437	10.166	9.886	9.386	10.188	9.755
191	10.779	10.745	10.539	11.340	10.291	10.400	10.543	10.647	10.368	9.854	10.622	10.415
201	10.620	10.487	9.833	10.085	10.033	10.011	10.173	9.734	9.324	8.508	9.779	9.249
197	10.609	10.456	9.804	10.135	9.900	10.050	10.215	9.797	9.338	8.430	9.777	9.138
61	9.014	8.989	8.957	8.449	8.725	8.742	8.965	8.825	8.912	8.624	9.111	8.983
86	9.383	9.311	9.140	9.177	9.111	9.135	9.353	9.261	9.282	9.125	9.343	5.149
106	9.704	9.657	9.635	9.730	9.434	9.411	9.608	9.711	9.697	9.178	9.792	9.882
114	9.760	9.718	9.708	9.832	9.478	9.532	9.692	9.831	9.836	9.312	9.861	10.030
143	9.885	9.806	9.564	9.624	9.593	9.589	9.880	9.707	9.741	8.957	9.786	9.662
141	10.069	10.031	9.880	9.922	9.750	9.707	9.888	9.894	9.849	9.217	10.069	9.928
137	10.124	10.056	9.958	9.916	9.814	9.715	9.951	9.905	9.915	9.259	10.138	10.046
129	10.261	10.178	10.028	10.131	9.967	9.968	10.291	10.193	10.259	9.482	10.292	10.271
159	10.384	10.311	10.378	10.336	10.029	9.887	10.021	10.264	10.204	9.736	10.485	10.522
156	10.627	10.555	10.585	10.760	10.354	10.381	10.553	10.737	10.750	10.235	10.780	10.965
182	10.407	10.317	10.203	9.964	9.998	9.862	10.096	9.872	9.839	9.163	10.400	10.009
174	10.666	10.470	10.242	10.348	10.202	10.207	10.478	10.391	10.344	9.527	10.548	10.245
172	10.810	10.684	10.644	10.370	10.414	10.299	10.470	10.471	10.447	9.720	10.826	10.615
180	10.874	10.775	10.732	10.755	10.485	10.398	10.577	10.641	10.570	9.972	10.950	10.791
170	11.033	10.959	10.871	11.079	10.690	10.732	11.029	10.997	10.929	10.342	11.183	11.064
189	11.333	11.310	11.370	11.515	10.983	10.947	11.135	11.479	11.410	10.810	11.618	11.724
199	11.174	11.052	10.664	10.771	10.724	10.558	10.765	10.566	10.366	9.464	10.775	10.558
196	11.164	11.022	10.636	10.821	10.591	6.501	10.807	10.629	10.380	9.385	10.733	10.447
194	11.697	11.587	11.467	11.508	13.089	9.906	10.531	8.997	8.931	4.909	12.122	11.755
116	9.292	9.387	9.140	9.161	9.106	9.237	9.440	9.173	9.168	8.482	9.570	9.429
142	9.667	9.582	9.273	9.445	9.330	9.348	9.575	9.088	9.139	8.936	9.594	9.030
160	9.992	9.944	9.767	9.998	9.654	9.625	9.728	9.538	9.553	8.989	10.044	9.612
166	10.053	9.990	9.841	10.100	9.698	9.746	9.811	9.658	10.211	9.124	10.113	9.760
186	10.173	10.078	9.696	9.892	9.631	9.803	9.999	9.534	9.598	8.769	10.038	9.393
185	10.357	10.302	10.012	10.190	9.969	9.920	10.007	9.716	9.706	9.029	10.321	9.659
181	10.412	10.327	10.091	10.184	10.033	9.929	10.070	9.727	9.772	9.070	10.390	9.776
173	10.550	10.450	10.160	10.399	10.186	10.181	10.927	10.020	10.116	9.293	10.543	10.001
192	10.667	10.572	10.496	10.574	10.232	10.073	10.625	10.058	10.022	9.497	10.720	10.205

Table 5.7 Cont.

190	10.916	10.826	10.718	11.028	10.574	10.594	10.672	10.564	10.607	10.046	11.032	10.696
204	10.889	10.796	10.641	10.849	10.561	10.655	10.901	10.394	10.507	10.053	11.009	10.738
200	10.909	10.741	10.374	6.531	10.421	10.420	10.597	8.260	10.159	9.338	10.800	9.975
198	11.098	10.956	10.776	6.554	10.634	10.512	10.589	10.298	10.304	9.531	11.078	10.345
203	11.134	11.012	10.813	10.920	10.648	11.027	10.582	10.352	10.291	9.604	11.142	10.355
195	11.321	11.230	11.003	11.342	10.909	10.946	11.148	10.825	10.785	10.153	11.435	10.794
205	11.621	11.582	11.503	11.783	11.203	11.161	11.254	11.306	11.267	10.621	11.870	11.454
208	11.462	11.324	10.388	11.039	10.944	10.772	10.884	10.393	10.223	9.275	11.026	10.288
207	11.452	11.293	10.768	11.090	10.811	10.811	10.926	10.456	10.237	9.197	11.025	10.177
206	11.935	11.784	11.490	11.555	11.380	11.152	11.273	11.039	10.990	9.767	11.893	11.129
209	12.294	12.130	11.732	12.044	11.722	11.572	11.637	11.115	11.136	9.964	12.272	11.216
266	5.665	5.648	5.618	5.621	5.706	5.602	5.538	5.555	5.507	5.509	5.690	5.509
268	6.680	6.666	6.640	6.642	6.715	6.627	6.571	6.586	6.546	6.547	6.701	6.547
270	7.695	7.683	7.662	7.663	7.724	7.651	7.605	7.617	7.584	7.585	7.712	7.585
272	8.710	8.701	8.684	8.684	8.733	8.675	8.639	8.648	8.622	8.622	8.723	8.622
274	9.725	9.718	9.706	9.705	9.742	9.699	9.673	9.679	9.660	9.660	9.734	9.660
276	10.740	10.736	10.728	10.726	10.751	10.724	10.707	10.710	10.698	10.698	10.745	10.698
278	11.755	11.753	11.750	11.748	11.760	11.748	11.741	11.740	11.736	11.735	11.756	11.735
280	12.770	12.771	12.772	12.769	12.769	12.772	12.775	12.771	12.774	12.773	12.767	12.773
282	13.785	13.788	13.794	13.790	13.778	13.796	13.808	13.802	13.812	13.811	13.778	13.810
284	14.801	14.806	14.816	14.811	14.787	14.821	14.842	14.833	14.850	14.848	14.789	14.848
286	15.816	15.824	15.838	15.832	15.796	15.845	15.876	15.864	15.888	15.886	15.800	15.886
289	17.338	17.350	17.371	17.364	17.310	17.381	17.427	17.411	17.445	17.442	17.316	17.442

The second step was to take the average of the first three phases, i e. log L (c1+c2+c3). The average values were taken again to do the regression for the first three phases, OV-101, F-50, APIEZON. Then the values for these three phases were averaged again, and these values were taken along with the few original ones in order to get the best values for log c avg. , (log L best), as shown in Table 5.8.

Table 5.8. Average values for log L^{16} (log c123) from phases OV-101 (c1), F-50- (c2) ,and Aplezon (c3), together with the average values from repeated regressions (log c avg.).

IUPAC	Log 123 avg	Log c1 w-avg	Log c2 w-avg	Log c3 w-avg	Log c avg
-	6.010	6.001	6.022	6.095	6.060
1	6.650	6.491	6.502	6.451	6.513
4	6.923	6.981	6.982	6.806	6.966
2	6.871	6.803	6.857	6.955	6.905
6	7.313	7.293	7.337	7.310	7.358
11	7.877	7.604	7.691	8.335	7.921
3	6.480	6.859	6.903	7.030	6.964
8	7.372	7.349	7.383	7.385	7.417
13	7.763	7.661	7.737	7.889	7.809
15	7.920	7.813	7.877	8.065	7.952
10	6.905	6.927	6.940	6.848	6.953
19	7.386	7.456	7.457	7.244	7.439
27	7.769	7.761	7.805	7.742	7.826
32	7.835	7.824	7.858	7.823	7.890
54	7.848	7.930	7.932	7.682	7.913
9	7.183	7.142	7.195	7.212	7.228
18	7.625	7.632	7.675	7.567	7.681
26	8.015	7.944	8.030	8.071	8.073
31	8.242	8.000	8.580	8.146	8.301
53	8.087	8.107	8.150	8.005	8.154
52	8.326	8.283	8.369	8.328	8.395
7	7.239	7.199	7.227	7.291	7.283
17	7.679	7.688	7.702	7.646	7.734
25	8.069	8.000	8.056	8.151	8.126
28	8.128	8.057	8.103	8.225	8.184
51	8.142	8.163	8.177	8.085	8.207
49	8.800	8.339	8.395	8.407	8.448
47	8.435	8.396	8.421	8.487	8.502
5	7.346	7.333	7.342	7.362	7.391
16	7.787	7.822	7.822	7.717	7.844
20	8.177	8.134	8.176	8.222	8.236
22	8.237	8.191	8.223	8.296	8.294
46	8.250	8.297	8.297	8.156	8.317
44	8.489	8.473	8.515	8.478	8.558
42	8.543	8.530	8.541	8.558	8.611
40	8.651	8.664	8.661	8.629	8.721
14	7.541	7.445	7.465	7.713	7.587
34	7.976	7.929	7.939	8.061	8.034
36	8.379	8.253	8.306	8.579	8.437

Table 5.8 cont.

39	8.426	8.297	8.340	8.640	8.484
73	8.439	8.403	8.414	8.499	8.507
72	8.678	8.580	8.632	8.822	8.748
68	8.732	8.636	8.659	8.902	8.802
58	8.840	8.770	8.779	8.973	8.911
80	9.029	8.876	8.896	9.316	9.102
12	7.951	7.691	7.712	8.451	7.994
33	8.220	8.181	8.192	8.286	8.277
35	8.610	8.492	8.547	8.791	8.669
37	8.669	8.549	8.593	8.865	8.728
71	8.682	8.655	8.667	8.724	8.751
70	8.941	8.851	8.904	9.067	9.009
66	8.976	8.888	8.912	9.127	9.045
56	9.084	9.022	9.032	9.198	9.155
79	9.273	9.128	9.149	9.541	9.345
77	9.516	9.380	9.402	9.766	9.588
30	7.488	7.453	7.465	7.548	7.542
50	7.930	7.943	7.945	7.903	7.995
69	8.320	8.254	8.299	8.407	8.387
75	8.379	8.311	8.346	8.482	8.446
104	8.399	8.437	8.420	8.341	8.475
103	8.632	8.594	8.638	8.664	8.710
100	8.686	8.650	8.665	8.743	8.763
98	8.794	8.784	8.784	8.814	8.873
121	8.985	8.895	8.902	9.158	9.065
119	9.227	9.142	9.155	9.383	9.306
155	8.937	8.904	8.908	9.000	9.024
24	7.637	7.707	7.615	7.588	7.692
45	8.078	8.197	8.095	7.943	8.145
59	8.462	8.502	8.443	8.441	8.532
69	8.528	8.565	8.496	8.522	8.596
96	8.541	8.672	8.570	8.381	8.619
95	8.780	8.848	8.788	8.704	8.860
91	8.834	8.904	8.815	8.783	8.913
84	8.942	9.038	8.934	8.854	9.023
113	9.131	9.145	9.052	9.198	9.213
110	9.375	9.397	9.305	9.423	9.457
150	9.085	9.159	9.058	9.040	9.175
136	9.233	9.413	9.208	9.080	9.325
23	7.890	7.848	7.823	7.999	7.947
43	8.332	8.338	8.303	8.354	8.400
57	8.722	8.650	8.658	8.858	8.793
63	8.781	8.706	8.704	8.933	8.851
94	8.794	8.813	8.778	8.792	8.874
92	9.050	9.039	8.996	9.115	9.132
90	9.104	9.046	9.073	9.194	9.185
83	9.196	9.180	9.143	9.266	9.278
111	9.385	9.286	9.260	9.609	9.468
107	9.628	9.538	9.513	9.834	9.711
148	9.339	9.300	9.266	9.451	9.430
135	9.487	9.554	9.416	9.491	9.580
133	9.740	9.695	9.624	9.902	9.835
29	7.951	7.900	7.895	8.057	8.007

Table 5.8 cont.

48	8.392	8.390	8.375	8.413	8.460
67	8.783	8.701	8.729	8.917	8.853
74	8.842	8.758	8.776	8.991	8.911
102	8.855	8.864	8.850	8.851	8.934
101	9.230	9.046	9.068	9.174	9.177
99	9.167	9.102	9.095	9.305	9.247
97	9.257	9.231	9.214	9.324	9.338
120	9.446	9.337	9.332	9.668	9.528
118	9.689	9.589	9.585	9.893	9.771
154	9.399	9.351	9.338	9.510	9.490
149	9.548	9.606	9.488	9.549	9.640
146	9.803	9.752	9.696	9.961	9.896
153	9.890	9.798	9.768	10.019	9.955
21	8.299	8.572	8.097	8.229	8.358
41	8.590	8.560	8.627	8.584	8.659
55	8.964	8.872	8.931	9.089	9.034
60	9.023	8.928	8.977	9.163	9.092
89	9.036	9.035	9.052	9.022	9.115
87	9.275	9.211	9.270	9.345	9.356
85	9.329	9.268	9.296	9.425	9.410
82	9.438	9.402	9.416	9.496	9.519
108	9.646	9.527	9.552	9.860	9.727
105	9.883	9.773	9.799	10.078	9.964
140	9.561	9.503	9.521	9.661	9.654
132	9.729	9.776	9.689	9.721	9.821
130	9.982	9.917	9.898	10.132	10.076
138	10.043	9.969	9.969	10.191	10.136
128	10.224	10.139	10.171	10.362	10.318
38	8.514	8.362	8.441	8.739	8.573
76	8.962	8.858	8.927	9.101	9.031
78	9.346	9.163	9.275	9.598	9.418
81	9.405	9.220	9.322	9.673	9.476
125	9.418	9.326	9.396	9.532	9.499
124	9.657	9.503	9.614	9.855	9.740
123	9.692	9.540	9.622	9.914	9.777
122	9.820	9.693	9.760	10.006	9.903
127	10.009	9.799	9.878	10.349	10.094
118	10.272	10.071	10.150	10.595	10.354
168	9.963	9.813	9.884	10.191	10.055
164	10.111	10.068	10.034	10.231	10.205
162	10.377	10.222	10.254	10.655	10.471
167	10.425	10.260	10.314	10.701	10.520
157	10.606	10.431	10.515	10.872	10.702
169	11.007	10.742	10.878	11.402	11.102
65	8.470	8.465	8.476	8.470	8.538
93	8.570	8.677	8.652	8.381	8.651
112	8.961	8.989	9.007	8.886	9.043
117	9.020	9.046	9.053	8.960	9.102
152	9.033	9.152	9.127	8.820	9.125
151	9.369	9.424	9.438	9.244	9.451
147	9.326	9.385	9.372	9.222	9.419
134	9.435	9.519	9.492	9.293	9.529
165	9.624	9.625	9.609	9.637	9.719

Table 5.8 cont.

163	9.867	9.877	9.862	9.862	9.962
188	9.577	9.639	9.615	9.478	9.680
179	9.706	9.874	9.746	9.498	9.814
178	9.986	10.041	9.979	9.936	10.091
187	10.040	10.086	10.045	9.988	10.145
177	10.699	10.276	11.641	10.180	10.807
193	10.603	10.548	10.591	10.670	10.711
202	10.218	10.374	10.322	9.957	10.336
62	8.421	8.455	8.365	8.444	8.489
88	8.548	8.669	8.623	8.352	8.628
109	8.938	8.980	8.977	8.856	9.020
115	8.997	9.037	9.024	8.931	9.078
145	9.011	9.143	9.098	8.790	9.101
144	9.250	9.320	9.316	9.113	9.343
139	9.304	9.376	9.343	9.192	9.396
131	9.412	9.510	9.463	9.264	9.505
161	9.601	9.616	9.580	9.607	9.696
158	9.845	9.869	9.833	9.832	9.939
184	9.555	9.630	9.586	9.449	9.657
176	9.684	9.866	9.717	9.468	9.790
175	9.957	10.026	9.944	9.900	10.062
183	10.019	10.083	10.016	9.959	10.124
171	10.199	10.248	10.217	10.130	10.304
191	10.580	10.540	10.562	10.640	10.688
201	10.195	10.365	10.293	9.928	10.313
197	10.173	10.357	10.264	9.898	10.290
61	8.916	8.867	8.876	9.005	8.987
86	9.197	9.211	9.179	9.200	9.278
106	9.582	9.523	9.518	9.704	9.665
114	9.646	9.579	9.580	9.778	9.729
143	9.659	9.686	9.654	9.638	9.752
141	9.898	9.862	9.872	9.961	9.993
137	9.953	9.919	9.899	10.040	10.046
129	10.061	10.053	10.019	10.111	10.156
159	10.263	10.172	10.148	10.468	10.357
156	10.493	10.411	10.389	10.680	10.589
182	10.205	10.178	10.142	10.297	10.309
174	10.354	10.432	10.292	10.337	10.459
172	10.605	10.568	10.500	10.748	10.713
180	10.690	10.640	10.597	10.833	10.793
170	10.847	10.790	10.773	10.978	10.954
189	11.229	11.082	11.118	11.488	11.338
199	10.844	10.908	10.849	10.775	10.963
196	10.822	10.899	10.820	10.746	10.940
194	11.464	11.421	11.376	11.593	11.584
116	9.192	9.121	9.255	9.200	9.273
142	9.415	9.470	9.432	9.342	9.507
160	9.807	9.787	9.787	9.846	9.901
166	9.867	9.848	9.833	9.921	9.961
186	9.879	9.950	9.907	9.780	9.982
185	10.118	10.126	10.126	10.103	10.224
181	10.172	10.183	10.152	10.182	10.277
173	10.281	10.317	10.272	10.253	10.386

Table 5.8 cont.

192	10.471	10.428	10.389	10.597	10.579
190	10.713	10.675	10.642	10.822	10.820
204	10.695	10.706	10.656	10.724	10.776
200	10.558	10.651	10.545	10.479	10.675
198	10.825	10.832	10.753	10.890	10.943
203	10.866	10.865	10.806	10.928	10.986
195	11.067	11.054	11.027	11.120	11.185
205	11.449	11.346	11.371	11.630	11.569
208	10.925	11.172	11.102	10.502	11.058
207	11.041	11.163	11.073	10.888	11.171
206	11.593	11.610	11.536	11.634	11.736
209	11.910	11.970	11.882	11.877	12.052
266	5.700	5.889	5.817	5.490	5.644
268	6.710	6.892	6.826	6.530	6.662
270	7.710	7.894	7.834	7.569	7.680
272	8.720	8.897	8.842	8.609	8.698
274	9.730	9.900	9.850	9.648	9.716
276	10.740	10.902	10.858	10.688	10.735
278	11.760	11.905	11.866	11.728	11.753
280	12.770	12.908	12.874	12.767	12.771
282	13.780	13.911	13.883	13.807	13.789
284	14.790	14.913	14.891	14.846	14.807
286	15.790	15.916	15.899	15.886	15.826
289	17.320	17.420	17.411	17.445	17.353

5.4 The calculation of the solute dipolarity/polarisability parameter- π^{H}_{2}

In order to find the best values for π^{H}_{2}, similar calculations were started using the fourth and subsequent phases, which are all somewhat polar. Then equation 5.3, recast as equation 5.5, could be used to find π^{H}_{2}

$$\pi^{H}_{2} = [I - c - r R_2 - l \log L^{16}]/ s \qquad (5.5)$$

For eight phases from OV-210, up to POLMPE, multiple linear regressions were carried out, and used to back-calculate π^{H}_{2} values through equation 5.5. The obtained π^{H}_{2} values are given in Table 5.9. Unfortunately, the π^{H}_{2} values were not constant across the phases. For example, values for PCB 66 range form 1.403 to -0.138, the latter negative value being quite unrealistic. The most consistent values were obtained from phases 4,5,7 and 11, and therefore π^{H}_{2} values were averaged from these four phases only. These values are denoted as π 1st - rd .

Table 5.9 Values of π^{H}_{2}, for eight phases from (OV-210) up to POLMPE ,

based on equation 5.5 .

IUPAC	π c4 OV-210	π c5 OV-3	π c6 OV-17	πç7 OV-25	π c8 AN-600	π c9 OV-225	πç10 CHOMS	πç11 HK-325	πç12 POLMPE
	1.089	0.988	1.147	0.954	0.925	0.901	1.182	1.146	0.796
1	1.495	1.001	0.999	1.082	1.259	1.123	1.002	1.341	1.163
4	1.335	1.225	1.660	1.040	0.996	1.029	1.168	1.222	1.208
2	0.223	1.083	2.271	1.089	0.971	0.980	1.355	1.515	0.870
6	1.108	1.210	1.432	1.125	0.964	1.031	1.362	1.195	1.063
11	1.147	1.096	0.822	1.291	1.110	1.183	1.393	1.316	1.070
3	0.242	1.325	2.264	0.862	0.244	0.518	1.843	0.767	0.389
8	1.035	1.194	1.561	1.106	0.916	0.955	1.425	1.179	0.977
13	0.808	1.179	1.333	1.192	0.812	0.958	1.619	1.151	0.832
15	0.434	1.062	1.587	0.990	0.340	0.604	1.839	0.995	0.405
10	1.473	1.241	1.393	1.139	1.270	1.185	1.085	1.361	1.331
19	1.452	1.328	1.733	1.102	1.112	1.124	1.154	1.330	1.387
27	1.245	1.320	1.497	1.199	1.102	1.146	1.338	1.312	1.265
32	1.152	1.297	1.635	1.168	0.988	1.051	1.412	1.287	1.157
54	1.569	1.432	1.807	1.164	1.206	1.220	1.141	1.439	1.567
9	1.285	1.177	1.199	1.196	1.206	1.209	1.191	1.291	1.194
18	1.385	1.304	1.488	1.232	1.271	1.260	1.197	1.316	1.387
26	1.158	1.289	1.260	1.317	1.175	1.262	1.392	1.289	1.242
31	1.343	1.176	1.020	1.376	1.368	1.286	1.297	1.417	1.304
53	1.502	1.408	1.562	1.294	1.351	1.356	1.184	1.425	1.567
52	1.434	1.384	1.317	1.424	1.418	1.491	1.227	1.411	1.566
7	1.372	1.174	1.088	1.185	1.268	1.193	1.169	1.272	1.133
17	1.469	1.302	1.380	1.218	1.287	1.242	1.178	1.296	1.324
25	1.242	1.287	1.152	1.306	1.227	1.245	1.372	1.268	1.179
28	1.169	1.271	1.282	1.287	1.157	1.169	1.435	1.252	1.093
51	1.586	1.435	1.454	1.283	1.403	1.338	1.165	1.404	1.504
49	2.163	1.141	0.286	1.607	2.083	1.833	0.813	1.749	1.826
47	1.603	1.379	1.101	1.401	1.529	1.456	1.188	1.370	1.441
5	1.213	1.209	1.417	1.085	1.024	0.997	1.287	1.240	1.037
16	1.313	1.336	1.706	1.121	1.046	1.048	1.294	1.265	1.229
20	1.086	1.321	1.478	1.206	0.986	1.050	1.488	1.238	1.084
22	1.013	1.304	1.607	1.187	0.894	0.975	1.552	1.222	0.999
46	1.430	1.439	1.779	1.183	1.162	1.143	1.281	1.374	1.409
44	1.362	1.415	1.534	1.313	1.257	1.279	1.324	1.359	1.409
42	1.447	1.413	1.427	1.302	1.309	1.261	1.304	1.339	1.346
40	1.291	1.447	1.752	1.202	1.060	1.067	1.420	1.308	1.251
14	1.236	1.143	0.794	1.323	1.228	1.244	1.334	1.264	1.024
34	1.357	1.277	1.075	1.371	1.279	1.314	1.330	1.299	1.240
36	1.089	1.249	0.864	1.432	1.176	1.279	1.545	1.253	1.049
39	1.057	1.245	0.976	1.438	1.127	1.241	1.588	1.255	1.009
73	1.474	1.380	1.148	1.433	1.395	1.365	1.317	1.407	1.419
72	1.406	1.356	0.903	1.563	1.490	1.545	1.360	1.393	1.419
68	1.491	1.354	0.795	1.552	1.542	1.527	1.341	1.222	1.356
58	1.335	1.388	1.121	1.409	1.300	1.333	1.237	1.342	1.261
80	1.379	1.329	0.490	1.702	1.534	1.599	1.493	1.376	1.272

Table 5.9 Cont.

12	1.193	1.099	1.008	1.260	1.118	1.111	1.442	1.356	0.975
33	1.026	1.326	1.678	1.215	0.906	1.014	1.612	1.233	1.016
35	0.799	1.311	1.450	1.301	0.846	1.016	1.806	1.206	0.871
37	0.727	1.294	1.580	1.282	0.754	0.940	1.869	1.190	0.785
71	1.143	1.429	1.752	1.278	1.022	1.109	1.598	1.342	1.195
70	1.015	1.385	1.532	1.436	1.052	1.189	1.673	1.299	1.126
66	1.160	1.403	1.399	1.396	1.169	1.227	-0.138	1.307	1.132
56	1.004	1.436	1.724	1.297	0.927	1.033	1.738	1.276	1.037
79	1.048	1.377	1.093	1.547	1.161	1.299	1.774	1.310	1.047
77	0.718	1.426	1.697	1.391	0.709	0.998	2.056	1.244	0.823
30	1.772	1.229	0.954	1.325	1.747	1.564	0.936	1.353	1.476
50	1.873	1.356	1.243	0.239	1.776	1.615	0.943	1.379	1.668
69	1.645	1.341	1.015	1.447	1.716	2.062	0.111	1.351	1.523
75	1.573	1.324	1.144	1.428	1.624	1.542	1.201	1.335	1.437
104	2.000	1.455	1.301	1.427	1.901	1.716	0.924	1.493	1.854
103	1.922	1.435	1.071	1.554	1.987	1.846	0.973	1.473	1.847
100	2.007	1.433	0.963	1.542	2.039	1.828	0.953	1.453	1.785
98	1.850	1.467	1.289	1.443	1.797	1.634	1.070	1.422	1.690
121	1.897	1.407	0.654	1.694	2.033	1.901	1.104	1.457	1.702
119	1.564	1.456	1.261	1.537	1.658	1.600	1.387	1.390	1.476
155	2.410	1.486	0.826	1.683	2.528	2.201	0.719	1.536	2.129
24	1.419	1.269	1.394	1.225	1.238	1.266	1.147	1.361	1.407
45	1.519	1.396	1.683	1.261	1.267	1.316	1.154	1.387	1.599
59	1.312	1.387	1.447	1.359	1.228	1.338	1.338	1.369	1.477
69	1.219	1.364	1.585	1.328	1.115	1.243	1.412	1.343	1.369
96	1.636	1.499	1.757	1.323	1.383	1.408	1.141	1.495	1.779
95	1.568	1.475	1.512	1.454	1.478	1.548	1.184	1.481	1.779
91	1.653	1.473	1.404	1.442	1.530	1.530	0.724	1.460	1.716
84	1.496	1.506	1.730	1.343	1.934	1.736	1.280	1.430	1.621
113	1.540	1.447	1.098	1.593	1.522	2.002	1.317	1.464	1.631
110	1.210	1.496	1.702	1.437	1.148	1.301	1.598	1.457	1.407
150	2.056	1.526	1.266	1.583	2.018	1.902	1.418	1.543	2.060
136	1.702	1.566	1.707	1.483	1.509	1.604	1.140	1.508	1.991
23	1.797	1.268	1.061	1.369	1.460	1.418	1.113	1.364	1.328
43	1.897	1.395	1.350	1.405	1.533	1.469	1.120	1.389	1.521
57	1.670	1.380	1.122	1.491	1.472	1.471	1.314	1.362	1.376
63	1.597	1.393	1.252	1.472	1.381	1.396	1.378	1.346	1.290
94	2.014	1.498	1.424	1.467	1.649	1.564	1.107	1.498	1.700
92	1.972	1.465	1.142	1.605	1.767	1.714	1.134	1.498	1.715
90	2.057	1.463	1.034	1.594	1.819	1.697	1.114	1.477	1.652
83	1.875	1.506	1.397	1.463	1.554	1.488	1.246	1.432	1.542
111	1.919	1.447	0.765	1.737	1.787	1.754	1.283	1.466	1.553
107	1.588	1.525	1.369	1.581	1.414	1.454	1.564	1.400	1.328
148	2.435	1.526	0.933	1.727	2.284	2.055	0.895	1.546	1.981
135	2.081	1.566	1.374	1.627	1.775	1.757	1.106	1.554	1.912
133	2.459	1.565	1.041	1.771	2.048	1.909	1.072	1.556	1.834
29	1.382	1.248	1.018	1.370	1.414	1.423	1.190	1.331	1.303
48	1.482	1.375	1.307	1.406	1.465	1.474	1.197	1.357	1.496
67	1.255	1.360	1.079	1.492	1.404	1.878	1.391	1.330	1.350
74	1.182	1.343	1.209	1.473	1.313	1.401	1.454	1.313	1.265
102	1.599	1.478	1.381	1.468	1.581	1.570	1.144	1.465	1.675
101	1.740	2.032	2.303	1.661	1.872	1.822	1.588	1.568	1.794
99	1.645	1.441	0.986	1.596	1.761	1.704	1.189	1.447	1.628

Table 5.9 Cont.

97	1.459	1.486	1.353	1.487	3.638	1.494	1.323	1.400	1.517
120	1.503	1.427	0.722	1.738	1.719	1.760	1.359	1.434	1.527
118	1.173	1.475	1.326	1.582	1.346	1.459	1.641	1.351	1.303
154	2.019	1.505	0.890	1.728	2.216	2.060	0.972	1.514	1.956
149	1.665	1.545	1.331	1.628	1.707	1.762	0.225	1.521	1.641
146	2.046	1.544	0.994	1.772	1.975	1.916	1.147	1.525	1.810
153	1.672	1.508	0.893	1.786	1.944	1.945	1.199	1.516	1.808
21	1.337	1.184	1.109	1.293	1.332	1.349	1.307	1.459	1.695
41	1.206	1.398	1.729	1.259	1.152	1.271	1.455	1.297	1.346
55	0.953	1.392	1.538	1.337	1.068	1.259	1.665	1.256	1.186
60	0.880	1.376	1.667	1.318	0.977	1.183	1.734	1.239	1.101
89	1.297	1.510	1.839	1.313	1.245	1.352	1.458	1.391	1.511
87	1.229	1.486	1.594	1.444	1.376	1.487	1.501	1.377	1.511
85	1.314	1.484	1.486	1.432	1.392	1.470	1.481	1.357	1.448
82	1.158	1.518	1.812	1.333	1.150	1.275	1.597	1.326	1.353
108	1.141	1.439	1.206	1.546	1.318	1.485	1.665	1.332	1.295
105	0.831	1.494	1.801	1.403	0.967	1.204	1.936	1.275	1.094
140	1.778	1.558	1.323	1.610	1.945	1.898	1.215	1.468	1.860
132	1.363	1.578	1.789	1.473	1.371	1.544	1.457	1.448	1.723
130	1.742	1.577	1.456	1.617	1.637	1.696	1.423	1.450	1.644
138	1.326	1.557	1.413	1.618	1.569	1.702	1.500	1.418	1.619
128	1.025	1.589	1.872	1.463	1.133	1.484	1.774	1.379	1.455
38	1.012	1.253	1.132	1.366	0.985	1.143	1.569	1.236	0.918
76	1.092	1.373	1.429	1.390	0.992	1.175	1.586	1.252	1.088
78	0.885	1.365	1.193	1.487	0.954	1.197	1.769	1.234	0.966
81	0.813	1.348	1.322	1.469	0.862	1.121	1.833	1.218	0.880
125	1.229	1.483	1.494	1.464	1.130	1.290	1.562	1.370	1.290
124	1.162	1.459	1.249	1.594	1.225	0.980	1.605	1.356	1.290
123	1.307	1.477	1.116	1.619	1.342	1.463	1.554	1.363	1.296
122	1.090	1.490	1.467	1.483	1.035	1.213	1.702	1.305	1.132
127	1.134	1.431	0.836	1.734	1.269	1.479	1.738	1.338	1.143
118	0.743	1.460	1.465	1.541	0.830	1.123	2.051	1.244	0.850
168	1.650	1.510	1.004	1.724	1.765	-2.671	1.351	1.418	1.571
164	1.296	1.550	1.444	1.624	1.256	1.482	1.562	1.426	1.502
162	1.634	1.536	1.128	1.743	1.479	1.597	1.549	1.410	1.378
167	1.259	1.529	1.068	1.769	1.454	1.640	1.604	1.396	1.398
157	0.957	1.562	1.527	1.614	1.118	1.421	1.879	1.322	1.235
169	0.829	1.514	1.207	1.728	0.938	1.303	2.014	1.273	0.945
65	1.656	1.417	0.899	1.456	1.666	1.537	0.982	1.696	1.464
93	1.740	1.528	1.488	1.471	1.824	1.835	0.745	1.729	1.872
112	1.513	1.513	1.260	1.557	1.700	1.838	0.940	1.702	1.727
117	1.440	1.497	1.390	1.538	1.608	1.762	1.003	1.686	1.641
152	1.857	1.632	1.562	1.533	1.940	1.931	0.732	1.838	2.051
151	1.486	1.508	1.445	1.480	1.710	1.787	0.932	1.683	1.709
147	1.874	1.606	1.209	1.652	2.087	2.048	0.756	1.803	1.988
134	1.718	1.639	1.534	1.552	1.846	1.854	0.872	1.773	2.258
165	1.762	1.580	0.903	1.803	2.079	2.120	0.908	1.806	1.904
163	1.431	1.629	1.507	1.647	1.706	1.820	1.190	1.741	1.680
188	2.278	1.659	1.071	1.793	2.576	2.421	0.521	1.886	2.332
179	1.984	1.719	1.487	1.729	2.132	2.179	0.700	1.922	2.332
178	2.282	1.692	1.188	1.824	2.311	2.257	0.708	1.887	2.162
187	1.887	1.678	1.136	1.838	2.265	2.281	0.775	1.864	2.160
177	2.229	1.427	0.610	1.859	2.503	2.401	0.649	2.155	2.330

Table 5.9 Cont.

193	1.517	1.683	1.249	1.834	1.814	2.000	1.153	1.769	1.775
202	2.145	1.832	1.317	1.903	2.617	2.641	0.323	2.237	2.536
62	1.534	1.364	1.300	1.367	1.584	1.499	0.930	1.282	1.389
88	1.621	1.457	1.617	1.434	1.698	1.796	0.685	1.704	1.942
109	1.393	1.442	1.389	1.519	1.638	1.799	0.880	1.677	1.797
115	1.321	1.426	1.518	1.500	1.546	1.723	0.943	1.660	1.711
145	1.737	1.560	1.690	1.496	1.290	1.892	0.672	1.812	2.122
144	1.670	1.536	1.445	1.626	1.385	2.027	0.715	1.798	2.121
139	1.754	1.534	1.338	1.614	1.437	2.009	1.184	1.778	1.603
131	1.598	1.568	1.663	1.515	1.195	1.815	0.812	1.747	1.964
161	1.642	1.509	1.032	1.765	1.429	2.081	0.848	1.781	1.974
158	1.312	1.558	1.636	1.609	1.056	1.336	1.129	1.715	1.750
184	2.158	1.588	1.200	1.755	2.449	2.378	0.461	1.861	2.403
176	1.865	1.647	1.615	1.692	2.005	2.140	0.640	1.897	2.402
175	2.182	1.627	1.308	1.799	2.206	1.791	0.638	1.871	2.255
183	1.770	1.606	1.261	1.801	2.140	2.243	0.713	1.840	2.231
171	1.465	1.639	1.723	1.645	1.802	2.024	0.989	1.765	2.066
191	0.613	1.612	1.378	1.796	1.687	1.961	1.093	1.743	1.845
201	2.025	1.760	1.446	1.865	2.498	2.602	0.263	2.211	2.606
197	1.906	1.689	1.574	1.828	2.371	2.563	0.203	2.186	2.676
61	2.181	1.353	1.079	1.441	1.590	1.467	1.187	1.297	1.326
86	1.587	1.506	1.418	1.483	1.467	1.482	1.487	1.431	5.027
106	1.352	1.493	1.201	1.567	1.400	1.480	1.197	1.399	1.237
114	1.287	1.474	1.319	1.550	1.315	1.409	1.256	1.387	1.156
143	1.704	1.609	1.491	1.546	1.583	1.578	0.985	1.539	1.566
141	1.636	1.585	1.246	1.676	1.678	1.713	1.028	1.525	1.566
137	1.721	1.583	1.139	1.664	1.730	1.696	1.008	1.505	1.503
129	1.564	1.616	1.464	1.565	1.488	1.501	1.125	1.474	1.408
159	1.568	1.544	0.850	1.791	1.678	1.730	1.182	1.489	1.373
156	1.278	1.606	1.436	1.659	1.348	1.467	1.442	1.442	1.195
182	2.127	1.635	0.997	1.806	2.221	2.070	0.772	1.589	1.849
174	1.773	1.675	1.438	1.706	1.712	1.771	0.983	1.597	1.780
172	2.149	1.676	1.109	1.849	1.975	1.922	0.950	1.598	1.700
180	1.650	1.630	1.103	1.800	1.818	1.852	1.071	1.527	1.582
170	1.424	1.688	1.524	1.695	1.571	1.710	1.302	1.492	1.511
189	1.364	1.660	1.179	1.846	1.456	1.647	1.406	1.470	1.290
199	1.992	1.809	1.246	1.915	2.267	2.289	0.576	1.938	2.051
196	1.872	1.738	-7.650	1.878	2.140	2.249	0.516	1.947	2.121
194	1.828	2.828	-1.539	2.326	5.329	4.066	-4.284	1.331	1.560
116	1.603	1.505	1.654	1.441	1.582	1.576	0.885	1.232	1.269
142	1.602	1.598	1.499	1.573	2.103	1.884	1.196	1.494	1.907
160	1.378	1.582	1.268	1.707	2.045	1.888	0.899	1.468	1.763
166	1.307	1.565	1.394	1.689	1.956	1.369	0.961	1.453	1.679
186	1.721	1.596	1.569	1.684	2.221	1.981	0.692	1.604	2.088
185	1.654	1.677	1.324	1.814	2.324	2.117	0.735	1.590	2.087
181	1.739	1.675	1.217	1.803	2.375	2.099	0.715	1.569	2.024
173	1.582	1.708	1.542	1.464	2.127	1.905	0.832	1.539	1.930
192	1.629	1.648	0.907	1.715	2.362	2.172	0.866	1.574	1.942
190	1.296	1.698	1.514	1.798	1.987	1.870	1.149	1.507	1.716
204	1.291	1.449	1.436	1.431	1.946	1.688	0.920	1.258	1.411
200	8.043	1.775	1.549	1.837	5.055	2.198	0.704	1.649	2.288
198	8.442	1.767	1.187	1.987	2.614	2.326	0.657	1.663	2.221
203	1.812	1.767	2.246	2.025	2.610	2.387	0.703	1.659	2.264

Table 5.9 Cont.

195	1.449	1.779	1.602	1.834	2.210	2.113	1.009	1.556	2.032
205	1.382	1.752	1.257	1.984	2.095	2.051	1.113	1.535	1.811
208	1.796	1.980	1.630	1.989	2.712	2.573	0.414	1.884	2.451
207	1.890	1.829	1.453	2.016	2.779	2.653	0.223	1.977	2.642
206	2.160	1.977	1.126	2.249	2.873	2.619	0.379	1.845	2.429
209	1.874	1.970	1.332	2.204	3.186	2.742	0.243	1.769	2.608
266	0.114	-0.004	-0.222	0.068	0.194	0.157	-0.187	0.001	0.081
268	0.098	-0.003	-0.189	0.058	0.167	0.135	-0.159	0.001	0.058
270	0.067	0.003	-0.135	0.043	0.125	0.103	-0.123	-0.007	0.026
272	0.051	0.004	-0.102	0.034	0.097	0.080	-0.095	-0.007	0.003
274	0.035	0.005	-0.070	0.024	0.069	0.058	-0.068	-0.006	-0.020
276	0.019	0.005	-0.037	0.014	0.041	0.035	-0.041	-0.006	-0.043
278	0.019	0.000	-0.026	0.009	0.027	0.021	-0.023	0.003	-0.057
280	0.003	0.001	0.006	-0.001	-0.001	-0.002	0.004	0.004	-0.080
282	-0.013	0.001	0.039	-0.011	-0.029	-0.025	0.031	0.004	-0.103
284	-0.029	0.002	0.071	-0.021	-0.057	-0.048	0.059	0.005	-0.126
286	-0.060	0.008	0.126	-0.035	-0.098	-0.079	0.095	-0.004	-0.158
289	-0.061	0.001	0.142	-0.043	-0.119	-0.100	0.122	0.010	-0.179

Then in the second round, regressions were carried out on all twelve phases using the π Ist-rd values as starting values. There were still a number of PCBs that had to be deleted from one or other phase regressions. Detail of the regression equations are in Table 5.10, where it can be seen that only the equations for three phases (1,2 and 5) had the required positive s- coefficient. These phases are OV-101, F-50 and OV-3.

Table 5.10. Regression details for the second round of π^{H}_{2} calculations

Phase	**Coefficient**						
No	**l**	**s**	**r**	**c**	**F**	**r^2**	**n**
1	200.45	49.62	80.25	35.06	12894.3	0.997	217
2	198.37	66.61	63.38	65.50	14343.5	0.998	215
3	194.47	-187.26	271.87	121.73	8716.4	0.996	215
4	195.21	-251.4	461.48	121.24	889.9	0.962	217
5	197.20	72.77	95.33	81.06	5571.3	0.994	217
6	183.86	-169.42	367.52	236.28	1493.5	0.977	216
7	182.58	-140.51	415.77	248.33	2736.4	0.987	216
8	184.02	-372.88	570.86	248.39	1793.3	0.980	217
9	182.37	-501.78	713.43	270.78	952.0	0.964	216
10	165.54	-745.93	951.74	474.57	776.6	0.956	216
11	198.07	-128.90	164.73	71.25	1163.8	0.970	217
12	190.76	-428.79	744.57	184.10	1526.4	0.977	217

The next step was to average the back-calculated π^{H_2} values from the three selected phases as shown in Table 5.11, with the average values now denoted as π 2nd -rd . It can be seen that there are some considerable changes on going from π Ist - rd to π 2nd - rd .

Table 5.11 The back-calculation of π for (OV-101), (F-50), (OV-3),with average, π (1st-rd), π (2nd - rd).

IUPAC	π calc. OV-101	π calc. F -50	π calc. OV-3	π avg. 101,50,3	π Sd	π 1st - rd	π 2nd-rd
-	0.994	0.993	0.963	0.983	0.017	1.04	0.98
1	0.767	0.489	0.707	0.654	0.146	1.22	1.12
4	1.196	1.179	1.289	1.221	0.059	1.21	1.42
6	1.215	1.372	1.353	1.313	0.086	1.16	1.29
11	1.234	1.565	1.417	1.406	0.166	1.21	0.67
3	1.919	2.712	2.187	2.273	0.403	0.81	1.09
8	1.205	1.324	1.309	1.279	0.064	1.13	1.21
13	1.225	1.517	1.373	1.372	0.146	1.08	1.11
15	0.861	0.903	0.976	0.913	0.059	1.02	1.20
10	1.247	1.279	1.300	1.275	0.027	1.30	1.34
19	1.288	1.294	1.425	1.336	0.078	1.30	1.59
27	1.315	1.497	1.494	1.435	0.104	1.27	1.47
32	1.297	1.439	1.446	1.394	0.084	1.23	1.41
54	1.380	1.408	1.562	1.450	0.098	1.40	1.76
9	1.218	1.408	1.252	1.293	0.101	1.24	1.14
18	1.310	1.484	1.403	1.399	0.087	1.31	1.42
26	1.329	1.677	1.467	1.491	0.175	1.26	1.22
31	1.319	3.575	1.423	2.106	1.273	1.33	1.32
53	1.401	1.599	1.54	1.513	0.101	1.04	1.56
52	1.423	1.789	1.517	1.577	0.190	1.41	1.37
7	1.208	1.301	1.263	1.258	0.047	1.25	1.14
17	1.300	1.358	1.414	1.357	0.057	1.27	1.36
25	1.319	1.551	1.478	1.450	0.119	1.28	1.29
28	1.310	1.503	1.434	1.416	0.098	1.24	1.23
51	1.392	1.473	1.688	1.518	0.153	1.43	1.49
49	1.436	1.114	1.279	1.276	0.161	1.44	1.45
47	1.404	1.537	1.539	1.494	0.077	1.38	1.38
5	1.214	1.237	1.327	1.259	0.060	1.22	1.22
16	1.306	1.313	1.478	1.365	0.097	1.26	1.41
20	1.325	1.506	1.542	1.458	0.116	1.23	1.28

Table 5.11 Cont.

22	1.316	1.458	1.498	1.424	0.096	1.21	1.24
46	1.398	1.428	1.614	1.480	0.117	1.37	1.55
44	1.42	1.618	1.592	1.543	0.108	1.34	1.55
42	1.41	1.492	1.603	1.502	0.097	1.37	1.41
40	1.416	1.447	1.667	1.510	0.137	1.27	1.46
14	1.229	1.299	1.188	1.238	0.056	1.24	0.96
34	1.329	1.385	1.343	1.352	0.029	1.32	1.21
36	1.331	1.558	1.399	1.429	0.116	1.26	1.07
39	1.339	1.530	1.363	1.411	0.104	1.25	1.04
73	1.421	1.500	1.480	1.467	0.041	1.40	1.37
72	1.443	1.690	1.457	1.530	0.139	1.39	1.27
68	1.433	1.564	1.468	1.489	0.068	1.42	1.21
58	1.439	1.519	1.532	1.497	0.050	1.37	1.30
80	1.462	1.591	1.397	1.484	0.099	1.36	1.07
12	1.224	1.304	1.429	1.319	0.103	1.22	0.70
33	1.316	1.380	1.580	1.425	0.138	1.20	1.23
35	1.335	1.573	1.644	1.518	0.162	1.27	1.23
37	1.326	1.525	1.600	1.484	0.142	1.25	1.14
71	1.408	1.495	1.717	1.540	0.159	1.25	1.37
70	1.404	1.654	1.682	1.580	0.153	1.28	1.31
66	1.420	1.559	1.705	1.562	0.143	1.32	1.31
56	1.426	1.514	1.769	1.57	0.178	1.29	1.29
79	1.449	1.586	1.634	1.557	0.096	1.34	1.19
77	1.436	1.581	1.872	1.629	0.222	1.31	1.32
30	1.305	1.353	1.187	1.281	0.086	1.30	1.23
50	1.396	1.429	1.338	1.388	0.046	1.37	1.42
69	1.415	1.623	1.402	1.480	0.124	1.35	1.33
75	1.406	1.574	1.358	1.446	0.114	1.33	1.29
104	1.488	1.467	1.420	1.458	0.035	1.46	1.55
103	1.510	1.735	1.452	1.565	0.149	1.45	1.45
100	1.500	1.609	1.463	1.524	0.076	1.44	1.45
98	1.506	1.563	1.527	1.532	0.029	1.44	1.49
121	1.529	1.616	1.378	1.508	0.120	1.43	1.32
119	1.516	1.631	1.629	1.592	0.066	1.55	1.37
155	1.597	1.680	1.386	1.554	0.151	1.51	1.53
24	1.308	0.960	1.061	1.110	0.179	1.25	1.24
45	1.400	1.036	1.212	1.216	0.182	1.39	1.36
59	1.427	1.240	1.281	1.316	0.099	1.36	1.39
69	1.409	1.182	1.233	1.275	0.120	1.34	1.33
96	1.492	1.151	1.349	1.331	0.171	1.50	1.68
95	1.513	1.342	1.327	1.394	0.104	1.47	1.59
91	1.504	1.216	1.338	1.352	0.145	1.46	1.56
84	1.510	1.171	1.401	1.361	0.173	1.42	1.64
113	1.533	1.243	1.267	1.347	0.161	1.46	1.56

Table 5.11 Cont.

110	1.520	1.238	1.504	1.420	0.159	1.47	1.56
150	1.600	1.287	1.261	1.383	0.189	1.53	1.59
136	1.604	0.894	1.136	1.211	0.361	1.50	1.73
23	1.331	1.247	1.285	1.288	0.042	1.36	1.21
43	1.422	1.323	1.436	1.394	0.062	1.39	1.41
57	1.441	1.517	1.501	1.486	0.040	1.37	1.30
63	1.432	1.469	1.594	1.498	0.085	1.37	1.33
94	1.514	1.438	1.573	1.508	0.068	1.49	1.52
92	1.535	1.435	1.415	1.462	0.064	1.48	1.45
90	1.527	1.697	1.562	1.595	0.090	1.47	1.43
83	1.532	1.457	1.625	1.538	0.084	1.45	1.49
111	1.556	1.530	1.491	1.525	0.033	1.47	1.47
107	1.542	1.525	1.865	1.644	0.192	1.57	1.47
148	1.623	1.574	1.485	1.561	0.070	1.54	1.45
135	1.626	1.181	1.360	1.389	0.224	1.56	1.49
133	1.649	1.468	1.584	1.567	0.092	1.56	1.51
29	1.321	1.316	1.241	1.293	0.045	1.36	1.17
48	1.413	1.392	1.392	1.399	0.012	1.37	1.39
67	1.432	1.585	1.457	1.491	0.082	1.35	1.27
74	1.423	1.537	1.413	1.457	0.069	1.32	1.23
102	1.505	1.507	1.529	1.513	0.013	1.47	1.54
101	1.135	0.966	4.101	2.068	1.763	1.61	1.60
99	1.517	1.552	1.504	1.524	0.025	1.44	1.35
97	1.523	1.526	1.581	1.543	0.033	1.46	1.47
120	1.546	1.598	1.446	1.530	0.077	1.43	1.45
118	1.533	1.593	1.684	1.603	0.076	1.52	1.48
154	1.613	1.643	1.441	1.566	0.109	1.51	1.49
149	1.617	1.250	1.316	1.394	0.196	1.53	1.47
146	1.639	1.517	1.526	1.561	0.068	1.53	1.46
153	1.435	1.251	1.247	1.311	0.107	1.62	1.63
21	1.308	-0.499	0.066	0.292	0.925	1.27	1.22
41	1.410	1.707	1.576	1.564	0.149	1.25	1.42
55	1.429	1.705	1.641	1.592	0.145	1.36	1.33
60	1.419	1.657	1.597	1.558	0.124	1.35	1.32
89	1.501	1.627	1.713	1.614	0.106	1.33	1.55
87	1.523	1.817	1.691	1.677	0.148	1.46	1.54
85	1.514	1.691	1.702	1.636	0.106	1.40	1.49
82	1.520	1.646	1.765	1.644	0.123	1.33	1.54
108	1.517	1.688	1.618	1.608	0.086	1.36	1.53
105	1.513	1.693	1.859	1.688	0.173	1.45	1.42
140	1.636	1.794	1.638	1.689	0.091	1.60	1.54
132	1.613	1.370	1.500	1.494	0.122	1.46	1.59
130	1.636	1.657	1.724	1.672	0.046	1.60	1.53
138	1.627	1.725	1.680	1.677	0.049	1.48	1.48

Table 5.11 Cont.

128	1.623	1.846	1.864	1.778	0.134	1.42	1.48
38	1.338	1.668	1.462	1.489	0.167	1.24	1.07
76	1.421	1.734	1.608	1.588	0.158	1.38	1.33
78	1.448	1.937	1.677	1.687	0.245	1.43	1.21
81	1.439	1.889	1.633	1.654	0.226	1.40	1.60
125	1.521	1.859	1.749	1.710	0.172	1.47	1.50
124	1.543	2.049	1.727	1.773	0.256	1.39	1.38
123	1.559	1.954	1.750	1.755	0.197	1.33	1.35
122	1.539	1.878	1.801	1.740	0.178	1.49	1.43
127	1.563	1.950	1.667	1.726	0.201	1.41	1.13
118	1.524	1.914	1.891	1.776	0.219	1.50	1.37
168	1.630	1.995	1.661	1.762	0.202	1.56	1.37
164	1.633	1.602	1.536	1.59	0.049	1.47	1.47
162	1.639	1.868	1.752	1.753	0.115	1.58	1.30
167	1.646	1.957	1.716	1.773	0.163	1.49	1.30
157	1.643	2.077	1.900	1.873	0.218	1.50	1.41
169	1.637	2.278	1.923	1.946	0.321	1.62	1.24
65	1.411	1.491	1.601	1.501	0.095	1.56	1.49
93	1.517	1.474	1.473	1.488	0.025	1.62	1.75
112	1.536	1.668	1.537	1.580	0.076	1.54	1.61
117	1.527	1.619	1.493	1.546	0.066	1.47	1.57
152	1.609	1.589	1.609	1.602	0.011	1.71	1.90
151	1.502	1.626	1.523	1.551	0.066	1.48	1.64
147	1.621	1.654	1.598	1.624	0.028	1.73	1.75
134	1.627	1.608	1.662	1.632	0.027	1.76	1.85
165	1.650	1.681	1.527	1.619	0.081	1.80	1.67
163	1.637	1.675	1.764	1.692	0.065	1.64	1.68
188	1.717	1.725	1.521	1.655	0.115	1.78	1.83
179	1.746	1.363	1.409	1.506	0.209	1.84	1.93
178	1.735	1.609	1.616	1.653	0.071	1.80	1.81
187	1.734	1.688	1.576	1.666	0.081	1.82	1.80
177	1.705	7.089	1.748	3.514	3.096	1.92	1.75
193	1.750	2.040	1.796	1.862	0.155	1.71	1.70
202	1.838	1.770	1.656	1.755	0.092	1.87	2.13
62	1.412	1.101	1.243	1.252	0.155	1.36	1.36
88	1.508	1.386	1.124	1.340	0.196	1.44	1.60
109	1.528	1.579	1.188	1.432	0.212	1.51	1.55
115	1.518	1.531	1.144	1.398	0.220	1.48	1.64
145	1.600	1.501	1.261	1.454	0.175	1.65	1.75
144	1.622	1.691	1.238	1.517	0.244	1.65	1.72
139	1.613	1.565	1.249	1.476	0.198	1.67	1.68
131	1.619	1.520	1.313	1.484	0.156	1.61	1.70
161	1.642	1.592	1.178	1.471	0.255	1.67	1.66
158	1.629	1.587	1.415	1.544	0.113	1.55	1.68

Table 5.11 Cont.

184	1.709	1.637	1.173	1.506	0.291	1.74	1.73
176	1.738	1.274	1.060	1.358	0.346	1.78	1.76
175	1.735	1.531	1.272	1.512	0.232	1.77	1.71
183	1.725	1.580	1.214	1.506	0.264	1.75	1.84
171	1.722	1.719	1.412	1.618	0.179	1.68	1.76
191	1.742	1.951	1.448	1.714	0.253	1.72	1.73
201	1.829	1.682	1.308	1.606	0.269	1.97	1.98
197	1.821	1.593	0.959	1.458	0.447	1.90	1.99
61	1.429	1.511	1.338	1.426	0.086	1.36	1.32
86	1.523	1.467	1.567	1.519	0.050	1.50	1.54
106	1.543	1.602	1.631	1.592	0.045	1.45	1.44
114	1.533	1.612	1.587	1.577	0.040	1.43	1.40
143	1.615	1.582	1.704	1.634	0.063	1.60	1.68
141	1.637	1.772	1.681	1.697	0.069	1.61	1.60
137	1.628	1.647	1.692	1.655	0.033	1.62	1.58
129	1.633	1.601	1.756	1.663	0.081	1.58	1.60
159	1.640	1.653	1.613	1.635	0.021	1.63	1.62
156	1.643	1.668	1.858	1.723	0.117	1.68	1.64
182	1.724	1.699	1.602	1.675	0.064	1.68	1.63
174	1.727	1.306	1.477	1.503	0.212	1.69	1.65
172	1.750	1.612	1.714	1.692	0.072	1.71	1.64
180	1.706	1.659	1.667	1.677	0.025	1.65	1.60
170	1.737	1.801	1.854	1.797	0.059	1.58	1.60
189	1.757	2.032	1.891	1.893	0.138	1.59	1.47
199	1.844	1.763	1.751	1.786	0.051	1.91	1.95
196	1.836	1.674	1.402	1.638	0.219	1.86	1.86
194	1.851	1.833	6.823	3.503	2.876	2.08	1.90
116	1.525	2.107	1.798	1.810	0.291	1.45	1.60
142	1.619	1.558	1.573	1.584	0.032	1.57	1.72
160	1.639	1.732	1.624	1.665	0.059	1.53	1.61
166	1.629	1.665	1.566	1.620	0.050	1.50	1.56
186	1.711	1.654	1.201	1.522	0.279	1.65	1.78
185	1.733	1.844	1.674	1.750	0.086	1.68	1.77
181	1.724	1.718	1.685	1.709	0.021	1.70	1.74
173	1.729	1.673	1.748	1.717	0.039	1.61	1.82
192	1.753	1.726	1.600	1.693	0.081	1.64	1.61
190	1.739	1.740	1.851	1.777	0.064	1.67	1.67
204	1.461	1.359	1.430	1.417	0.052	1.44	1.44
200	1.824	1.551	1.592	1.656	0.147	1.80	1.87
198	1.846	1.683	1.707	1.745	0.088	1.81	1.72
203	1.862	1.783	1.676	1.773	0.093	1.82	1.82
195	1.833	1.872	1.847	1.851	0.020	1.81	1.81
205	1.853	2.104	1.883	1.947	0.137	1.86	1.67
208	1.940	1.834	1.743	1.839	0.099	1.91	1.99

Table 5.11 Cont.

207	1.932	1.746	1.395	1.691	0.273	1.93	1.96
206	2.075	1.981	1.901	1.986	0.087	2.06	2.03
209	2.043	1.899	1.830	1.924	0.109	2.02	2.05
266	0.270	0.109	-0.070	0.103	0.170	0	0
268	0.236	0.101	-0.059	0.093	0.147	0	0
270	0.222	0.133	-0.020	0.111	0.123	0	0
272	0.187	0.125	-0.009	0.101	0.100	0	0
274	0.153	0.118	0.002	0.091	0.079	0	0
276	0.118	0.111	0.014	0.081	0.058	0	0
278	0.062	0.065	-0.002	0.041	0.038	0	0
280	0.027	0.057	0.009	0.031	0.024	0	0
282	-0.008	0.050	0.021	0.021	0.029	0	0
284	-0.042	0.042	0.032	0.011	0.046	0	0
286	-0.056	0.074	0.070	0.029	0.074	0	0
289	-0.140	0.005	0.047	-0.029	0.098	0	0

Then the averaged π^{H}_{2} 2nd-rd values were used in another round of regressions to yield the set of equations given in Table 5.12. These equations are very satisfactory as regards the sign of the coefficients and the statistics.

Table 5.12. Recalculated equations for phases OV-101, F-50 and OV-3

Phase		Coefficient						
Name	No	l	s	r	c	F	r^2	n
OV-101	1	201.28	94.81	47.79	27.05	43544	0.9992	210
F-50	2	198.39	51.39	74.31	63.56	22521	0.9996	212
OV-3	3	197.20	72.71	95.40	81.05	33846	0.9989	214

Values of π^{H}_{2} were again back-calculated and the process repeated until there was little change in the calculated π^{H}_{2} values. The final π^{H}_{2} values are given in Table 5.13.

Table (5.13) IUPAC no. R_2 estimate, π final, β estimate and Vx

IUPAC	R_2 estm.	π final	β est.	Vx
-	1.36	0.99	0.26	1.324
1	1.48	1.12	0.19	1.447
2	1.51	1.02	0.20	1.447
3	1.50	1.09	0.20	1.447
4	1.60	1.40	0.14	1.569
9	1.63	1.18	0.16	1.569
6	1.63	1.27	0.14	1.569
11	1.66	1.18	0.14	1.569
7	1.62	1.16	0.16	1.569
8	1.62	1.22	0.14	1.569
13	1.65	1.09	0.14	1.569
15	1.49	1.20	0.13	1.569
5	1.63	1.24	0.16	1.569
14	1.65	0.99	0.16	1.569
12	1.65	1.15	0.16	1.569
10	1.66	1.35	0.16	1.569
19	1.72	1.55	0.10	1.691
27	1.76	1.42	0.10	1.691
32	1.74	1.37	0.10	1.691
18	1.75	1.42	0.10	1.691
26	1.78	1.29	0.10	1.691
31	1.77	1.34	0.10	1.691
17	1.74	1.40	0.10	1.691
25	1.77	1.27	0.10	1.691
28	1.76	1.23	0.10	1.691
16	1.75	1.48	0.10	1.691
20	1.78	1.35	0.10	1.691
22	1.77	1.31	0.10	1.691
34	1.78	1.23	0.01	1.691
36	1.79	1.09	0.01	1.691
39	1.80	1.06	0.01	1.691
33	1.77	1.34	0.01	1.691
30	1.74	1.19	0.13	1.691
35	1.80	1.21	0.01	1.691
37	1.79	1.17	0.01	1.691
24	1.75	1.35	0.13	1.691
23	1.78	1.19	0.13	1.691
29	1.77	1.17	0.13	1.691
21	1.77	1.16	0.13	1.691
38	1.80	1.09	0.13	1.691
54	1.84	1.69	0.07	1.814
53	1.87	1.57	0.06	1.814

Table 5.13 Cont.

52	1.90	1.45	0.06	1.814
51	1.86	1.60	0.06	1.814
49	1.89	1.45	0.05	1.814
47	1.88	1.40	0.07	1.814
46	1.87	1.63	0.07	1.814
44	1.90	1.51	0.07	1.814
42	1.89	1.48	0.07	1.814
40	1.90	1.57	0.06	1.814
73	1.90	1.38	0.06	1.814
72	1.93	1.26	0.06	1.814
68	1.92	1.24	0.06	1.814
58	1.93	1.32	0.06	1.814
80	1.96	1.07	0.06	1.814
71	1.89	1.29	0.06	1.814
70	1.89	1.35	0.06	1.814
66	1.91	1.34	0.06	1.814
56	1.92	1.43	0.06	1.814
79	1.95	1.18	0.06	1.814
77	1.94	1.29	0.06	1.814
50	1.86	1.43	0.07	1.814
69	1.89	1.30	0.07	1.814
75	1.88	1.26	0.07	1.814
45	1.87	1.57	0.07	1.814
59	1.91	1.45	0.07	1.814
69	1.89	1.40	0.07	1.814
43	1.90	1.44	0.07	1.814
57	1.93	1.30	0.07	1.814
63	1.92	1.30	0.07	1.814
48	1.89	1.41	0.07	1.814
67	1.92	1.28	0.07	1.814
74	1.91	1.24	0.07	1.814
41	1.89	1.48	0.07	1.814
55	1.92	1.35	0.07	1.814
60	1.91	1.31	0.07	1.814
76	1.91	1.31	0.07	1.814
78	1.95	1.21	0.07	1.814
81	1.94	1.14	0.07	1.814
65	1.89	1.51	0.13	1.814
62	1.89	1.38	0.13	1.814
61	1.92	1.30	0.13	1.814
104	1.98	1.58	0.03	1.936
103	2.01	1.46	0.03	1.936
100	2.00	1.43	0.03	1.936
98	2.01	1.52	0.03	1.936
121	2.04	1.27	0.03	1.936
119	2.03	1.38	0.03	1.936
96	1.99	1.72	0.03	1.936
95	2.02	1.60	0.03	1.936

Table 5.13 cont.

91	2.01	1.58	0.03	1.936
84	2.02	1.66	0.03	1.936
113	2.05	1.41	0.03	1.936
110	2.04	1.52	0.03	1.936
94	2.02	1.58	0.03	1.936
92	2.05	1.45	0.03	1.936
90	2.04	1.44	0.03	1.936
83	2.05	1.52	0.03	1.936
111	2.08	1.27	0.03	1.936
107	2.07	1.43	0.03	1.936
102	2.01	1.55	0.03	1.936
101	2.04	1.60	0.02	1.936
99	2.03	1.36	0.03	1.936
97	2.04	1.49	0.03	1.936
120	2.07	1.24	0.03	1.936
118	2.06	1.35	0.03	1.936
89	2.01	1.63	0.03	1.936
87	2.04	1.51	0.03	1.936
85	2.03	1.48	0.03	1.936
82	2.04	1.57	0.03	1.936
108	2.04	1.29	0.03	1.936
105	2.04	1.41	0.03	1.936
125	2.04	1.46	0.03	1.936
124	2.07	1.35	0.03	1.936
123	2.09	1.33	0.03	1.936
122	2.07	1.40	0.03	1.936
127	2.10	1.15	0.03	1.936
118	2.06	1.24	0.03	1.936
93	2.02	1.80	0.07	1.936
112	2.05	1.67	0.07	1.936
117	2.04	1.63	0.07	1.936
88	2.01	1.69	0.07	1.936
109	2.04	1.53	0.07	1.936
115	2.03	1.53	0.07	1.936
86	2.04	1.59	0.07	1.936
106	2.07	1.44	0.07	1.936
114	2.06	1.41	0.07	1.936
116	2.04	1.60	0.13	1.936
150	2.13	1.56	0.03	2.059
136	2.14	1.75	0.00	2.059
155	2.12	1.47	0.00	2.059
148	2.16	1.47	0.00	2.059
135	2.17	1.61	0.00	2.059
133	2.20	1.48	0.00	2.059
154	2.15	1.44	0.00	2.059
149	2.16	1.57	0.00	2.059
146	2.19	1.45	0.00	2.059
153	2.18	1.63	0.00	2.059

Table 5.13 cont.

140	2.18	1.54	0.00	2.059
132	2.16	1.65	0.03	2.059
130	2.19	1.52	0.00	2.059
138	2.18	1.49	0.00	2.059
128	2.18	1.56	0.00	2.059
168	2.18	1.35	0.00	2.059
164	2.19	1.49	0.00	2.059
162	2.20	1.34	0.00	2.059
167	2.21	1.31	0.00	2.059
157	2.21	1.40	0.00	2.059
169	2.21	1.21	0.00	2.059
152	2.14	1.95	0.03	2.059
151	2.02	1.70	0.03	2.059
147	2.16	1.80	0.03	2.059
134	2.17	1.88	0.03	2.059
165	2.20	1.63	0.03	2.059
163	2.19	1.74	0.03	2.059
145	2.13	1.85	0.03	2.059
144	2.16	1.68	0.03	2.059
139	2.15	1.62	0.03	2.059
131	2.16	1.76	0.03	2.059
161	2.19	1.68	0.03	2.059
158	2.18	1.62	0.03	2.059
143	2.16	1.73	0.03	2.059
141	2.19	1.61	0.03	2.059
137	2.18	1.58	0.03	2.059
129	2.19	1.67	0.03	2.059
159	2.20	1.41	0.03	2.059
156	2.21	1.53	0.03	2.059
142	2.16	1.76	0.07	2.059
160	2.19	1.62	0.07	2.059
166	2.18	1.58	0.07	2.059
188	2.28	1.83	0.00	2.181
179	2.32	1.95	0.00	2.181
178	2.31	1.83	0.00	2.181
187	2.31	1.81	0.00	2.181
177	2.28	1.82	0.00	2.181
193	2.34	1.71	0.00	2.181
184	2.27	1.74	0.00	2.181
176	2.31	1.72	0.00	2.181
175	2.31	1.63	0.00	2.181
183	2.30	1.60	0.00	2.181
171	2.30	1.76	0.00	2.181
191	2.33	1.63	0.00	2.181
182	2.30	1.62	0.00	2.181
174	2.31	1.78	0.00	2.181
172	2.34	1.62	0.00	2.181
186	2.28	1.74	0.03	2.181

Table 5.13 cont.

185	2.31	1.78	0.03	2.181
181	2.30	1.77	0.03	2.181
173	2.31	1.84	0.03	2.181
180	2.29	1.56	0.00	2.181
170	2.33	1.66	0.00	2.181
189	2.36	1.50	0.00	2.181
192	2.34	1.59	0.03	2.181
190	2.33	1.70	0.03	2.181
199	2.46	1.98	0.00	2.303
196	2.45	1.86	0.00	2.303
194	2.48	1.90	0.00	2.303
201	2.43	1.89	0.00	2.303
197	2.42	1.92	0.00	2.303
202	2.44	1.91	0.00	2.303
204	2.00	1.45	0.00	2.303
200	2.43	1.92	0.00	2.303
198	2.46	1.79	0.00	2.303
203	2.48	1.79	0.00	2.303
195	2.45	1.84	0.00	2.303
205	2.48	1.67	0.00	2.303
208	2.58	1.91	0.00	2.426
207	2.57	1.95	0.00	2.426
206	2.75	2.05	0.00	2.426
209	2.72	2.11	0.00	2.548

Chapter 6 The Second Calculation of Descriptors for PCBs

6.0 Introduction

In the previous chapter the first estimation of the descriptors was given. In this chapter the calculation of the descriptors is continued in more specific ways in order to obtain better estimates. Octanol-water partition coefficients (Poct) of many PCBs congeners have been determined, either by direct measurement[1] or indirectly by reverse-phase high-performance liquid chromatography. In addition predictions of log Poct can be made[2] by the use of models based on chemical structure.[3] From the point of view of the general solvation equation one could say that the use of log Poct would be a very good way to obtain estimates of descriptors, and would be a complimentary method to the GLC procedure.

6.1 The calculation of $\Sigma\beta^{H}_{2}$ values from water-octanol partition coefficients, as log Poct.

Because the GLC phases are all non-acidic, the $b.\Sigma\beta^{H}_{2}$ term is redundant. This means that it is not possible to obtain $\Sigma\beta^{H}_{2}$ values for the PCBs from the GLC data. The other main source of data that could be used for the calculation of $\Sigma\beta^{H}_{2}$ values is that of water-octanol partition coefficients, as log Poct values, for which the solvation equation [4] is known :

$$\log \text{Poct} = 0.088 + 0.562\, R_2 - 1.054\, \pi^{H}_{2} + 0.034\, \Sigma\alpha^{H}_{2} - 3.460\, \Sigma\beta^{H}_{2} + 3.814\, V_x \qquad (6.1)$$

Values of log Poct for the PCBs were obtained from a number of sources, the main ones being the Med Chem[1] listed values , and those listed by Sangster [5] in the LOGKOW data base. For the PCBs, $\Sigma\alpha^H{}_2$ is zero and the truncated solvation equation can be used,

$$\log \text{Poct} = 0.088 + 0.562\, R_2 - 1.054\, \pi^H{}_2 - 3.460\, \Sigma\beta^H{}_2 + 3.814\, V_x \qquad (6.2)$$

Hence for any PCB, if log Poct is known, and if R_2, $\pi^H{}_2$ and V_x are available, then $\Sigma\beta^H{}_2$ can be calculated through equation (6.2). However, as a start, $\Sigma\beta^H{}_2$ was first roughly estimated as shown in Table (5.3), see column β est. Then not only $\Sigma\beta^H{}_2$ but also sometimes $\pi^H{}_2$ was altered in order to reproduce the correct values of log Poct. Results are in the last two columns of Table 6.1.

Table 6.1. Values for R_2 est., π final calc., β est, V_x calc., log P calc., 1st log P calc.2nd , (using altered π ,β) log P(a), log P(b) ,π altered and β altered .

IUPAC	R_2 est.	πfinal calc.	β est.	V_x	Log P calc. 1st	LogP calc.2nd	LogP (a)	logP (b)	π altered	β altered
–	1.36	0.99	0.26	1.324	3.96		3.98		0.99	0.26
1	1.48	1.12	0.19	1.447	4.60		4.52	4.53d	1.12	0.19
2	1.51	1.02	0.20	1.447	4.69		4.58	4.66c	1.02	0.20
3	1.50	1.09	0.20	1.447	4.61		4.61		1.09	0.20
4	1.60	1.40	0.14	1.569	4.92		4.73	4.86c	1.35	0.18
9	1.63	1.18	0.16	1.569	5.19		5.10	5.18c	1.18	0.16
6	1.63	1.27	0.14	1.569	5.16		4.84	5.02c	1.27	0.14
11	1.66	1.18	0.14	1.569	5.28		5.30		1.18	0.14
7	1.62	1.16	0.16	1.569	5.21		5.16	5.15d	1.16	0.16
8	1.62	1.22	0.14	1.569	5.21		5.09	5.10d	1.22	0.14
13	1.65	1.09	0.14	1.569	5.37		5.15	4.96c	1.09	0.14
15	1.64	1.20	0.13	1.569	4.99		5.23	5.32d	1.20	0.13
5	1.63	1.24	0.16	1.569	5.13		4.99		1.24	0.16
14	1.65	0.99	0.16	1.569	5.40		5.41		0.99	0.16
12	1.65	1.15	0.16	1.569	5.23		5.30		1.15	0.16
10	1.66	1.35	0.16	1.569	5.02		4.99	4.98d	1.35	0.16
19	1.72	1.55	0.10	1.691	5.52	5.17	5.04	5.48d	1.55	0.20
27	1.76	1.42	0.10	1.691	5.68		5.52		1.42	0.10
32	1.74	1.37	0.10	1.691	5.72		5.49	5.75d	1.37	0.10
18	1.75	1.42	0.10	1.691	5.52		5.44	5.60c	1.42	0.10
26	1.78	1.29	0.10	1.691	5.83		5.65	5.76d	1.29	0.10
31	1.77	1.34	0.10	1.691	5.77		5.70	5.69d	1.34	0.10
17	1.74	1.40	0.10	1.691	5.69		5.50	5.76e	1.40	0.10
25	1.77	1.27	0.10	1.691	5.84	5.54	5.54		1.27	0.15
28	1.76	1.23	0.10	1.691	5.88		5.71	5.69d	1.23	0.10
16	1.75	1.48	0.10	1.691	5.62	5.13	5.12	5.31e	1.48	0.22
20	1.78	1.35	0.10	1.691	5.77		5.62	5.57d	1.35	0.10
22	1.77	1.31	0.10	1.691	5.81	5.46	5.45	5.63e	1.31	0.20

Table 6.1 Cont.

34	1.78	1.23	0.01	1.691	5.89		5.76	5.18e	1.23	0.01
36	1.79	1.09	0.01	1.691	6.36	5.82	5.81	5.70e	1.09	0.13
39	1.80	1.06	0.01	1.691	6.39				1.06	0.01
33	1.77	1.34	0.01	1.691	6.08	5.73	5.71	5.80e	1.34	0.11
30	1.74	1.19	0.13	1.691	5.92	5.61	6.61	5.71c	1.19	0.15
35	1.80	1.21	0.01	1.691	6.24				1.21	0.01
37	1.79	1.17	0.01	1.691	6.27	5.79	5.78	5.90e	1.17	0.14
24	1.75	1.35	0.13	1.691	5.65		5.44	5.50c	1.35	0.13
23	1.78	1.19	0.13	1.691	5.84	5.40	5.53		1.19	0.16
29	1.77	1.17	0.13	1.691	5.84		5.81	5.90e	1.17	0.13
21	1.77	1.16	0.13	1.691	5.86	5.47	5.45		1.16	0.18
38	1.80	1.09	0.13	1.691	5.95				1.09	0.13
54	1.84	1.69	0.07	1.814	6.02	5.28	5.24	5.90c	1.69	0.23
53	1.87	1.57	0.06	1.814	6.19	5.56	5.55	5.23e	1.57	0.22
52	1.90	1.45	0.06	1.814	6.33	5.80	5.79	6.10e	1.45	0.17
51	1.86	1.60	0.06	1.814	6.15	5.52	5.51		1.60	0.22
49	1.89	1.45	0.05	1.814	6.37	5.88	5.87	6.23e	1.45	0.17
47	1.88	1.40	0.07	1.814	6.34	5.95	5.94	6.29e	1.40	0.16
46	1.87	1.63	0.07	1.814	6.09	5.36	4.84	5.68e	1.63	0.22
44	1.90	1.51	0.07	1.814	6.24	5.74	5.73	6.00e	1.51	0.18
42	1.89	1.48	0.07	1.814	6.26	5.73	5.72		1.48	0.17
40	1.90	1.57	0.06	1.814	6.21	5.68	5.67	6.18c	1.57	0.18
73	1.90	1.38	0.06	1.814	6.41				1.38	0.06
72	1.93	1.26	0.06	1.814	6.55	6.12	6.11	6.50e	1.26	0.15
68	1.92	1.24	0.06	1.814	6.57				1.24	0.06
58	1.93	1.32	0.06	1.814	6.49				1.32	0.06
80	1.96	1.07	0.06	1.814	6.77		6.60	6.58c	1.07	0.06
71	1.89	1.29	0.06	1.814	6.50				1.29	0.06
70	1.89	1.35	0.06	1.814	6.43		6.23	6.20e	1.35	0.06
66	1.91	1.34	0.06	1.814	6.46		6.12	6.10e	1.34	0.06
56	1.92	1.43	0.06	1.814	6.37	5.92	5.85	6.11e	1.43	0.17
79	1.95	1.18	0.06	1.814	6.65				1.18	0.06
77	1.94	1.29	0.06	1.814	6.53	6.23	6.11	6.30e	1.29	0.12
50	1.86	1.43	0.07	1.814	6.30	5.78	5.75	5.95e	1.43	0.18

Table 6.1 Cont.

69	1.89	1.30	0.07	1.814	6.45	6.04	6.03	5.89e	1.30	0.15
75	1.88	1.26	0.07	1.814	6.49	6.05	6.03	5.94e	1.26	0.14
45	1.87	1.57	0.07	1.814	6.16	5.48	4.84		1.57	0.25
59	1.91	1.45	0.07	1.814	6.31				1.45	0.07
69	1.89	1.40	0.07	1.814	6.35	5.77	5.76	6.35c	1.40	0.19
43	1.90	1.44	0.07	1.814	6.31				1.44	0.07
57	1.93	1.30	0.07	1.814	6.48				1.30	0.07
63	1.92	1.30	0.07	1.814	6.47	6.12	6.10		1.30	0.14
48	1.89	1.41	0.07	1.814	6.34	5.99	5.99	5.69c	1.41	0.14
67	1.92	1.28	0.07	1.814	6.49		6.32		1.28	0.07
74	1.91	1.24	0.07	1.814	6.53	6.10	6.10	6.67e	1.24	0.16
41	1.89	1.48	0.07	1.814	6.21		6.11	5.79e	1.48	0.07
55	1.92	1.35	0.07	1.814	6.42				1.35	0.07
60	1.91	1.31	0.07	1.814	6.45	6.06	6.01	5.95e	1.31	0.14
76	1.91	1.31	0.07	1.814	6.45				1.31	0.07
78	1.95	1.21	0.07	1.814	6.58				1.21	0.07
81	1.94	1.14	0.07	1.814	6.65				1.14	0.07
65	1.89	1.51	0.13	1.814	5.96		5.96	5.94e	1.51	0.13
62	1.89	1.38	0.13	1.814	6.63				1.38	0.13
61	1.92	1.30	0.13	1.814	6.30		6.40		1.30	0.13
104	1.98	1.58	0.03	1.936	6.86				1.58	0.03
103	2.01	1.46	0.03	1.936	6.95	6.12	6.11		1.46	0.2
100	2.00	1.43	0.03	1.936	6.98	6.23	6.23		1.43	0.18
98	2.01	1.52	0.03	1.936	6.89				1.52	0.03
121	2.04	1.27	0.03	1.936	7.17	6.43	6.43		1.27	0.16
119	2.03	1.38	0.03	1.936	7.05	6.42	6.4			0.16
96	1.99	1.72	0.03	1.936	6.67					0.03
95	2.02	1.60	0.03	1.936	6.81	5.99	5.92			0.2
91	2.01	1.58	0.03	1.936	6.83	6.32	6.31	5.87c		0.15
84	2.02	1.66	0.03	1.936	6.75	6.25	6.24	5.96e		0.15
113	2.05	1.41	0.03	1.936	7.01	6.45	6.45			0.15
110	2.04	1.52	0.03	1.936	6.91	6.45	6.22			0.15
94	2.02	1.58	0.03	1.936	6.83					0.03
92	2.05	1.45	0.03	1.936	6.99	6.32	6.32	6.05e		0.17

Table 6.1 Cont.

90	2.04	1.44	0.03	1.936	6.99	6.32	6.32		0.17
83	2.05	1.52	0.03	1.936	6.92	6.52	6.51		0.12
111	2.08	1.27	0.03	1.936	7.19	6.33	6.32	6.11	0.19
107	2.07	1.43	0.03	1.936	7.02				0.03
102	2.01	1.55	0.03	1.936	6.86				0.03
101	2.04	1.60	0.02	1.936	6.82	6.51	6.50	6.16e	0.12
99	2.03	1.36	0.03	1.936	7.07	6.42	6.41	7.21c	0.16
97	2.04	1.49	0.03	1.936	6.94	6.34	6.31	6.67e	0.17
120	2.07	1.24	0.03	1.936	7.22	5.68	5.68		0.26
118	2.06	1.35	0.03	1.936	7.10	6.58	6.57	6.24e	0.14
89	2.01	1.63	0.03	1.936	6.78				0.03
87	2.04	1.51	0.03	1.936	6.92	6.24	6.23	6.80e	0.20
85	2.03	1.48	0.03	1.936	6.94		6.63	6.61e	0.03
82	2.04	1.57	0.03	1.936	6.86				0.03
108	2.04	1.29	0.03	1.936	7.16				0.03
105	2.04	1.41	0.03	1.936	7.02	6.79	6.79		0.09
125	2.04	1.46	0.03	1.936	6.97				0.03
124	2.07	1.35	0.03	1.936	7.11				0.03
123	2.09	1.33	0.03	1.936	7.14				0.03
122	2.07	1.40	0.03	1.936	7.06				0.03
127	2.10	1.15	0.03	1.936	7.34				0.03
118	2.06	1.24	0.03	1.936	7.21	6.59	6.57	6.24c	0.18
93	2.02	1.80	0.07	1.936	6.47		6.58	6.06e	0.07
112	2.05	1.67	0.07	1.936	6.62		6.41		0.07
117	2.04	1.63	0.07	1.936	6.65		6.40		0.07
88	2.01	1.69	0.07	1.936	6.57				0.07
109	2.04	1.53	0.07	1.936	6.76				0.07
115	2.03	1.53	0.07	1.936	6.75		6.45		0.07
86	2.04	1.59	0.07	1.936	6.70				0.07
106	2.07	1.44	0.07	1.936	6.87				0.07
114	2.06	1.41	0.07	1.936	6.90		6.72		0.07
116	2.04	1.60	0.13	1.936	6.48		6.30	6.14c	0.13
150	2.13	1.56	0.03	2.059	7.39	6.65	6.64	6.31e	0.20
136	2.14	1.75	0.00	2.059	7.30	6.67	6.45	7.14c	0.18

Table 6.1 Cont.

155	2.12	1.47	0.00	2.059	7.58	6.56	6.54	7.55c	0.21
148	2.16	1.47	0.00	2.059	7.60	6.89	6.89	5.74e	0.15
135	2.17	1.61	0.00	2.059	7.46	7.15	7.15		0.09
133	2.20	1.48	0.00	2.059	7.62	7.02	7.00		0.17
154	2.15	1.44	0.00	2.059	7.63	7.04	7.04		0.17
149	2.16	1.57	0.00	2.059	7.5		7.28		0.00
146	2.19	1.45	0.00	2.059	7.61	6.85	6.85		0.22
153	2.18	1.63	0.00	2.059	7.44	6.82	6.8	7.75c	0.18
140	2.18	1.54	0.00	2.059	7.54	6.63	6.58		0.20
132	2.16	1.65	0.03	2.059	7.42	6.79	6.78	6.43e	0.18
130	2.19	1.52	0.00	2.059	7.57		7.12	7.39e	0.00
138	2.18	1.49	0.00	2.059	7.59	6.73	6.72	7.93e	0.20
128	2.18	1.56	0.00	2.059	7.52	6.96	6.96	7.32c	0.16
168	2.18	1.35	0.00	2.059	7.74	6.96	7.18		0.18
164	2.19	1.49	0.00	2.059	7.6	6.74	6.63		0.20
162	2.20	1.34	0.00	2.059	7.76	7.21	7.21		0.16
167	2.21	1.31	0.00	2.059	7.8	7.29	7.29		0.12
157	2.21	1.40	0.00	2.059	7.7				0.00
169	2.21	1.21	0.00	2.059	7.9	7.57	7.55		0.07
152	2.14	1.95	0.03	2.059	7.08	6.63	6.61		0.13
151	2.02	1.70	0.03	2.059	7.28		7.15		0.03
147	2.16	1.80	0.03	2.059	7.25	6.91	6.89		0.10
134	2.17	1.88	0.03	2.059	7.17	6.69	6.68		0.14
165	2.20	1.63	0.03	2.059	7.45		7.37		0.03
163	2.19	1.74	0.03	2.059	7.33	6.78	6.78		0.16
145	2.13	1.85	0.03	2.059	7.18	6.77	6.76		0.03
144	2.16	1.68	0.03	2.059	7.38	6.83	6.82		0.16
139	2.15	1.62	0.03	2.059	7.44	6.61	6.58		0.03
131	2.16	1.76	0.03	2.059	7.3	6.78	6.78		0.03
161	2.19	1.68	0.03	2.059	7.30				0.03
158	2.18	1.62	0.03	2.059	7.45	7.00	6.99		0.13
143	2.16	1.73	0.03	2.059	7.33	6.77	6.76		0.16
141	2.19	1.61	0.03	2.059	7.47	6.86	6.85		0.18
137	2.18	1.58	0.03	2.059	7.50		7.46	6.83e	0.03

Table 6.1 Cont.

129	2.19	1.67	0.03	2.059	7.41		7.32	6.76e	0.03
159	2.20	1.41	0.03	2.059	7.69	7.17	7.17		0.15
156	2.21	1.53	0.03	2.059	7.57		7.44		0.03
142	2.16	1.76	0.07	2.059	7.30	6.85	6.85		0.13
160	2.19	1.62	0.07	2.059	7.46	6.91	6.88		0.16
166	2.18	1.58	0.07	2.059	7.50	7.18	7.16		0.09
188	2.28	1.83	0.00	2.181	7.75	6.79	6.78		0.28
179	2.32	1.95	0.00	2.181	7.65	6.54	6.41		0.32
178	2.31	1.83	0.00	2.181	7.77	6.94	6.85		0.24
187	2.31	1.81	0.00	2.181	7.79	7.01	6.99		0.23
177	2.28	1.82	0.00	2.181	7.76				0.00
193	2.34	1.71	0.00	2.181	7.91	7.22	7.21		0.20
184	2.27	1.74	0.00	2.181	7.84				0.00
176	2.31	1.72	0.00	2.181	7.89				0.00
175	2.31	1.63	0.00	2.181	7.98	6.94	6.92		0.30
183	2.30	1.60	0.00	2.181	8.01	7.14	7.05		0.25
171	2.30	1.76	0.00	2.181	7.84	7.01	6.99		0.24
191	2.33	1.63	0.00	2.181	7.99	7.23	7.21		0.22
182	2.30	1.62	0.00	2.181	7.99	7.09	6.92		0.26
174	2.31	1.78	0.00	2.181	7.82	6.92	6.85		0.20
172	2.34	1.62	0.00	2.181	8.01	7.14	7.03		0.25
186	2.28	1.74	0.03	2.181	7.85	7.09	6.78		0.22
185	2.31	1.78	0.03	2.181	7.82	6.99	6.99		0.24
181	2.30	1.77	0.03	2.181	7.83	7.00	6.92		0.24
173	2.31	1.84	0.03	2.181	7.66				0.03
180	2.29	1.56	0.00	2.181	8.04	7.21	7.21		0.24
170	2.33	1.66	0.00	2.181	8.02	7.13	7.08		0.26
189	2.36	1.50	0.00	2.181	8.15	7.28	7.24		0.25
192	2.34	1.59	0.03	2.181	8.04	7.28	7.21		0.22
190	2.33	1.70	0.03	2.181	7.92	7.09	7.08		0.24
199	2.46	1.98	0.00	2.303	8.16	7.44	7.43		0.21
196	2.45	1.86	0.00	2.303	8.28	7.38	7.35		0.26
194	2.48	1.90	0.00	2.303	8.26				0.00
201	2.43	1.89	0.00	2.303	8.24				0.00

Table 6.1 Cont.

197	2.42	1.92	0.00	2.303	8.21				0.00
202	2.44	1.91	0.00	2.303	8.23				0.00
204	2.38	1.85	0.00	2.303	8.50	7.60	7.48		0.26
200	2.43	1.92	0.00	2.303	8.21	7.31	7.21	7.11c	0.26
198	2.46	1.79	0.00	2.303	8.36	7.46	7.43		0.26
203	2.48	1.79	0.00	2.303	8.37	7.51	7.49		0.25
195	2.45	1.84	0.00	2.303	8.30	7.41	7.35		0.26
205	2.48	1.67	0.00	2.303	8.50	7.64	7.62		0.25
208	2.58	1.91	0.00	2.426	8.77				0.00
207	2.57	1.95	0.00	2.426	8.73				0.00
206	2.60	2.05	0.00	2.426	8.25		8.16		0.00
209	2.72	2.11	0.00	2.548	8.18		8.26	7.73c	0.00

a- Log P listed by Sangster [5], as log KOW

b- Values of log P from ref. paper (c- from Opperhuizen [6], e- from Rapaport [2], d- from Sabiljic [3].)

6.2 Adjustment of the estimated $\Sigma\beta^{H}_{2}$ values

In order to check the obtained values of $\Sigma\beta^{H}_{2}$ from the above procedure, β1st, and π^{H}_{2} from Table 6.1, other data were also used. The first set was that of the log P data of Opperhuizen; [6] in this paper the values for water-octanol partition coefficients for alkyl benzenes, chlorinated benzene, naphthalenes and biphenyls, were given. So by using the initial descriptors for PCBs, and for the other compounds, a multiple linear regression was obtained, equation 6.3,

$$\log Poct = 0.722 + 0.469\, R_2 - 1.267\, \pi^{H}_{2} - 3.920\, \Sigma\beta^{H}_{2} + 3.569 V_x \qquad (6.3)$$

$n = 58$ $\quad r^2 = 0.9759$ $\quad sd = 0.220$ $\quad F = 409.3$

Another set of log Poct values from Rapaport et al.[2] was also used, to give the following equation.

$$\log Poct = -0.183 + 1.149\, R_2 - 2.602\, \pi^{H}_{2} - 0.707\, \Sigma\beta^{H}_{2} + 3.950\, V_x \qquad (6.4)$$

$n = 67$ $\quad r^2 = 0.8350$ $\quad sd = 0.421$ $\quad F = 78.2$

In this case the regression equation was very poor, but by leaving out some of the PCBs a good regression equation could be found, equation 6.5.

$$\log P = 1.135 + 1.400\, R_2 - 2.040\, \pi^{H}_{2} - 2.286\, \Sigma\beta^{H}_{2} + 2.487\, V_x \qquad (6.5)$$

$n = 45$ $\quad r^2 = 0.9902$ $\quad sd = 0.137$ $\quad F = 302.6$

In the final step, the back-calculated $\Sigma\beta^{H}_{2}$ values found from equations 6.3 and 6.5 were compared to the values obtained from the Sangster and the Med Chem data base log Poct values. A new averaged set of $\Sigma\beta^{H}_{2}$ values was obtained and the data from Opperhuizen and Rapaport et al. were recalculated to give equations 6.6 and 6.7. In addition data by Sablijic et al.[3] and by Parks et al.[7] on HPLC capacity factors were also used to provide two extra regression equations, equations 6.8 and 6.9.

Equation (6.6), Opperhuizen values

$$\log Poct = 0.552 + 0.166R_2 - 0.758\pi^{H}_{2} - 3.963\ \Sigma\beta^{H}_{2} + 3.649\ V_x \qquad (6.6)$$

$n = 58$ $\quad r^2 = 0.9936$ $\quad sd = 0.201$ $\quad F = 450.8$

Equation (6.7), Rapaport et al. values

$$\log Poct = 1.038 + 1.772\ R_2 - 3.300\ \pi^{H}_{2} + 3.277\ \Sigma\beta^{H}_{2} + 3.265\ V_x \qquad (6.7)$$

$n = 67$ $\quad r^2 = 0.9506$ $\quad sd = 0.231$ $\quad F = 2117$

Equation (6.8), Sablijic et al. values

$$\log k' = 1.473 + 4.731\ R_2 + 0.141\ \pi^{H}_{2} - 5.275\Sigma\beta^{H}_{2} - 2.047\ V_x \qquad (6.8)$$

$n = 20$ $\quad r^2 = 0.9872$ $\quad sd = 0.155$ $\quad F = 309.2$

Equation (6.9), Parks et al. values

$$\log k' = 0.602 + 0.388\ R_2 - 0.836\ \pi^{H}_{2} - 1.167\ \Sigma\beta^{H}_{2} + 1.266\ V_x \qquad (6.9)$$

$n = 39$ $\quad r^2 = 0.9542$ $\quad sd = 0.120$ $\quad F = 178.9$

6.3 Individual calculations for the PCBs

The regression equations obtained to data are summarized in Table 5.6 [This will give the GLC, log P, log k' etc. equations]. Then for each PCB, the values of the dependent variable, I , log Poct , or log k' were back-calculated from the equations. If the back-calculated values did not entirely agree with the observed values, then the descriptor values were adjusted accordingly. As found before, unsatisfactory results were obtained with the more polar GLC phases, so most recalculations were carried out with the non-polar GLC phases and the various phases used in the calculation of $\Sigma\beta^{H}_{2}$. As an example, the individual calculation for PCB 172 (2,3,4,5- tetrachlorobiphenyl) is given in Table 6.2.

Table 6.2. Individual calculation of descriptors for PCB 172 (2,3,4,5-tetrachlorobiphenyl).

6.2 (A) Comparison of observed and calculated values

System	Obs. Values	Calc. Values
log P_{oct}	6.450	6.393
log k'(3) [a]	6.406	6.586
GLC phase 1[b]	2.039	1.898
GLC phase 2	2.043	1.908
GLC phase 3	2.127	1.998
GLC phase 4	2.306	2.277
GLC phase 5	2.110	2.026
GLC phase 11	2.000	2.200

sd :	0.118

a Reference number.
b For the GLC phases I/1000 is entered.

6.3 (B) Descriptor values used in the recalculation

Descriptor values	Original values	Recalculated
R_2	1.92	1.92
$\pi^H{}_2$	1.30	1.31
$\Sigma\beta^H{}_2$	0.09	0.09
Log L^{16}	8.30	8.28
V_x	1.814	1.814

6.4 Re-examination of the polar GLC phases

Because a number of polar GLC phases had not yielded satisfactory results, new regression equations were obtained with the descriptors found in 6.4. An example is phase 8 (An-600).

$$I = 324.626 + 363.005\, R_2 + 421.229\, \pi^H{}_2 + 157.589 \log L^{16} \qquad (6.10)$$

$n = 49$ $\quad r^2 = 0.963$ $\quad sd = 0.203$ $\quad F = 209.7$

This is still not satisfactory, and so most of the polar GLC phases were not further used.

6.5 References

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Chapter 7 The Final (Third) Calculation of Descriptors for PCBs

7.0 Introduction

This chapter is a continuation of the work which was described in the previous two chapters (Chapters 5 and 6). In this chapter most of the calculations will be done by using Solver, the Microsoft Excel computer program which is fast and easy to use. In the first part of the Chapter, the PCBs studied by Opperhuizen[1] will be dealt with, and in the second part all the 209 PCBs will be considered.

7.1 Using Solver program to get the final values for (π^H_2 , $\Sigma\beta^H_2$ and log L^{16})

The Solver program is a program in Excel that automatically carries out the procedure for the calculation of descriptors that was done by hand previously. Regression coefficients for all systems examined were entered into the Excel spreadsheet. Then for any given PCB, the dependent variables were entered. The descriptors R_2 and V_x were taken as fixed values, and Solver then calculates the values of π^H_2 , $\Sigma\beta^H_2$ and log L^{16} that give the best fit of observed and calculated dependent variables. It is possible to over-ride the Solver calculations, and fix descriptors either within a range or as a definite value. For example, from the previous work, it was clear that $\Sigma\beta^H_2$ for all the dichlorobiphenyls was within the range 0.11 to 0.19, and so this range for dichlorobiphenyls was fixed in Solver.

The range for values of log L^{16} for the PCBs was estimated using data on the polychlorobenzenes, (see Table 7.1). The log L^{16} values fall into a definite pattern. This a pattern was used to estimate log L^{16} values for the PCBs as a first assessment, in the Solver program. The PCBs listed in the paper of Opperhuizen paper[1] and studied using Solver are given in Table (7.2).

Table (7.1) The pattern of values of log L^{16} for the chlorobenzenes

Name	**log L^{16}**	**Difference**	**Est. log L^{16}**
Benzene	2.79		
Chlorobenzene	3.63	0.87	3.66
1,2-Dichlorobenzene	4.47	0.98	4.44
1,2,3-Trichlorobenzene	5.31	0.81	5.25
1,2,3,5-Tetrachlorobenzene	6.15	0.75	6.00
Pentachlorobenzene	6.99	0.72	6.72
Hexachlorobenzene	7.83	0.90	7.62

In Table 7.2 are given a number of different sets of values for the descriptors for the PCBs listed in the paper of Opperhuizen.[1] The first set of results (1) was by use of the Solver program, which had to be done two or three times in order to get the best set according to the limitation of the values of $\Sigma\beta_2^H$. The second sets (2) were by hand calculation using an in-house method (LPCALC). The third set was the one that was chosen to give the 'best' values for all the descriptors. There is not much difference

between the values, and the set with the smallest sd value (in Solver) was taken as the final set of values (shown as '3' in the Table 7.2).

Table (7.2) Values for (π^{H}_{2}, $\Sigma\beta_2^{H}$, log L^{16}, and sd) using Solver calculations, with previous values and the values finally taken .

Name	R_2	Vx	π^{H}_{2}	$\Sigma\beta_2^{H}$	Log L^{16}	Sd
Biphenyl	1.36	1.32	0.87	0.32	4.62	0.28
1			0.94	0.25	5.19	0.19
			0.98	0.25	5.44	0.15
			0.98	0.24	5.44	0.16
2			0.98	0.25	5.40	0.16
3			0.98	0.25	5.44	0.15
2-Monochlorobiphenyl	1.48	1.45	0.94	0.26	6.36	0.05
1			1.08	0.20	6.44	0.04
			1.08	0.18	6.44	0.07
			1.08	0.18	6.35	0.09
2			1.11	0.19	6.30	0.66
3			1.08	0.20	6.35	0.04
3-Monochlorobiphenyl	1.51	1.45	0.62	0.38	6.62	0.13
1			1.06	0.17	6.35	0.18
			1.06	0.20	6.35	0.18
			1.06	0.18	6.35	0.18
2			1.02	0.20	6.40	0.17
3			1.06	0.18	6.35	0.18
4-Monochlorobiphenyl	1.50	1.45	1.08	0.28	6.67	0.17
1			0.64	0.38	6.72	0.09
			1.01	0.20	6.57	0.13
			1.01	0.18	6.57	0.15
2			1.09	0.17	6.48	0.15
3			1.01	0.20	6.57	0.13
2,2'-Dichlorobiphenyl	1.60	1.57	1.29	0.22	4.80	0.47
1			1.34	0.15	6.79	0.06
			1.34	0.14	6.79	0.07
2			1.46	0.10	6.66	0.86
3			1.29	0.15	6.79	0.06

2,5-Dichlorobiphenyl	1.63	1.57	1.00	0.29	5.52	0.37
1			0.81	0.32	6.87	0.12
			1.17	0.15	6.72	0.16
			1.17	0.16	6.72	0.15
2			1.19	0.15	7.00	0.17
3			1.17	0.16	6.72	0.15
2,6-Dichlorobiphenyl	1.66	1.57	1.20	0.25	4.88	0.43
1			0.81	0.36	6.59	0.11
			1.26	0.16	6.41	0.16
			1.26	0.15	6.41	0.17
2			1.38	0.12	6.40	0.53
3			1.26	0.16	6.41	0.16
4,4'-Dichlorobiphenyl	1.64	1.57	1.24	0.20	7.12	0.14
1			1.20	0.21	7.20	0.14
			1.24	0.20	7.02	0.16
2			1.20	0.16	7.03	0.13
3			1.20	0.16	7.03	0.13
2,2',5-Trichlorobiphenyl	1.75	1.69	0.22	0.67	7.40	0.11
1			1.31	0.16	7.67	0.07
			1.31	0.11	7.67	0.14
			1.31	0.15	7.67	0.74
2			1.38	0.13	7.56	0.07
3			1.31	0.16	7.67	0.07
2,4,5-Trichlorobiphyl	1.77	1.69	0.31	0.51	7.51	0.17
1			1.12	0.16	7.83	0.05
			1.12	0.13	7.83	0.10
2			1.17	0.14	7.80	0.05
3			1.12	0.16	7.83	0.05
2,4,6-Trichlorobiphenyl	1.74	1.69	1.63	0.14	6.31	0.39
1			1.17	0.10	7.30	0.06
			1.17	0.07	7.30	0.08
			1.17	0.14	7.30	0.08
2			1.32	0.06	7.30	0.06
3			1.17	0.10	7.30	0.06
2,2',4,5'-Tetrachlorobiphenyl	1.89	1.81	1.16	0.29	6.40	0.48
1			1.28	0.16	8.26	0.13
			1.28	0.14	8.26	0.14
			1.28	0.15	8.26	0.13
2			1.49	0.07	8.20	0.17
3			1.28	0.15	8.26	0.13
2,3,4,5-Tetrachlorobiphenyl	1.92	1.81	1.42	0.10	6.44	0.51
1			1.20	0.16	8.74	0.17
			1.31	0.09	8.30	0.13
2			1.31	0.09	8.30	0.12
3			1.20	0.09	8.30	0.13

2,2',4,5,5'-Pentachlorobiphenyl	2.04	1.94	1.60	0.10	9.18	0.17
1			1.61	0.09	9.20	0.13
2			1.59	0.11	9.14	0.15
3			1.61	0.09	9.20	0.13
2,3,4,5,6-Pentachlorobiphenyl	2.04	1.94	1.48	0.10	6.70	0.51
1			1.76	0.10	9.08	0.11
			1.76	0.07	9.08	0.15
			1.76	0.05	9.08	0.18
2			1.65	0.12	9.10	0.04
3			1.76	0.10	9.08	0.11
2,2',3,3',4,4'-Hexachlorobiphenyl	2.18	2.06	1.64	0.10	7.62	0.51
1			1.68	0.10	10.19	0.07
			1.88	0.07	10.17	0.12
2			1.58	0.14	10.20	0.06
3			1.68	0.10	10.19	0.07
2,2',3,3',6,6'-Hexachlorobiphenyl	2.14	2.06	1.53	0.34	6.61	0.62
1			1.86	0.10	9.07	0.10
			1.93	0.07	9.07	0.11
			1.82	0.12	9.08	0.09
2			1.75	0.14	9.10	0.11
3			1.82	0.12	9.08	0.09
2,2'4,4,5,5'-Hexachlorobiphenyl	2.19	2.06	1.26	0.32	7.74	0.52
1			1.71	0.10	9.72	0.13
			1.79	0.07	9.71	0.14
2			1.67	0.17	9.80	0.04
3			1.71	0.10	9.72	0.13
2,2',4,4'6,6'-Hexachlorobiphenyl	2.12	2.06	1.61	0.18	5.87	0.70
1			1.69	0.04	8.69	0.11
			1.73	0.02	8.68	0.12
			1.78	0.00	8.68	0.13
2			1.74	0.02	8.70	0.08
3			1.69	0.04	8.69	0.11
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	2.48	2.30	1.39	0.35	7.51	0.62
1			1.98	0.01	9.95	0.13
			1.98	0.00	9.95	0.13
			1.98	0.02	9.95	0.14
2			1.91	0.04	9.90	0.12
3			2.00	0.01	9.95	0.13
2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	2.58	2.43	0.17	0.77	10.71	0.38
1			1.83	0.03	10.88	0.10
			1.89	0.01	10.88	0.10
2			1.91	0.00	10.80	0.10
3			2.22	0.01	10.88	0.10

Decachlorobiphenyl	2.75	2.55	1.64	0.37	8.78	0.79
1			2.05	0.03	11.78	0.37
			2.05	0.00	11.78	0.39
			2.05	0.01	11.78	0.38
2			1.84	0.15	11.70	0.28
3			2.35	0.00	11.78	0.37

1-Values for descriptors using Solver program.
2-Values for descriptors calculated by hand.
3-Taken values for the descriptors.

The final set of values of (π^{H}_{2} , $\Sigma\beta^{H}_{2}$ and log L^{16}) were plotted against the number of chlorine atoms (N) in the biphenyl. The graph of π^{H}_{2} versus N shows three nearly straight lines, see Figure (7.1). The same type of effect is noticed in the plot of log L^{16} versus N. In the case of the plot of $\Sigma\beta^{H}_{2}$ against N, three straight lines are again observed. The three straight lines in the graph for π^{H}_{2} were clearer than those of log L^{16} or for $\Sigma\beta^{H}_{2}$ although the difference between the three lines is very small.

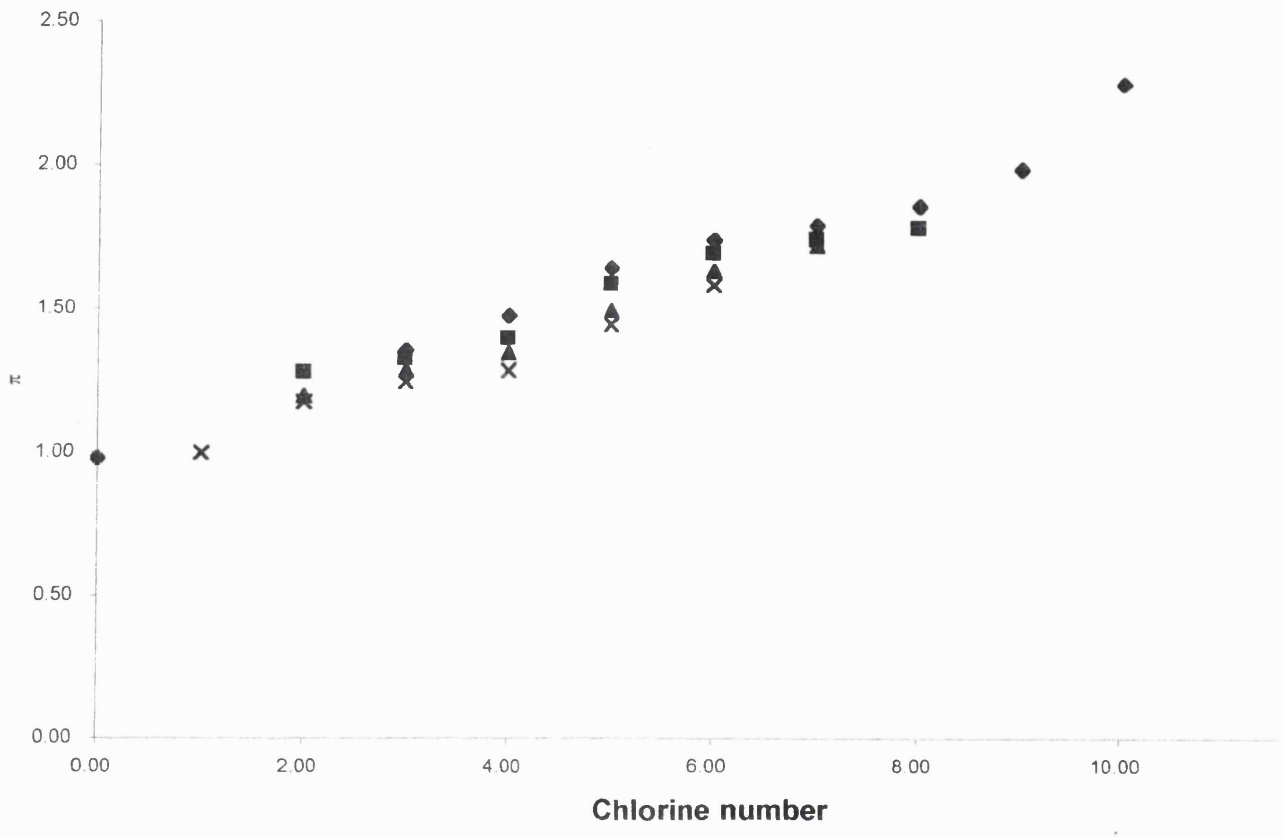

Figure (7.1) Plot of π vs chlorine number.

For ortho-substituted congeners (◆) 2,2',6,6'-substituted congeners, (■) 2,2'-substituted congeners, (▲) 2- substituted congeners and (X) non-substituted .

These effects appear to be due to the positions of the chlorine substituents, especially with respect to the ortho-position. Restriction of rotation about the 1,1' bond (i.e in the 2,2' compounds) [2-5] leads to an increase in polarity. Interestingly, the effect of ortho-substituents has been noted in various high -performance liquid chromatographic HPLC systems[6,4,5] Brinkman and Devries[4] observed little or no effect of PCBs planarity but did observe an obvious increased polarity with ortho substitution. This increase was noted for 2, 6,2'- and 2,6,2', 6'-congeners compared to other PCBs with the same chlorine number. Experiments of Dekok et al[5] produced similar results. Two possible explanations for the pronounced Roth effects observed in this work are increased polarity due to Roth chlorine substitution or decrease in contact area resulting from persistence of the biphenyl moiety in a non planar form. Therefore, the increasing effect of ortho-substitution might reflect a decrease in substrate-compound contact area and /or increased congener polarity.

7.2 Recalculation of the log P oct equation from data in Opperhuizen's and Sablijic's papers.

In order to recalculate the equation, all the PCBs in Opperhuizen's paper[1] plus all the aromatic compounds in Sablijic's paper[7] were used in a multiple linear regression equation, as shown below:

$$\text{Log Poct} = 0.710 + 1.154\, R_2 - 1.068\, \pi^{H}{}_2 - 3.613\, \Sigma\beta^{H}{}_2 + 2.855\, V_x \qquad (7.1)$$

$n = 35$ $\quad r^2 = 0.974$ $\quad sd = 0.241$ $\quad F = 618.9$

This equation was then used as a reference equation in the Solver program, together with previous equations. New values for the descriptors for compounds in Opperhuizen's paper were then calculated. A new graph for each descriptor verses the number of chlorine atoms, N, was drawn. Using the linear regression the equation for each line was found, The first one represented the (2,2',6,6') ortho-substituted PCBs, the second line represented the 2,2' substituted PCBs, and the last line was for one substituted or non - substituted, as shown in Table (7.3). From the equations for the line, new calculated values for (π_2^H, $\Sigma\beta^H_2$ and $\log L^{16}$) were obtained.

Table (7.3)

Linear equations of π_2^H, $\Sigma\beta_2^H$, $\log L$ for the PCBs in Opperhuizen's paper[1]

Linear equations of π^H_2

g + N, where g is a constant and N is the number of chlorine atoms in the PCB

0.98 + 0.13 N, for (2,2',6,6') ortho-substituted PCBs

n = 9 $r^2 = 1.00$ sd = 0.01 F = 1691.5

0.96 + 0.13 N, for (2,2') ortho-substituted PCBs

n = 6 $r^2 = 1.00$ sd = 0.01 F = 1106.5

0.96 + 0.11 N, for one substituted or, non substituted

n = 7 $r^2 = 1.00$ sd = 0.01 F = 1053.4

Linear equations for β^H_2

0.24 – 0.02 N, for (2,2',6,6') ortho-substituted PCBs

n = 9 $r^2 = 0.99$ sd = 0.02 F = 4329.7

0.22 – 0.02 N, for (2,2') substituted PCBs

n = 6 $r^2 = 0.99$ sd = 0.02 F = 1721.8

0.20 - 0.02 N, for one substituted or, non substituted

n = 7 $r^2 = 0.99$ sd = 0.02 F = 934.3

Linear equations for log L^{16}.

5.66 + 0.68 N, for (2,2',6,6') ortho-substituted PCBs

n = 9 $r^2 = 0.99$ sd = 0.09 F = 3724.6

5.66 + 0.66 N, for (2,2') ortho-substituted PCBs

n = 6 $r^2 = 1.00$ sd = 0.01 F = 7291.4

5.65 + 0.62 N, for one substituted or, non substituted

n = 7 $r^2 = 1.00$ sd = 0.01 F = 7961.3

The next step was to compare the calculated values of the descriptors in this second round, with the ones first calculated by using the Solver program ,and to compare also the sd values, as shown in Table (7.4). The final values for the descriptors are indicated.

Table (7.4) The values for (π^{H}_{2}, $\Sigma\beta^{H}_{2}$, log L^{16}) first calc., (π^{H}_{2}, $\Sigma\beta^{H}_{2}$, log L^{16}) second calc. and the values for sd.

Name	N	π^{H}_{2}	$\Sigma\beta^{H}_{2}$	$\log L^{16}$	Sd	π^{H}_{2}	$\Sigma\beta^{H}_{2}$	$\log L^{16}$	sd
		2nd	2nd	2nd	2nd	**1st**	**1st**	**1st**	**1st**
Biphenyl	0.00	0.97	0.24	5.530	0.106	0.98	0.25	5.444	0.097
2-Monochlorobiphenyl	1.00	1.13	0.22	6.320	0.096	1.10	0.22	6.340	0.094
3-Monochlorobiphenyl	1.00	1.11	0.22	6.230	0.130	1.01	0.22	6.440	0.117
4-Monochlorobiphenyl	1.00	1.10	0.22	6.320	0.125	1.00	0.21	6.400	0.097
2,2'-Dichlorobiphenyl	2.00	1.24	0.17	6.980	0.086	1.20	0.18	6.800	0.070
2,5-Dichlorobiphenyl	2.00	1.18	0.20	7.220	0.096	1.25	0.19	6.900	0.094
2,6-Dichlorobiphenyl	2.00	1.23	0.20	7.220	0.121	1.25	0.19	6.746	0.120
4,4'-Dichlorobiphenyl	2.00	1.06	0.19	7.220	0.117	1.07	0.19	6.900	0.116
2,2',5-Trichlorobiphenyl	3.00	1.34	0.15	7.640	0.074	1.30	0.16	7.500	0.063
2,4,5-Trichlorobiphenyl	3.00	1.27	0.18	7.720	0.093	1.28	0.16	7.500	0.082
2,4,6-Trichlorobipheny	3.00	1.36	0.17	7.720	0.152	1.35	0.17	7.400	0.127
2,2',4,5'-Tetrachlorobipheny	4.00	1.47	0.14	8.300	0.124	1.48	0.13	8.251	0.098
2,3,4,5-Tetrachlorobiphen	4.00	1.39	0.15	8.330	0.103	1.53	0.15	8.300	0.098
2,2',3,4,5'Pentachlorobipheny	5.00	1.64	0.11	8.960	0.142	1.62	0.11	9.160	0.101
2,3,4,5,6-Pentachlorobiphenyl	5.00	1.59	0.13	9.030	0.101	1.55	0.12	9.090	0.084
2,2',3,3',4,4'-Hexachlorobiphenyl	6.00	1.65	0.09	9.620	0.143	1.75	0.08	9.900	0.095

2,2',4,4'6,6'-Hexachlorobiphenylc	6.00	1.80	0.05	9.000	0.159	1.84	0.03	9.500	0.088
2,2'4,4,5,5'-Hexachlorobipheny	6.00	1.73	0.09	9.620	0.126	1.74	0.08	9.800	0.090
2,2',3,3',5,5',6,6'-Octachlorobipheny	8.00	2.	0.01	10.360	0.111	2.00	0.00	9.980	0.084
2,2',3,3',4,5,5',6,6'-Nanochlorobipheny	9.00	2.20	0.00	10.930	0.164	2.21	0.00	10.875	0.097
Decachlorobipheny	10.00	2.40	0.00	11.500	0.117	2.45	0.00	11.789	0.111

7. 3 Calculation of the descriptors for the rest of the PCBs.

Once the best values of the descriptors for the compounds in Opperhuizen's paper were found, plots against N were again carried out. The various equations from linear regressions were found in the same way as before. Using these equations, calculated values for the descriptors for the rest of the PCBs could be obtained. Values for all 209 PCBs are shown in Table (7.5).

Using these calculated descriptors, it was possible to predict values for the water-octanol partition coefficients for all the PCBs, through equation (5.2). Results are also shown in Table (7.5). Comparison of the calculated logPoct values with those observed (Table 6.1, log P calculated using the altered π , β values) gave a standard deviation in observed- predicted values of only 0.122, which is a very acceptable value.

Table (7.5) Calculated values for (π_2^H, $\Sigma\beta_2^H$ and log L^{16}) the values of log P first calc. Predicted values for log P.

Name	IUPAC	Log L^{16} cal	Log P cal(a)	Log P prd(b)	π_2^H cal	$\Sigma\beta_2^H$ cal	Log P(cal-prd)
Biphenyl	-	5.660	3.890	4.06	0.98	0.24	0.17
2-Monochloro	1	6.430	4.600	4.54	1.11	0.22	-0.06
3-Monochloro	2	6.430	4.690	4.60	1.00	0.20	-0.09
4-Monochloro	3	6.340	4.610	4.58	1.00	0.20	-0.03
2,2'-Dichloro	4	7.020	5.060	5.07	1.28	0.22	0.01
2,3-Dichloro	5	6.980	5.130	5.08	1.20	0.18	-0.05
2,3'-Dichloro	6	6.980	5.165	5.08	1.20	0.18	-0.08
2,4-Dichloro	7	6.980	5.010	5.06	1.20	0.18	0.05
2,4'-Dichloro	8	6.980	5.130	5.06	1.20	0.18	0.07
2,5-Dichloro	9	6.980	5.150	5.08	1.20	0.18	0.07
2,6-Dichloro	10	6.980	5.090	5.14	1.20	0.18	0.05
3,3'-Dichloro	11	6.880	5.280	5.30	1.18	0.16	-0.02
3,4-Dichloro	12	6.880	5.230	5.30	1.18	0.16	0.07
3,4'-Dichloro	13	6.880	5.250	5.18	1.18	0.16	-0.07
3,5-Dichloro	14	6.880	5.320	5.37	1.18	0.16	0.05
4,4'-Dichloro	15	6.880	5.300	5.35	1.18	0.16	0.05
2,2',3-Trichloro	16	7.640	5.620	5.62	1.33	0.15	0.00
2,2',4-Trichloro	17	7.640	5.620	5.60	1.33	0.15	-0.02
2,2',5-Trichloro	18	7.640	5.527	5.62	1.33	0.15	0.09
2,2',6-Trichloro	19	7.640	5.550	5.62	1.33	0.15	0.07
2,3,3'-Trichloro	20	7.510	5.590	5.57	1.29	0.14	0.02
2,3,4-Trichloro	21	7.510	5.670	5.61	1.29	0.14	0.04
2,3,4'-Trichloro	22	7.510	5.590	5.61	1.29	0.14	-0.02
2,3,5-Trichloro	23	7.510	5.690	5.61	1.29	0.14	-0.08

Table 7.5 cont.

2,3,6-Trichloro	24	7.510	5.660	5.67	1.29	0.14	-0.01
2,3',4-Trichloro	25	7.510	5.540	5.61	1.29	0.14	0.07
2,3',5-Trichloro	26	7.510	5.710	5.63	1.29	0.14	-0.07
2,3',6-Trichloro	27	7.510	5.684	5.59	1.29	0.14	-0.10
2,4,4'-Trichloro	28	7.510	5.600	5.59	1.29	0.14	-0.01
2,4,5-Trichloro	29	7.510	5.690	5.61	1.29	0.14	-0.08
2,4,6-Trichloro	30	7.510	5.710	5.61	1.29	0.14	-0.10
2,4',5-Trichloro	31	7.510	5.770	5.61	1.29	0.14	-0.16
2,4',6-Trichloro	32	7.510	5.750	5.75	1.29	0.14	-0.00
2',3,4-Trichloro	33	7.510	5.730	5.71	1.29	0.14	-0.02
2',3,5-Trichloro	34	7.510	5.700	5.63	1.29	0.14	-0.07
3,3',4-Trichloro	35	7.400	5.700	5.66	1.25	0.13	-0.04
3,3',5-Trichloro	36	7.400	5.720	5.64	1.25	0.13	-0.08
3,4,4'-Trichloro	37	7.400	5.670	5.64	1.25	0.13	-0.03
3,4,5-Trichloro	38	7.400	5.700	5.66	1.25	0.13	-0.04
3,4',5-Trichloro	39	7.400	5.710	5.66	1.25	0.13	-0.14
2,2',3,3'-Tetachloro	40	8.130	6.180	6.16	1.40	0.12	0.02
2,2',3,4-Tetrachloro	41	8.130	6.110	6.14	1.40	0.12	0.03
2,2',3,4'-Tetrachloro	42	8.130	6.180	6.14	1.40	0.12	-0.04
2,2',3,5-Tetrachloro	43	8.130	6.200	6.16	1.40	0.12	-0.04
2,2',3,5'-Tetrachloro	44	8.130	6.180	6.16	1.40	0.12	0.02
2,2',3,6-Tetrachloro	45	8.300	6.080	6.15	1.48	0.15	0.07
2,2',3,6'-Tetrachloro	46	8.300	6.090	6.15	1.48	0.15	0.06
2,2',4,4'-Tetrachloro	47	8.130	6.190	6.12	1.40	0.12	-0.07
2,2',4,5-Tetrachloro	48	8.130	6.160	6.14	1.40	0.12	-0.02
2,2',4,5'-Tetrachloro	49	8.130	5.210	6.14	1.40	0.12	0.07
2,2',4,6-Tetrachloro	50	8.300	6.040	6.13	1.48	0.15	0.09

Table 7.5 cont.

2,2',4,6'-Tetrachloro	51	8.300	6.150	6.13	1.48	0.15	-0.02
2,2',5,5'-Tetrachloro	52	8.130	6.230	6.26	1.40	0.12	0.03
2,2',5,6'-Tetrachloro	53	8.300	6.060	6.15	1.48	0.15	0.08
2,2',6,6'-Tetrachloro	54	8.300	5.940	5.94	1.48	0.15	0.00
2,3,3',4-Tetrachloro	55	7.720	6.120	6.15	1.35	0.10	0.03
2,3,3',4'-Tetrachloro	56	7.720	6.200	6.15	1.35	0.10	-0.05
2,2',4,5-Tetrachloro	57	8.380	6.120	6.17	1.40	0.12	0.05
2,3,3',5'-Tetrachloro	58	7.720	6.170	6.17	1.35	0.10	0.00
2,3,3',6-Tetrachloro	59	7.720	6.210	6.13	1.35	0.10	-0.08
2,3,4,4'-Tetrachloro	60	7.720	6.300	6.13	1.35	0.10	-0.17
2,3,4,5-Tetrachloro	61	7.720	6.250	6.15	1.35	0.10	-0.10
2,3,4,6-Tetrachloro	62	7.720	6.230	6.09	1.35	0.10	-0.14
2,3,4',5-Tetrachloro	63	7.720	6.210	6.15	1.35	0.10	-0.06
2,3,4',6-Tetrachloro	64	7.720	6.250	6.18	1.35	0.10	-0.07
2,3,5,6-Tetrachloro	65	7.720	6.090	6.09	1.35	0.10	0.00
2,3,4,4'-Tetrachloro	66	7.720	6.250	6.15	1.35	0.10	-0.10
2,3,4',5-Tetrachloro	67	7.720	6.270	6.15	1.35	0.10	-0.08
2,3',4,5'-Tetrachloro	68	7.720	6.270	6.15	1.35	0.10	-0.08
2,3',4,6-Tetrachloro	69	7.720	6.200	6.09	1.35	0.10	-0.11
2,3',4',5-Tetrachloro	70	7.720	6.130	6.15	1.35	0.10	0.02
2,3',4',6-Tetrachloro	71	7.720	6.130	6.15	1.35	0.10	0.02
2,3,5,5'-Tetrachl;oro	72	7.720	6.120	6.17	1.35	0.10	0.05

Table 7.5 cont.

2,3',5',6-Tetrachloro	73	7.720	6.230	6.11	1.35	0.10	-0.12
2,4,4',5-Tetrachloro	74	7.720	6.100	6.13	1.35	0.10	0.03
2,4,4',6-Tetrachloro	75	7.720	6.200	6.07	1.35	0.10	-0.13
2',3,4,5-Tetrachloro	76	7.720	6.120	6.13	1.35	0.10	0.01
3,3',4,4'-Tetrachloro	77	7.500	6.530	6.60	1.29	0.07	0.07
3,3',4,5-Tetrachloro	78	7.500	6.300	6.21	1.29	0.07	-0.09
3,3',4,5'-Tetrachloro	79	7.500	6.30	6.21	1.29	0.07	-0.09
3,3',5,5'-Tetrachloro	80	7.500	6.770	6.85	1.29	0.07	-0.07
3,4,4',5-Tetrachloro	81	7.500	6.320	6.19	1.29	0.07	-0.13
2,2',3,3',4-Pentachloro	82	8.960	6.660	6.68	1.59	0.08	0.02
2,2',3,3',5-Pentachloro	83	8.960	6.720	6.70	1.59	0.08	0.02
2,2',3,3',6-Pentachloro	84	9.060	6.250	6.24	1.65	0.10	0.01
2,2',3,4,4'-Pentachloro	85	8.960	6.610	6.66	1.59	0.08	0.05
2,2',3,4,5-Pentachloro	86	8.960	6.600	6.68	1.59	0.08	0.08
2,2',3,4,5'-Pentachloro	87	8.960	6.600	6.68	1.59	0.08	0.08
2,2',3,4,6-Pentachloro	88	9.060	6.650	6.66	1.65	0.10	-0.02
2,2',3,4,6'-Pentachloro	89	9.060	6.650	6.66	1.65	0.10	-0.02
2,2',3,4',5-Pentachloro	90	8.960	6.700	6.68	1.59	0.08	0.02
2,2',3,4',6-Pentachloro	91	9.060	6.610	6.66	1.65	0.10	0.05
2,2',3,5,5'-Pentachloro	92	8.960	6.690	6.70	1.59	0.08	0.02
2,2',3,5,6-Pentachloro	93	9.060	6.570	6.68	1.65	0.10	0.11
2,2',3,5,6'-Pentachloro	94	9.060	6.700	6.68	1.65	0.10	-0.02
2,2',3,5',6-Pentachloro	95	9.060	6.600	6.68	1.65	0.10	0.08
2,2',3,6,6'-Pentachloro	96	9.060	6.670	6.64	1.65	0.10	-0.03
2,2',3',4,5-Pentachloro	97	8.960	6.650	6.66	1.59	0.08	0.01
2,2',3',4,6-Pentachloro	98	9.060	6.610	6.66	1.65	0.10	0.05
2,2',4,4',5-Pentachloro	99	8.960	6.650	6.66	1.59	0.08	0.01
2,2'4,4'6-Pentachloro	100	9.060	6.600	6.64	1.65	0.10	0.04

Table 7.5 cont.

2,2',4,5,5'-Pentachloro	101	8.960	6.610	6.68	1.59	0.08	0.07
2,2',4,5,6'-Pentachloro	102	9.060	6.650	6.66	1.65	0.10	0.01
2,2',4,5',6-Pentachloro	103	9.060	6.610	6.66	1.65	0.10	0.05
2,2',4,6,6'-Pentachloro	104	9.060	6.670	6.62	1.65	0.10	-0.05
2,3,3',4,4'-Pentachloro	105	8.750	6.580	6.63	1.50	0.07	0.05
2,3,3',4,5-Pentachloro	106	8.750	6.670	6.69	1.50	0.07	0.02
2,3,3',4',5-Pentachloro	107	8.750	6.610	6.69	1.50	0.07	0.08
2,3,3',4,5'-Pentachloro	108	8.750	6.610	6.63	1.50	0.07	0.02
2,3,3',4,6-Pentachloro	109	8.750	6.610	6.63	1.50	0.07	0.02
2,3,3',4',6-Pentachloro	110	8.750	6.500	6.63	1.50	0.07	0.13
2,3,3',5,5'-Pentachloro	111	8.750	6.600	6.71	1.50	0.07	0.11
2,3,3',5,6-Pentachloro	112	8.750	6.620	6.65	1.50	0.07	0.03
2,3,3',5',6-Pentachloro	113	8.750	6.500	6.65	1.50	0.07	0.15
2,3,4,4',5-Pentachloro	114	8.750	6.620	6.67	1.50	0.07	0.05
2,3,4,4',6-Pentachloro	115	8.750	6.610	6.61	1.50	0.07	0.00
2,3,4,5,6-Pentachloro	116	8.750	6.480	6.63	1.50	0.07	0.15
2,3,4',5,6-Pentachloro	117	8.750	6.650	6.63	1.50	0.07	-0.02
2,3',4,4',5-Pentachloro	118	8.750	6.630	6.67	1.50	0.07	0.04
2,3',4,4',6-Pentachloro	119	8.750	6.520	6.61	1.50	0.07	0.09
2,3',4,5,5'-Pentachloro	120	8.750	6.600	6.74	1.50	0.07	0.14
2,3',4,5',6-Pentachloro	121	8.750	6.520	6.63	1.50	0.07	0.11
2',3,3',4,5-Pentachloro	122	8.750	6.610	6.69	1.50	0.07	0.08
2',3,4,4',5-Pentachloro	123	8.750	6.630	6.73	1.50	0.07	0.10
2',3,4,5,5'-Pentachloro	124	8.750	6.620	6.69	1.50	0.07	0.07
2',3,4,5,6'-Pentachloro	125	8.750	6.600	6.63	1.50	0.07	0.03
3,3',4,4',5-Pentachloro	126	8.750	6.470	6.44	1.45	0.06	-0.03

Table 7.5 cont.

3,3',4,5,5'-Pentachloro	127	8.750	6.720	6.75	1.45	0.06	0.03
2,2',3,3',4,4'Hexachloro	128	9.620	7.300	7.20	1.70	0.05	0.10
2,2',3,3',4,5-Hexachloro	129	9.620	7.310	7.22	1.70	0.05	-0.08
2,2',3,3',4,5'-Hexachloro	130	9.620	7.170	7.22	1.70	0.05	0.05
2,2',3,3',4,6-Hexachloro	131	9.740	7.320	7.19	1.75	0.06	-0.13
2,2',3,3',4,6'-Hexachloro	132	9.740	7.300	7.19	1.75	0.06	-0.11
2,2',3,3',5,5'Hexachloro	133	9.620	7.090	7.20	1.70	0.05	0.11
2,2',3,3',5,6-Hexachloro	134	9.740	7.150	7.21	1.75	0.06	0.06
2,2',3,3',5,6'-Hexachloro	135	9.740	7.230	7.21	1.75	0.06	-0.02
2,2',3,3',6,6'-Hexachloro	136	9.740	7.120	7.16	1.75	0.06	0.04
2,2',3,4,4',5-Hexachloro	137	9.620	7.340	7.20	1.70	0.05	-0.14
2,2',3,4,4',-Hexachloro	138	9.620	7.290	7.20	1.70	0.05	0.09
2,2',3,4,4',6-Hexachloro	139	9.740	7.290	7.17	1.75	0.06	-0.12
2,2',3,4,4',6'-Hexachloro	140	9.740	7.320	7.23	1.75	0.06	-0.09
2,2',3,4,5,5'-Hexachloro	141	9.620	7.190	7.22	1.70	0.05	0.03
2,2',3,4,5,6-Hexachloro	142	9.740	7.300	7.19	1.75	0.06	-0.11
2,2',3,4,5,6'-Hexachloro	143	9.740	7.330	7.19	1.75	0.06	-0.14
2,2',3,4,5',6-Hexachloro	144	9.740	7.300	7.21	1.75	0.06	-0.09
2,2',3,4,6,6'-Hexachloro	145	9.740	7.180	7.14	1.75	0.06	-0.04
2,2',3,4',5,5'-Hexchloro	146	9.620	7.200	7.20	1.70	0.05	0.00
2,2',3,4',5,6-Hexachloro	147	9.740	7.200	7.19	1.75	0.06	-0.01
2,2',3,4',5,6'-Hexachloro	148	9.740	7.250	7.19	1.75	0.06	-0.06
2,2',3,4',5',6-Hexachloro	149	9.740	7.320	7.19	1.75	0.06	-0.13
2,2',3,4',6,6'-Hexachloro	150	9.740	7.200	7.14	1.75	0.06	-0.06
2,2',3,5,5',6-Hexachloro	151	9.740	7.850	6.92	1.75	0.06	-0.07
2,2',3,5,6,6'-Hexachloro	152	9.740	7.080	7.16	1.75	0.06	0.08
2,2'4,4,5,5'-Hexachloro	153	9.620	6.300	7.22	1.70	0.05	0.08
2,2',4,4',5,6'-Hexachloro	154	9.740	7.170	7.17	1.75	0.06	0.00

Table 7.5 cont.

2,2',4,4'6,6'-Hexachloro	155	9.740	7.200	7.12	1.75	0.06	0.08
2,3,3',4,4',5-Hexachloro	156	9.620	7.300	7.20	1.70	0.05	-0.10
2,3,3',4,4',5'-Hexachloro	157	9.620	7.310	7.16	1.70	0.05	-0.15
2,3,3',4,4',6-Hexachloro	158	9.740	7.310	7.16	1.75	0.06	-0.15
2,3,3',4,5,5'-Hexachloro	159	9.620	7.150	7.20	1.70	0.05	0.05
2,3,3',4,5,6-Hexachloro	160	9.740	7.180	7.18	1.75	0.06	0.00
2,3,3',4,5',6-Hexachloro	161	9.740	7.300	7.18	1.75	0.06	-0.12
2,3,3',4',5,5'-Hexachloro	162	9.620	7.100	7.20	1.70	0.05	0.10
2,3,3',4',5,6-Hexaachloro	163	9.740	7.200	7.18	1.75	0.06	-0.02
2,3,3',4',5',6-Hexachloro	164	9.740	7.300	7.20	1.75	0.06	-0.10
2,3,3',5,5',6-Hexachloro	165	9.740	7.300	7.20	1.75	0.06	-0.10
2,3,4,4',5,6-Hexachloro	166	9.740	7.230	7.16	1.75	0.06	-0.07
2,3',4,4',5,5'-Hexachloro	167	9.620	7.350	7.21	1.70	0.05	-0.14
2,3',4,4',5',6-Hexachloro	168	9.740	7.170	7.16	1.75	0.06	0.01
3,3',4,4',5,5'-Hexachloro	169	9.620	7.400	7.27	1.70	0.05	-0.13
2,2',3,3',4,4',5-Hepachloro	170	9.990	7.820	7.80	1.75	0.04	-0.02
2,2',3,3',4,4',6-Hepachloro	171	10.420	7.700	7.70	1.80	0.05	-0.00
2,2',3,3',4,5,5'-Hepachloro	172	9.990	7.670	7.77	1.75	0.05	0.10
2,2',3,3',4,5,6-Hepachloro	173	10.420	7.660	7.72	1.80	0.05	0.06
2,2',3,3',4,5,6'-Hepachloro	174	10.420	7.820	7.72	1.80	0.05	-0.08
2,2',3,3',4,5',6-Hepachloro	175	10.420	7.770	7.72	1.80	0.05	-0.05
2,2',3,3',4,6,6'-Hepachloro	176	10.420	7.710	7.71	1.80	0.05	-0.00
2,2',3,3',4',5,6-Hepachloro	177	10.420	7.760	7.66	1.80	0.05	-0.10
2,2',3,3',5,5',6-Hepachloro	178	10.420	7.770	7.72	1.80	0.05	-0.05
2,2',3,3',5,6,6'-Hepachloro	179	10.420	7.710	7.73	1.80	0.05	0.02
2,2',3,4,4',5,5'-Hepachloro	180	9.990	7.640	7.67	1.75	0.04	0.03
2,2',3,4,4',5,6-Hepachloro	181	10.420	7.700	7.70	1.80	0.05	-0.00

Table 7.5 cont.

2,2',3,4,4',5,6'-Hepachloro	182	10.420	7.700	7.70	1.80	0.05	-0.00
2,2',3,4,4',5',6-Hepachloro	183	10.420	7.760	7.70	1.80	0.05	-0.06
2,2',3,4,4',6,6'-Hepachloro	184	10.420	7.630	7.64	1.80	0.05	-0.01
2,2',3,4,5,5',6-Hepachloro	185	10.420	7.720	7.72	1.80	0.05	-0.00
2,2',3,4,5,6,6'-Hepachloro	186	10.420	7.650	7.66	1.80	0.05	-0.01
2,2',3,4',5,5',6-Hepachloro	187	10.420	7.790	7.72	1.80	0.05	-0.07
2,2',3,4',5,6',6-Hepachloro	188	10.420	7.700	7.66	1.80	0.05	-0.04
2,3,3',4,4',5,5'-Hepachloro	189	9.640	7.728	7.76	1.75	0.04	0.03
2,3,3',4,4',5,6-Hepachloro	190	9.640	7.660	7.70	1.75	0.04	-0.02
2,3,3',4,4',5',6-Hepachloro	191	9.640	7.660	7.70	1.75	0.04	-0.04
2,3,3',4,5,5',6-Hepachloro	192	9.640	7.700	7.72	1.75	0.04	0.02
2,3,3',4',5,5',6-Hepachloro	193	9.640	7.680	7.72	1.75	0.04	-0.04
2,2',3,3',4,4',5,5'-Octachloro	194	10.640	8.260	8.29	1.79	0.02	0.03
2,2',3,3',4,4',5,6-Octachloro	195	10.940	8.160	8.25	1.87	0.03	0.03
2,2',3,3',4,4',5,6'-Octachloro	196	10.940	8.280	8.23	1.87	0.03	-0.05
2,2',3,3',4,4',6,6'-Octachloro	197	10.940	8.210	8.15	1.87	0.03	-0.06
2,2',3,3',4,5,5',6'-Octachloro	198	10.940	8.230	8.25	1.87	0.03	0.02
2,2',3,3',4,5,5',6'-Octachloro	199	10.940	8.160	8.25	1.87	0.03	0.09
2,2',3,3',4,5,6,6'-Octachloro	200	10.940	8.210	8.17	1.87	0.03	-0.04
2,2',3,3',4,5',6,6'-Octachloro	201	10.940	8.170	8.17	1.87	0.03	-0.00
2,2',3,3',5,5',6,6'-Octachloro	202	10.940	8.230	8.19	1.87	0.03	-0.04
2,2',3,4,4',5,5',6-Octachloro	203	10.940	8.250	8.29	1.87	0.03	-0.04
2,2',3,4,4',5,6,6'-Octachloro	204	10.940	8.200	8.15	1.87	0.03	-0.05
2,,3,3',4,4',5,5',6-Octachloro	205	10.940	8.200	8.27	1.87	0.03	0.07
2,2',3,3',4,4',5,5',6-Nonachloro	206	11.400	8.250	8.16	2.20	0.00	-0.08
2,2',3,3',4,4',5,6,6'-Nonachloro	207	11.400	8.430	8.25	2.20	0.00	0.10
2,2',3,3',4,5,5',6,6'-Nonachloro	208	11.400	8.130	8.16	2.20	0.00	-0.03

Table 7.5 cont.

Decachlorobiphenyl	209	11.600	8.340	8.28	2.30	0.00	0.06

a- Log P cal. using the altered π ,β , (Table 6.1)

b- Log P predicted using the last cal. values (Table 7.5)

The plots of (π^{H}_{2} , $\Sigma\beta^{H}_{2}$ and log L^{16}) versus the chlorine number for all 209 PCBs are shown in figures (7.2), (7.3) and (7.4), the effect of the ortho-substituents being very clear.

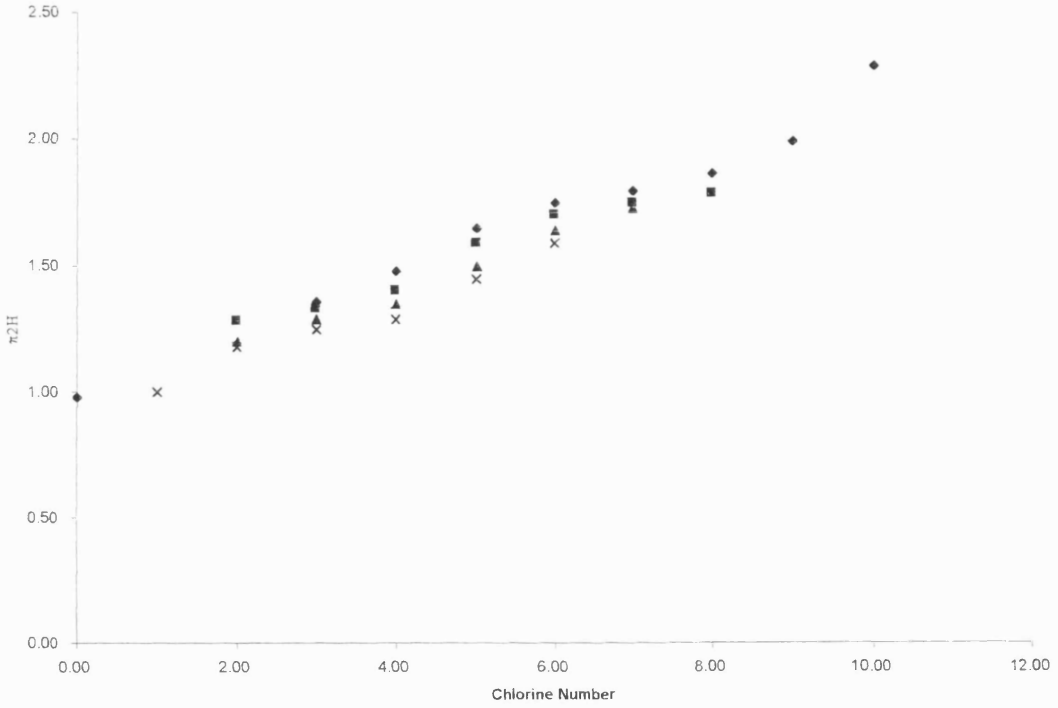

Figure (7.2) Plot of π_{2}^{H} vs chlorine number.

For ortho-substituted congeners (◆) 2,2',6,6'-substituted congeners, (■) 2,2'-substituted congeners, (▲) 2- substituted congeners and (**X**) non -substituted .

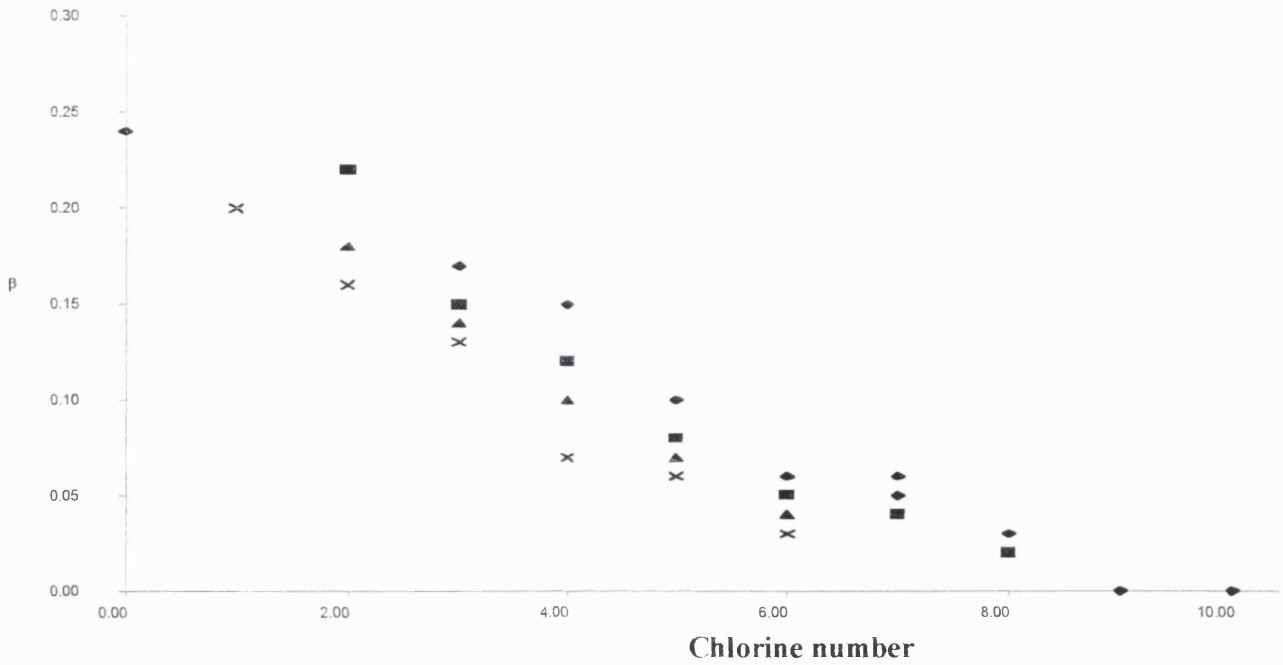

Figure (7.3) Plot of β vs chlorine number.

For ortho- substituted congeners (◆) 2,2',6,6'- substituted congeners, (■) 2,2'- substituted congeners, (▲) 2- substituted congeners and (**X**) non - substituted.

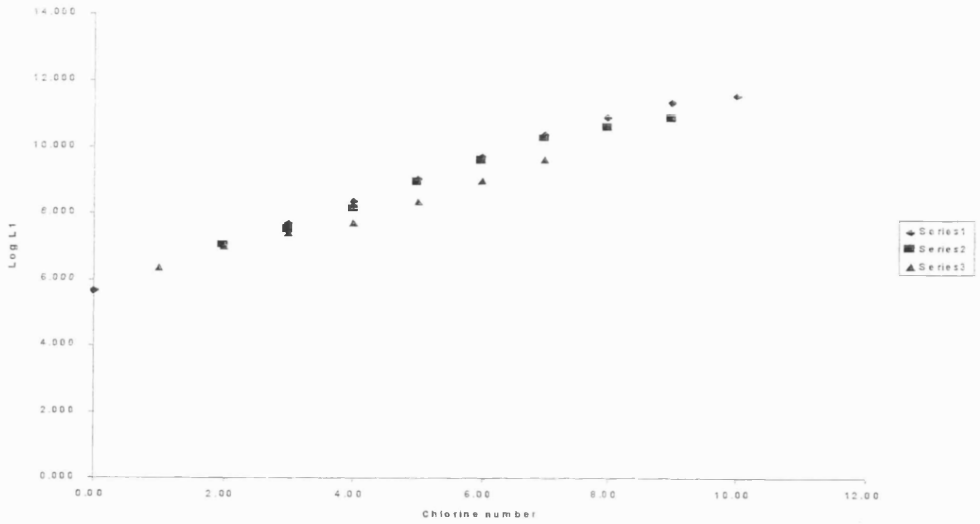

Figure (7.4) Plot of log L^{16} vs chlorine number.

For ortho- substituted congeners (◆) 2,2',6,6'- substituted congeners, (■) 2,2'- substituted congeners, (▲) 2- substituted congeners or non.

7.4 Testing the final set of the calculated descriptors.

The final set of (π^{H}_{2} , $\Sigma\beta^{H}_{2}$ and log L^{16}) values could be tested to see how good they are by comparison to the initial set. As before, data from the paper of Opperhuizen [1] were used, and a multiple linear regression for the aromatic compounds plus the PCBs carried out. In this case, the final set of values found for the descriptors was used. Comparing the obtained equation (7.2) with equation (6.6), shows that equation (7.2) was reasonable. Similar calculations were carried out using data from the paper of Sablijic[7] , see equation (7.3), and from the paper of Park, [8] equation (7.4). The obtained equations were better than the initial ones.

Equation (7.2) Opperhuizen values

$$\log P_{oct} = 0.609 + 0.288 R_2 - 0.752 \pi^{H}_{2} - 3.059 \Sigma\beta^{H}_{2} + 3.445 V_x \quad (7.2)$$

n = 58 $r^2 = 0.975$ sd = 0.239 F = 354.8

Equation (7.3) Sablijic values

$$\log k' = - 0.110 - 0.265 R_2 - 1.617 \pi^{H}_{2} - 4.455 \Sigma\beta^{H}_{2} + 5.360 V_x \quad (7.3)$$

n = 20 $r^2 = 0.992$ sd = 0.122 F = 498.8

Equation (7.4) Park values

$$\log k' = - 0.603 + 1.650 R_2 + 1.211 \pi^{H}_{2} + 0.252 \Sigma\beta^{H}_{2} + 1.591 V_x \quad (7.4)$$

n = 39 $r^2 = 0.976$ sd = 0.103 F = 272.1

The second test for the set of new descriptors involved recalculations for the GLC data on the twelve phases. As mentioned in section (5.3), applying equation (5.2) for the first three phases yielded negative b-coefficients, see Table (5.5). This is because these phases are non-polar and equation 5.2 should not really be applied.

Table (7.6) Details of the multiple linear regressions for (OV-101) and (F-50) based on equation (5.2).

Phase	**Coefficients**							
Name	**c**	**r**	**s**	**b**	**l**	**F**	**r^2**	**n**
OV-101	190.97	239.35	205.39	-136.94	302.83	2085.6	0.975	215
F-50	210.60	197.38	205.52	-90.85	421.57	1564.9	0.966	216

Even when the restricted equation (5.3) was used, some of the coefficients were again negative as shown in Table (7.7) as an example.

Table (7.7) Details of the multiple linear regression for (F-50) based on equation (5.3)

Phase	**c**	**r**	**s**	**l**	**F**	**r^2**	**n**
F-50	136.14	146.82	-192.87	123.44	1902.5	0.9633	217

Using equation (5.4) the best values for log L^{16}, for all twelve phases could be found, as shown in Table (7.8) because all the coefficients were positive as shown in Table (7.9).

Table (7.8) calculated values of log L^{16}, for twelve phases using equation (5.4).

IUPAC	Log Lcal w(OV-101)	Log Lcal w(F-50)	Log Lcal w(APTEZ)	Log Lcal w(OV-210)	logLcal w(OV-30)	Log Lcal w(OV-17)	Log Lcal W(OV-25)	Log Lcal w(AN-600)	Log Lcal w(OV-225)	Log Lcal w(CHOMS)	Log Lcal w(HK-325)	Log Lcal w(POLMP)
-	5.697	5.685	5.699	5.487	5.677	5.552	5.579	5.430	5.467	5.253	5.440	5.668
1	6.193	6.176	6.059	5.951	6.196	6.147	6.188	5.962	6.034	5.767	5.960	6.041
4	6.689	6.667	6.418	6.416	6.715	6.741	6.796	6.562	6.600	6.281	6.480	6.413
2	6.510	6.540	6.582	7.088	6.531	7.016	6.465	6.462	6.505	6.509	6.003	6.685
6	7.006	7.031	6.941	7.007	7.050	7.048	7.073	7.045	7.072	7.023	6.941	7.057
11	7.323	7.395	8.007	7.598	7.384	7.354	7.350	7.580	7.544	7.765	7.402	7.701
3	6.568	6.588	6.660	6.651	6.576	6.585	6.556	6.601	6.661	6.674	6.494	6.847
8	7.064	7.079	7.020	7.115	7.095	7.180	7.164	7.144	7.228	7.188	7.014	7.219
13	7.381	7.444	7.543	7.706	7.430	7.486	7.441	7.684	7.699	7.930	7.474	7.863
15	7.439	7.492	7.622	7.815	7.475	7.619	7.532	7.863	7.855	8.095	7.547	8.025
10	6.633	6.622	6.457	6.332	6.642	6.572	6.648	6.364	6.441	6.121	6.341	6.302
19	7.170	7.153	6.864	6.892	7.213	7.252	7.365	7.071	7.132	6.796	6.922	6.825
27	7.480	7.510	7.380	7.467	7.539	7.544	7.624	7.536	7.583	7.511	7.373	7.444
32	7.544	7.565	7.466	7.591	7.593	7.690	7.733	7.687	7.759	7.702	7.456	7.631
54	7.650	7.639	7.310	7.368	7.710	7.762	7.934	7.596	7.664	7.310	7.364	7.237
9	6.852	6.886	6.838	6.745	6.856	6.789	6.764	6.705	6.691	6.629	6.690	6.749
18	7.349	7.377	7.198	7.210	7.375	7.383	7.372	7.231	7.258	7.143	7.210	7.121
26	7.666	7.741	7.721	7.801	7.710	7.690	7.649	7.766	7.729	7.885	7.671	7.765
31	7.723	8.308	7.800	7.909	7.755	7.822	7.740	7.858	7.944	8.050	7.744	7.927
53	7.829	7.863	7.644	7.686	7.873	7.893	7.941	7.768	7.789	7.657	7.652	7.533
52	8.008	8.087	7.978	8.004	8.035	8.025	7.948	8.003	7.915	8.005	7.940	7.829
7	6.910	6.919	6.922	6.739	6.922	6.797	6.833	6.711	6.764	6.675	6.763	6.877
17	7.406	7.404	7.282	7.204	7.441	7.392	7.446	7.271	7.331	7.189	7.283	7.249
25	7.723	7.768	7.805	7.795	7.776	7.698	7.718	7.778	7.803	7.931	7.744	7.893
28	7.781	7.817	7.884	7.903	7.821	7.831	7.809	7.893	7.958	8.096	7.817	8.055
51	7.887	7.890	7.728	7.680	7.991	7.902	8.010	7.780	7.863	7.704	7.725	7.661
49	8.066	8.114	8.062	7.998	8.101	8.034	8.017	7.992	7.988	8.051	8.013	8.014

Table 7.8 Cont.

47	8.124	8.142	8.145	7.992	8.167	8.042	8.086	8.021	8.062	8.098	8.086	8.085
5	7.047	7.036	6.996	6.969	7.081	7.076	7.202	7.034	7.154	6.964	6.920	7.126
16	7.543	7.527	7.355	7.434	7.600	7.670	7.810	7.594	7.721	7.478	7.440	7.498
20	7.860	7.892	7.878	8.024	7.935	7.977	8.087	8.100	8.193	8.220	7.901	8.142
22	7.918	7.940	7.957	8.133	7.980	8.109	8.179	8.233	8.348	8.385	7.974	8.304
46	8.024	8.013	7.801	7.909	8.098	8.181	8.379	8.102	8.253	7.993	7.882	7.910
44	8.202	8.237	8.135	8.227	8.260	8.312	8.387	8.314	8.378	8.340	8.170	8.206
42	8.260	8.265	8.219	8.221	8.326	8.321	8.455	8.326	8.452	8.386	8.243	8.334
40	8.397	8.388	8.292	8.451	8.485	8.599	8.825	8.654	8.842	8.675	8.400	8.583
14	7.161	7.163	7.359	7.172	7.137	6.974	6.891	7.102	7.072	7.266	7.109	7.378
34	7.650	7.648	7.710	7.621	7.647	7.554	7.481	7.639	7.618	7.753	7.619	7.725
36	7.981	8.025	8.250	8.243	7.999	7.889	7.794	8.180	8.131	8.549	8.100	8.419
39	8.025	8.060	8.312	8.320	8.027	7.993	7.849	8.278	8.245	8.660	8.152	8.531
73	8.131	8.133	8.157	8.096	8.145	8.065	8.050	8.147	8.208	8.268	8.060	8.137
72	8.310	8.357	8.490	8.414	8.307	8.196	8.057	8.359	8.275	8.615	8.349	8.433
68	8.368	8.385	8.574	8.408	8.373	8.205	8.126	8.371	8.349	8.661	11.556	8.561
58	8.504	8.508	8.647	8.638	8.532	8.483	8.596	8.694	8.738	8.654	8.578	8.810
80	8.612	8.628	9.003	8.825	8.579	8.368	8.165	8.738	8.635	9.225	8.757	9.037
12	7.411	7.418	8.128	7.641	7.482	7.531	7.486	7.650	7.711	7.930	7.422	7.892
33	7.907	7.909	7.946	8.106	8.001	8.126	8.094	8.204	8.278	8.444	7.942	8.264
35	8.224	8.273	8.469	8.696	8.335	8.432	8.371	8.710	8.750	9.186	8.403	8.908
37	8.282	8.321	8.548	8.805	8.381	8.565	8.463	8.843	8.905	9.351	8.476	9.070
71	8.388	8.394	8.392	8.581	8.498	8.636	8.663	8.712	8.810	8.959	8.384	8.676
70	8.588	8.638	8.750	8.947	8.687	8.811	8.573	8.978	8.997	9.386	8.703	9.048
66	8.625	8.646	8.810	8.893	8.727	8.776	8.739	8.936	9.009	6.985	8.745	9.100
56	8.761	8.769	8.883	9.123	8.886	9.055	9.109	9.259	9.399	9.641	8.902	9.349
79	8.869	8.889	9.238	9.310	8.933	8.939	8.779	9.304	9.295	9.916	9.081	9.576
77	9.126	9.150	9.474	9.795	9.287	9.510	9.393	9.933	9.955	10.607	9.404	10.115
30	7.166	7.160	7.179	6.789	7.112	6.970	6.986	6.689	6.692	6.624	7.017	6.849
50	7.662	7.651	7.538	7.254	7.630	7.564	10.235	7.244	7.259	7.138	7.537	7.221
69	7.979	8.016	8.062	7.845	7.965	7.871	7.871	7.750	7.144	6.499	7.997	7.866
75	8.037	8.064	8.140	7.954	8.011	8.003	7.962	7.883	7.886	8.045	8.070	8.028
104	8.163	8.137	7.984	7.730	8.128	8.075	8.163	7.752	7.790	7.653	7.979	7.634
103	8.322	8.361	8.318	8.048	8.291	8.206	8.170	7.964	7.916	8.000	8.267	7.929
100	8.380	8.389	8.402	8.042	8.357	8.215	8.239	7.976	7.989	8.046	8.340	8.057

Table 7.8 Cont.

98	8.516	8.512	8.475	8.272	8.515	8.493	8.608	8.298	8.379	8.335	8.497	8.306
121	8.629	8.632	8.831	8.459	8.563	8.377	8.279	8.343	8.276	8.610	8.675	8.534
119	8.881	8.893	9.066	8.944	8.916	8.949	8.892	8.909	8.936	9.301	8.999	9.073
155	8.636	8.636	8.658	8.092	8.546	8.387	8.392	7.948	7.917	7.995	8.593	8.030
24	7.425	7.315	7.220	7.199	7.323	7.350	7.400	7.271	7.263	7.090	7.169	7.109
45	7.921	7.806	7.579	7.664	7.841	7.944	8.008	7.825	7.830	7.605	7.689	7.482
59	8.231	8.163	8.094	8.239	8.168	8.236	8.267	8.314	8.281	8.320	8.139	8.101
69	8.296	8.218	8.181	8.363	8.221	8.383	8.377	8.465	8.458	8.511	8.222	8.288
96	8.402	8.291	8.025	8.140	8.339	8.454	8.577	8.334	8.368	8.119	8.131	7.894
95	8.581	8.515	8.359	8.458	8.502	8.586	8.585	8.546	8.487	8.466	8.419	8.190
91	8.639	8.543	8.443	8.452	8.568	8.595	8.653	8.558	8.561	7.921	8.492	8.318
84	8.775	8.666	8.516	8.681	8.726	8.873	9.023	8.361	8.423	8.802	8.649	8.567
113	8.883	8.786	8.871	8.868	8.774	8.757	8.693	8.925	8.320	9.077	8.827	8.794
110	9.140	9.047	9.107	9.353	9.127	9.329	9.307	9.490	9.508	9.768	12.599	9.333
150	8.895	8.790	8.699	8.502	8.757	8.767	8.807	8.530	8.488	9.119	8.745	8.290
136	9.154	8.944	8.740	8.912	8.968	9.147	9.221	9.112	9.060	8.928	8.949	8.551
23	7.568	7.528	7.645	7.223	7.542	7.453	7.391	7.397	7.383	7.352	7.451	7.519
43	8.064	8.019	8.005	7.687	8.061	8.048	7.999	7.916	7.950	7.866	7.972	7.892
57	8.381	8.383	8.528	8.278	8.396	8.354	8.276	8.423	8.422	8.608	8.432	8.536
63	8.439	8.431	8.607	8.387	8.494	8.486	8.367	8.556	8.577	8.773	8.505	8.698
94	8.545	8.505	8.451	8.163	8.559	8.558	8.568	8.425	8.482	8.381	8.413	8.304
92	8.775	8.729	8.785	8.481	8.721	8.690	8.575	8.637	8.607	8.728	8.702	8.600
90	8.782	8.808	8.868	8.475	8.788	8.698	8.644	8.649	8.681	8.775	8.774	8.728
83	8.918	8.879	8.942	8.705	8.946	8.977	9.070	8.971	9.071	9.063	8.931	8.977
111	9.026	9.000	9.297	8.892	8.994	8.861	8.684	9.016	8.967	9.338	9.110	9.204
107	9.283	9.261	9.533	9.377	9.399	9.432	9.297	9.581	9.628	10.029	9.433	9.743
148	9.038	9.003	9.125	8.525	8.977	8.871	8.797	8.621	8.608	8.723	9.028	8.700
135	9.297	9.158	9.166	8.935	9.188	9.251	9.212	9.203	9.180	9.190	9.180	8.961
133	9.440	9.371	9.592	8.959	9.408	9.354	9.202	9.288	9.300	9.452	9.463	9.371
29	7.621	7.602	7.708	7.571	7.582	7.501	7.437	7.495	7.433	7.537	7.545	7.607
48	8.117	8.093	8.067	8.036	8.101	8.096	8.045	8.032	8.000	8.051	8.065	7.980
67	8.434	8.457	8.590	8.627	8.436	8.402	8.322	8.538	7.944	8.793	8.526	8.624
74	8.492	8.506	8.669	8.735	8.481	8.534	8.413	8.671	8.627	8.958	8.599	8.786
102	8.598	8.579	8.513	8.512	8.599	8.606	8.614	8.540	8.532	8.513	8.507	8.392
101	8.782	8.803	8.847	8.830	9.943	9.469	8.621	8.747	8.657	9.570	8.795	8.688

Table 7.8 Cont.

99	8.840	8.831	8.985	8.824	8.828	8.746	8.690	8.759	8.731	8.959	8.868	8.816
97	8.971	8.954	9.004	9.053	8.986	9.025	9.060	7.357	9.121	9.248	9.025	9.065
120	9.079	9.074	9.359	9.240	9.034	8.909	8.730	9.132	9.017	9.523	9.204	9.292
118	9.336	9.335	9.595	9.725	9.387	9.480	9.344	9.697	9.678	10.214	9.548	9.831
154	9.091	9.078	9.187	8.874	9.017	8.919	8.843	8.737	8.658	8.908	9.122	8.788
149	9.350	9.232	9.228	9.284	9.228	9.299	9.258	9.318	9.230	8.085	9.274	9.049
146	9.498	9.445	9.654	9.307	9.448	9.402	9.248	9.409	9.350	9.636	9.557	9.459
153	9.546	9.520	9.716	9.656	9.488	9.450	9.295	9.525	9.400	9.821	9.650	9.547
21	8.306	7.810	7.886	7.975	7.828	7.929	7.999	7.951	7.926	8.135	10.069	7.499
41	8.291	8.353	8.246	8.440	8.347	8.523	8.607	8.505	8.493	8.650	8.342	8.385
55	8.608	8.665	8.769	9.030	8.682	8.830	8.884	9.011	8.964	9.391	8.803	9.029
60	8.666	8.713	8.848	9.139	8.727	8.962	8.975	9.144	9.120	9.563	8.876	9.191
89	8.772	8.787	8.692	8.915	8.845	9.034	9.176	9.013	9.024	9.164	8.784	8.797
87	8.951	9.011	9.026	9.233	9.007	9.165	9.183	9.196	9.150	9.511	9.072	9.093
85	9.009	9.038	9.109	9.227	9.073	9.174	9.252	9.237	9.223	9.558	9.145	9.221
82	9.145	9.161	9.183	9.457	9.232	9.452	9.622	9.560	9.613	9.847	9.302	9.470
108	9.273	9.301	9.562	9.691	9.305	9.379	9.346	9.658	9.572	10.202	9.511	9.773
105	9.523	9.556	9.790	10.160	9.650	9.936	9.942	10.205	10.212	10.866	9.825	10.287
140	9.244	9.265	9.342	9.230	9.237	9.304	9.351	9.156	9.089	9.426	9.368	9.118
132	9.524	9.439	9.407	9.687	9.474	9.726	9.820	9.791	9.723	9.973	9.551	9.454
130	9.667	9.653	9.833	9.711	9.693	9.830	9.810	9.882	9.842	10.235	9.833	9.864
138	9.719	9.727	9.895	10.059	9.733	9.878	9.856	9.998	9.892	10.419	9.927	9.952
128	9.893	9.935	10.073	10.463	9.979	10.306	10.418	10.551	10.385	11.018	10.162	10.357
38	8.092	8.164	8.415	8.445	8.132	8.168	8.113	8.491	8.474	8.745	8.267	8.743
76	8.594	8.661	8.783	8.926	8.659	8.776	8.739	9.063	9.061	9.287	8.797	9.140
78	8.905	9.019	9.298	9.501	8.985	9.068	8.998	9.552	9.512	10.002	9.248	9.759
81	8.962	9.067	9.376	9.609	9.030	9.201	9.089	9.685	9.668	10.167	9.321	9.921
125	9.068	9.140	9.221	9.386	9.148	9.272	9.290	9.554	9.572	9.774	9.229	9.527
124	9.247	9.364	9.554	9.704	9.311	9.404	9.297	9.766	10.285	10.121	9.517	9.823
123	9.285	9.372	9.614	9.651	9.351	9.370	9.312	9.725	9.709	10.088	9.559	9.875
122	9.442	9.515	9.712	9.928	9.535	9.691	9.736	10.100	10.161	10.457	9.747	10.200
127	9.549	9.635	10.067	10.115	9.583	9.575	9.406	10.145	10.058	10.732	9.925	10.427
118	9.827	9.916	10.326	10.647	9.962	10.189	10.074	10.764	10.780	11.503	10.280	11.042
168	9.561	9.639	9.895	9.748	9.566	9.585	9.519	9.750	15.565	10.117	9.844	9.923
164	9.820	9.793	9.935	10.158	9.777	9.965	9.934	10.332	10.271	10.583	9.995	10.184

Table 7.8 Cont.

162	9.977	10.020	10.377	10.213	10.014	10.097	9.961	10.458	10.432	10.898	10.299	10.644
167	10.016	10.081	10.423	10.530	10.037	10.117	9.971	10.539	10.440	11.029	10.372	10.682
157	10.190	10.288	10.602	10.934	10.283	10.544	10.532	11.011	10.933	11.628	10.649	11.087
169	10.507	10.662	11.155	11.452	10.612	10.826	10.701	11.605	11.543	12.318	11.125	11.892
65	8.194	8.197	8.127	7.998	8.258	7.978	8.012	7.957	8.006	7.860	7.736	8.105
93	8.407	8.375	8.023	8.114	8.381	8.344	8.315	8.033	7.872	7.611	7.901	7.841
112	8.724	8.739	8.546	8.705	8.716	8.650	8.592	8.591	8.343	8.353	8.362	8.486
117	8.782	8.788	8.625	8.813	8.761	8.783	8.683	8.724	8.499	8.518	8.435	8.648
152	8.888	8.861	8.469	8.590	8.879	8.854	8.884	8.541	8.403	8.126	8.343	8.254
151	9.169	9.185	8.922	9.145	9.171	9.200	9.163	9.019	8.839	8.874	8.784	8.926
147	9.125	9.112	8.886	8.902	9.108	8.995	8.960	8.765	8.602	8.519	8.704	8.677
134	9.261	9.236	8.960	9.131	9.266	9.273	9.330	9.087	8.992	8.808	8.861	8.470
165	9.369	9.356	9.315	9.319	9.314	9.157	9.000	9.132	8.889	9.083	9.040	9.154
163	9.626	9.617	9.551	9.803	9.667	9.729	9.614	9.698	9.549	9.774	9.363	9.693
188	9.381	9.360	9.143	8.952	9.297	9.167	9.113	8.737	8.530	8.468	8.958	8.650
179	9.619	9.494	9.160	9.314	9.482	9.504	9.473	9.266	9.039	8.854	9.079	8.835
178	9.790	9.734	9.618	9.401	9.737	9.665	9.536	9.428	9.242	9.223	9.403	9.346
187	9.836	9.801	9.672	9.734	9.768	9.698	9.564	9.526	9.271	9.381	9.486	9.408
177	10.030	11.446	9.874	10.185	10.039	10.169	5.945	10.052	9.826	10.060	9.794	9.889
193	10.306	10.363	10.379	10.608	10.317	10.365	10.240	10.539	10.312	10.590	10.208	10.544
202	10.126	10.083	9.628	9.812	10.048	9.947	9.834	9.532	9.143	8.941	9.322	9.270
62	8.184	8.083	8.099	8.030	8.112	8.124	8.169	7.969	8.000	7.729	8.186	8.145
88	8.399	8.346	7.993	8.168	8.244	8.386	8.361	8.102	7.886	7.507	7.901	7.718
109	8.716	8.710	8.516	8.759	8.579	8.693	8.638	8.608	8.358	8.248	8.362	8.362
115	8.774	8.758	8.595	8.867	8.624	8.825	8.730	8.741	8.514	8.413	8.435	8.524
145	8.879	8.831	8.439	8.644	8.742	8.897	8.930	9.031	8.418	8.021	8.343	8.130
144	9.058	9.055	8.773	8.962	8.904	9.028	8.938	9.244	8.544	8.368	8.631	8.426
139	9.116	9.083	8.857	8.956	8.970	9.037	9.006	9.255	8.617	9.072	8.704	9.125
131	9.253	9.206	8.930	9.185	9.129	9.315	9.376	9.578	9.007	8.704	8.861	8.803
161	9.360	9.326	9.285	9.373	9.176	9.200	9.046	9.623	8.904	8.978	9.039	9.030
158	9.617	9.587	9.521	9.857	9.530	9.771	9.660	10.188	10.151	9.669	9.363	9.569
184	9.372	9.330	9.113	9.006	9.159	9.209	9.159	8.807	8.550	8.363	8.958	8.527
176	9.611	9.464	9.130	9.368	9.345	9.546	9.519	9.336	9.054	8.750	9.079	8.712
175	9.774	9.698	9.580	9.439	9.590	9.693	9.564	9.480	9.823	9.092	9.392	9.197
183	9.832	9.772	9.642	9.788	9.630	9.741	9.611	9.595	9.286	9.276	9.486	9.285

Table 7.8 Cont.

171	10.001	9.979	9.821	10.191	9.876	10.169	10.172	10.068	9.779	9.875	9.763	9.690
191	10.297	10.333	10.349	11.207	10.179	10.407	10.287	10.609	10.327	10.485	10.208	10.420
201	10.117	10.054	9.598	9.866	9.910	9.989	9.880	9.596	9.157	8.837	9.322	9.147
197	10.108	10.024	9.568	9.920	9.773	10.031	9.927	9.665	9.172	8.732	9.322	9.023
61	8.603	8.608	8.682	8.125	8.562	8.548	8.586	8.538	8.636	8.688	8.704	8.801
86	8.951	8.917	8.874	8.901	8.960	8.991	9.004	9.035	9.068	9.393	8.926	4.593
106	9.268	9.266	9.397	9.491	9.295	9.297	9.281	9.541	9.540	9.477	9.386	9.806
114	9.326	9.330	9.476	9.600	9.340	9.430	9.372	9.674	9.695	9.642	9.459	9.968
143	9.431	9.403	9.320	9.376	9.458	-4.907	9.572	9.543	9.599	9.249	9.368	9.574
141	9.610	9.627	9.654	9.694	9.620	9.633	9.580	9.755	9.725	9.597	9.656	9.870
137	9.668	9.654	9.738	9.688	9.686	9.642	9.649	9.767	9.799	9.643	9.729	9.998
129	9.805	9.778	9.811	9.918	9.845	9.920	10.018	10.090	10.188	9.932	9.886	10.247
159	9.926	9.911	10.182	10.137	9.910	9.833	9.725	10.170	10.127	10.260	10.085	10.524
156	10.169	10.159	10.402	10.590	10.246	10.375	10.302	10.700	10.745	10.898	10.388	11.013
182	9.929	9.902	9.994	9.739	9.876	9.814	9.802	9.739	9.726	9.592	9.982	9.970
174	10.188	10.056	10.035	10.148	10.087	10.194	10.216	10.321	10.298	10.058	10.134	10.231
172	10.326	10.269	10.461	10.172	10.307	10.297	10.207	10.412	10.417	10.320	10.417	10.641
180	10.401	10.370	10.555	10.583	10.381	10.402	10.325	10.599	10.550	10.612	10.552	10.829
170	10.553	10.551	10.702	10.929	10.592	10.773	10.815	11.001	10.960	11.103	10.788	11.134
189	10.850	10.905	11.230	11.395	10.896	11.012	10.929	11.541	11.508	11.714	11.233	11.864
199	10.669	10.625	10.479	10.598	10.627	10.594	10.523	10.529	10.339	10.065	10.347	10.590
196	10.661	10.596	10.449	10.652	10.489	6.133	10.569	10.598	10.354	9.960	10.305	10.467
194	11.192	11.167	11.330	11.385	13.077	9.879	10.267	8.775	8.720	4.303	11.737	11.911
116	8.859	8.995	8.874	8.884	8.955	9.104	9.099	8.937	8.939	8.577	9.161	9.304
142	9.212	9.175	9.011	9.185	9.186	9.237	9.241	8.852	8.919	9.223	9.169	8.877
160	9.534	9.539	9.534	9.776	9.521	9.543	9.406	9.358	9.391	9.307	9.630	9.521
166	9.597	9.587	9.613	9.885	9.566	9.675	9.497	9.491	10.133	9.472	9.703	9.684
186	9.698	9.661	9.457	9.661	9.496	9.747	9.697	9.360	9.451	9.080	9.611	9.290
185	9.877	9.884	9.791	9.979	9.846	9.879	9.705	9.566	9.576	9.427	9.899	9.585
181	9.934	9.912	9.875	9.973	9.912	9.887	9.774	9.578	9.650	9.474	9.972	9.713
173	10.071	10.035	9.948	10.203	10.071	10.166	10.705	9.906	10.040	9.762	10.129	9.962
192	10.183	10.155	10.303	10.390	10.119	10.050	10.375	9.951	9.936	10.037	10.307	10.189
190	10.435	10.416	10.539	10.875	10.472	10.621	10.427	10.516	10.597	10.728	10.631	10.729
204	10.476	10.439	10.466	10.687	10.463	10.658	10.689	10.299	10.447	10.545	10.654	10.741
200	10.408	10.313	10.172	6.070	10.313	10.439	10.341	7.947	10.102	9.889	10.377	9.946

Table 7.8 Cont.

198	10.592	10.527	10.598	6.093	10.533	10.543	10.332	10.229	10.269	10.151	10.660	10.356
203	10.625	10.581	10.636	10.758	10.547	11.111	10.323	10.291	10.256	10.255	10.724	10.369
195	10.819	10.808	10.839	11.209	10.818	11.019	10.940	10.817	10.811	10.934	11.031	10.850
205	11.116	11.162	11.368	11.679	11.122	11.257	11.054	11.358	11.359	11.544	11.476	11.579
208	10.935	10.883	10.182	10.883	10.853	10.839	10.648	10.345	10.190	9.895	10.590	10.306
207	10.927	10.853	10.586	10.937	10.715	10.882	10.694	10.415	10.205	9.791	10.590	10.183
206	11.377	11.325	11.347	11.433	11.303	11.273	11.064	11.082	11.076	10.618	11.462	11.249
209	11.745	11.682	11.604	11.955	11.658	5.704	6.744	7.007	8.097	11.537	3.608	11.342
266	5.619	5.511	5.191	5.127	5.457	4.922	4.934	4.724	4.577	3.628	5.439	4.780
268	6.641	6.549	6.275	6.218	6.502	6.048	6.058	5.877	5.750	4.943	6.484	5.922
270	7.664	7.587	7.359	7.309	7.548	7.173	7.182	7.030	6.923	6.259	7.529	7.064
272	8.686	8.625	8.443	8.400	8.593	8.299	8.306	8.183	8.096	7.574	8.574	8.206
274	9.708	9.663	9.526	9.490	9.638	9.424	9.429	9.336	9.270	8.889	9.619	9.348
276	10.730	10.701	10.610	10.581	10.684	10.550	10.553	10.489	10.443	10.205	10.664	10.490
278	11.753	11.739	11.694	11.672	11.729	11.676	11.677	11.642	11.616	11.520	11.709	11.632
280	12.775	12.777	12.778	12.763	12.775	12.801	12.801	12.794	12.789	12.835	12.754	12.774
282	13.797	13.815	13.861	13.854	13.820	13.927	13.925	13.947	13.963	14.151	13.799	13.917
284	14.820	14.852	14.945	14.945	14.866	15.053	15.048	15.100	15.136	15.466	14.844	15.059
286	15.842	15.890	16.029	16.036	15.911	16.178	16.172	16.253	16.309	16.781	15.889	16.201
289	17.376	17.447	17.654	17.672	17.479	17.867	17.858	17.983	18.069	18.754	17.456	17.914

Finally, the very restricted equation (5.4) was applied to all the twelve phases. It would not be expected that this equation would apply to the polar-phases, but the statistics obtained can be used to identify the polar and nonpolar phases. In Table (7.9) are details of multiple linear regressions for the twelve phases based on equation (5.4).

Table (7.9) Details of the multiple linear regressions for all twelve phases based on equation (5.4).

Phase	**Coefficients**					
Name	**c**	**r**	**l**	**F**	**r^2**	**n**
OV-101	100.74	132.93	195.64	3926.8	0.9726	216
F-50	138.10	128.26	192.69	2866.1	0.9632	217
APIEZON	241.96	147.26	184.56	1353.1	0.9245	215
OV-210	259.96	289.77	183.35	692.4	0.8663	214
OV-3	156.05	164.60	191.31	2237.5	0.9533	215
OV-17	325.49	252.95	177.68	1176.5	0.9156	216
OV-25	321.81	322.94	177.97	1915.7	0.9459	215
AN-600	380.55	306.94	173.45	876.8	0.9221	213
OV -225	419.80	353.14	170.47	632.7	0.8517	216
CHOMS	648.31	406.60	152.06	473.57	0.8129	216
HK-325	159.12	195.38	191.39	1776.2	0.9223	214
POLMPE	362.90	440.04	175.12	798.87	0.8784	217

The same facts were noticed as mentioned before, that the best values of $\log L^{16}$ were for the first three phases (OV-101, F-50, Aplezon). The average of the back-calculated $\log L^{16}$ values were found as shown in Table (7.10). A plot of the final calculated $\log L^{16}$ values versus N is shown in Figure (7.5).

Table (7.10) IUPAC No. log L^{16} cal. from (OV-101, F-50, APLEZON) with their averages.

IUPAC	Log Lcal w(OV-101)	Log Lcal w(F-50)	Log Lcal w(APLEZON)	Log Lcal Avg
_	5.697	5.685	5.699	5.694
1	6.193	6.176	6.059	6.143
4	6.689	6.667	6.418	6.591
2	6.510	6.540	6.582	6.544
6	7.006	7.031	6.941	6.993
11	7.323	7.395	8.007	7.575
3	6.568	6.588	6.660	6.606
8	7.064	7.079	7.020	7.054
13	7.381	7.444	7.543	7.456
15	7.439	7.492	7.622	7.517
10	6.633	6.622	6.457	6.571
19	7.170	7.153	6.864	7.062
27	7.480	7.510	7.380	7.457
32	7.544	7.565	7.466	7.525
54	7.650	7.639	7.310	7.533
9	6.852	6.886	6.838	6.859
18	7.349	7.377	7.198	7.308
26	7.666	7.741	7.721	7.709
31	7.723	8.308	7.800	7.944
53	7.829	7.863	7.644	7.779
52	8.008	8.087	7.978	8.024
7	6.910	6.919	6.922	6.917
17	7.406	7.404	7.282	7.364
25	7.723	7.768	7.805	7.766
28	7.781	7.817	7.884	7.827
51	7.887	7.890	7.728	7.835
49	8.066	8.114	8.062	8.081
47	8.124	8.142	8.145	8.137
5	7.047	7.036	6.996	7.026
16	7.543	7.527	7.355	7.475
20	7.860	7.892	7.878	7.877
22	7.918	7.940	7.957	7.938
46	8.024	8.013	7.801	7.946
44	8.202	8.237	8.135	8.192
42	8.260	8.265	8.219	8.248
40	8.397	8.388	8.292	8.359
14	7.161	7.163	7.359	7.228
34	7.650	7.648	7.710	7.669
36	7.981	8.025	8.250	8.085
39	8.025	8.060	8.312	8.132
73	8.131	8.133	8.157	8.140
72	8.310	8.357	8.490	8.386
68	8.368	8.385	8.574	8.442
58	8.504	8.508	8.647	8.553
80	8.612	8.628	9.003	8.747
12	7.411	7.418	8.128	7.652

Table 7.10 cont.

33	7.907	7.909	7.946	7.921
35	8.224	8.273	8.469	8.322
37	8.282	8.321	8.548	8.384
71	8.388	8.394	8.392	8.392
70	8.588	8.638	8.750	8.659
66	8.625	8.646	8.810	8.693
56	8.761	8.769	8.883	8.804
79	8.869	8.889	9.238	8.999
77	9.126	9.150	9.474	9.250
30	7.166	7.160	7.179	7.168
50	7.662	7.651	7.538	7.617
69	7.979	8.016	8.062	8.019
75	8.037	8.064	8.140	8.080
104	8.163	8.137	7.984	8.095
103	8.322	8.361	8.318	8.334
100	8.380	8.389	8.402	8.390
98	8.516	8.512	8.475	8.501
121	8.629	8.632	8.831	8.697
119	8.881	8.893	9.066	8.947
155	8.636	8.636	8.658	8.643
24	7.425	7.315	7.220	7.320
45	7.921	7.806	7.579	7.769
59	8.231	8.163	8.094	8.163
69	8.296	8.218	8.181	8.232
96	8.402	8.291	8.025	8.240
95	8.581	8.515	8.359	8.485
91	8.639	8.543	8.443	8.541
84	8.775	8.666	8.516	8.652
113	8.883	8.786	8.871	8.847
110	9.140	9.047	9.107	9.098
150	8.895	8.790	8.699	8.795
136	9.154	8.944	8.740	8.946
23	7.568	7.528	7.645	7.581
43	8.064	8.019	8.005	8.030
57	8.381	8.383	8.528	8.431
63	8.439	8.431	8.607	8.492
94	8.545	8.505	8.451	8.500
92	8.775	8.729	8.785	8.763
90	8.782	8.808	8.868	8.820
83	8.918	8.879	8.942	8.913
111	9.026	9.000	9.297	9.108
107	9.283	9.261	9.533	9.359
148	9.038	9.003	9.125	9.055
135	9.297	9.158	9.166	9.207
133	9.440	9.371	9.592	9.468
29	7.621	7.602	7.708	7.644
48	8.117	8.093	8.067	8.093
67	8.434	8.457	8.590	8.494
74	8.492	8.506	8.669	8.555
102	8.598	8.579	8.513	8.563
101	8.782	8.803	8.847	8.811
99	8.840	8.831	8.985	8.885

Table 7.10 cont.

97	8.971	8.954	9.004	8.976
120	9.079	9.074	9.359	9.171
118	9.336	9.335	9.595	9.422
154	9.091	9.078	9.187	9.118
149	9.350	9.232	9.228	9.270
146	9.498	9.445	9.654	9.532
153	9.546	9.520	9.716	9.594
21	8.306	7.810	7.886	8.001
41	8.291	8.353	8.246	8.297
55	8.608	8.665	8.769	8.681
60	8.666	8.713	8.848	8.742
89	8.772	8.787	8.692	8.750
87	8.951	9.011	9.026	8.996
85	9.009	9.038	9.109	9.052
82	9.145	9.161	9.183	9.163
108	9.273	9.301	9.562	9.379
105	9.523	9.556	9.790	9.623
140	9.244	9.265	9.342	9.284
132	9.524	9.439	9.407	9.457
130	9.667	9.653	9.833	9.717
138	9.719	9.727	9.895	9.780
128	9.893	9.935	10.073	9.967
38	8.092	8.164	8.415	8.223
76	8.594	8.661	8.783	8.679
78	8.905	9.019	9.298	9.074
81	8.962	9.067	9.376	9.135
125	9.068	9.140	9.221	9.143
124	9.247	9.364	9.554	9.389
123	9.285	9.372	9.614	9.424
122	9.442	9.515	9.712	9.556
127	9.549	9.635	10.067	9.750
118	9.827	9.916	10.326	10.023
168	9.561	9.639	9.895	9.698
164	9.820	9.793	9.935	9.850
162	9.977	10.020	10.377	10.125
167	10.016	10.081	10.423	10.173
157	10.190	10.288	10.602	10.360
169	10.507	10.662	11.155	10.775
65	8.194	8.197	8.127	8.173
93	8.407	8.375	8.023	8.268
112	8.724	8.739	8.546	8.670
117	8.782	8.788	8.625	8.731
152	8.888	8.861	8.469	8.739
151	9.169	9.185	8.922	9.092
147	9.125	9.112	8.886	9.041
134	9.261	9.236	8.960	9.152
165	9.369	9.356	9.315	9.346
163	9.626	9.617	9.551	9.598
188	9.381	9.360	9.143	9.294
179	9.619	9.494	9.160	9.424
178	9.790	9.734	9.618	9.714
187	9.836	9.801	9.672	9.770

Table 7.10 cont.

177	10.030	11.446	9.874	10.450
193	10.306	10.363	10.379	10.349
202	10.126	10.083	9.628	9.946
62	8.184	8.083	8.099	8.122
88	8.399	8.346	7.993	8.246
109	8.716	8.710	8.516	8.647
115	8.774	8.758	8.595	8.709
145	8.879	8.831	8.439	8.717
144	9.058	9.055	8.773	8.962
139	9.116	9.083	8.857	9.019
131	9.253	9.206	8.930	9.129
161	9.360	9.326	9.285	9.324
158	9.617	9.587	9.521	9.575
184	9.372	9.330	9.113	9.272
176	9.611	9.464	9.130	9.402
175	9.774	9.698	9.580	9.684
183	9.832	9.772	9.642	9.749
171	10.001	9.979	9.821	9.934
191	10.297	10.333	10.349	10.327
201	10.117	10.054	9.598	9.923
197	10.108	10.024	9.568	9.900
61	8.603	8.608	8.682	8.631
86	8.951	8.917	8.874	8.914
106	9.268	9.266	9.397	9.310
114	9.326	9.330	9.476	9.377
143	9.431	9.403	9.320	9.385
141	9.610	9.627	9.654	9.630
137	9.668	9.654	9.738	9.687
129	9.805	9.778	9.811	9.798
159	9.926	9.911	10.182	10.006
156	10.169	10.159	10.402	10.243
182	9.929	9.902	9.994	9.942
174	10.188	10.056	10.035	10.093
172	10.326	10.269	10.461	10.352
180	10.401	10.370	10.555	10.442
170	10.553	10.551	10.702	10.602
189	10.850	10.905	11.230	10.995
199	10.669	10.625	10.479	10.591
196	10.661	10.596	10.449	10.568
194	11.192	11.167	11.330	11.230
116	8.859	8.995	8.874	8.909
142	9.212	9.175	9.011	9.133
160	9.534	9.539	9.534	9.536
166	9.597	9.587	9.613	9.599
186	9.698	9.661	9.457	9.605
185	9.877	9.884	9.791	9.851
181	9.934	9.912	9.875	9.907
173	10.071	10.035	9.948	10.018
192	10.183	10.155	10.303	10.214
190	10.435	10.416	10.539	10.464
204	10.476	10.439	10.466	10.460
200	10.408	10.313	10.172	10.298

Table 7.10 cont.

198	10.592	10.527	10.598	10.572
203	10.625	10.581	10.636	10.614
195	10.819	10.808	10.839	10.822
205	11.116	11.162	11.368	11.215
208	10.935	10.883	10.182	10.667
207	10.927	10.853	10.586	10.789
206	11.377	11.325	11.347	11.350
209	11.745	11.682	11.604	11.677
266	5.619	5.511	5.191	5.440
268	6.641	6.549	6.275	6.488
270	7.664	7.587	7.359	7.536
272	8.686	8.625	8.443	8.584
274	9.708	9.663	9.526	9.632
276	10.730	10.701	10.610	10.680
278	11.753	11.739	11.694	11.728
280	12.775	12.777	12.778	12.776
282	13.797	13.815	13.861	13.824
284	14.820	14.852	14.945	14.872
286	15.842	15.890	16.029	15.920
289	17.376	17.447	17.654	17.492

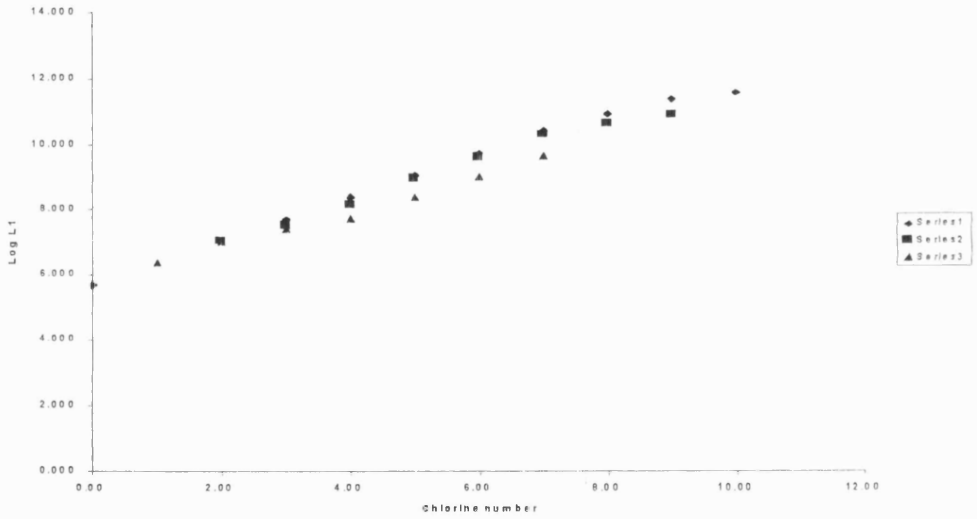

Figure (7.5) Plot of log L^{16} vs chlorine number.

For ortho- substituted congeners (◆) 2,2',6,6'- substituted congeners, (■) 2,2'- substituted congeners, (▲) 2- substituted congeners or non.

7.5 Conclusions

The solvation descriptors for the 209 PCBs have been determined, using data on the 209 compounds from GLC experiments, together with more limited data from HPLC experiments, and on log Poct values. The calculated descriptors for a number of PCBs were linearly related to the number of chlorine atoms, N, with due regard to the position of the chlorine atom. The effect for ortho- substitution was noted, so that the sets of the descriptors for the PCBs were divided into four groups. These groups were as follows: PCBs, 2,2'6-substituted, 2,2',6,6'-substituted PCBs, 2,2'-ortho-substituted PCBs, 2-ortho-subsituted and non substituted. From the obtained equations, descriptors for any of the 209 PCBs could be calculated by fitting a given PCB to a specific group. Using the calculated descriptors, values of log Poct were predicted for all the PCBs. Good agreement with experimentally obtained logPoct values was found. In the next Chapter, other properties of PCBs will be calculated from the descriptors, and, again, compared to experiment.

7.6 References

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Chapter 8 Comparison of Calculated and Observed Partition Coefficients for PCBs

8.0 Introduction

The environmental fate of organic chemicals is largely determined by their partitioning tendencies between aqueous, atmospheric and organic phases. The key parameter for assessing and describing the partitioning behaviour of organic chemicals between aqueous and organic phases is the water-octanol partition coefficient (Poct). For example, log Poct has been found to be highly correlated with the soil sorption [1-5] and bioconcentration factor [6-10] of aquatic organisms such as fish, daphnids and molluscs, for a diverse range of chemicals. In addition, log Poct has been correlated to biomagnification in beef cattle and swine[11] and to aqueous solubility.[12-15] This has resulted in the extensive use of log Poct in the development of Quantitative-Structure and Property Relationships (QSPRs). The importance of highly specific QSPRs becomes obvious when the fate and transport of structurally similar compounds are considered especially in the case of polychlorinated biphenyls (PCBs). PCBs were released into the environment in the form of multicongener mixtures referred to as Aroclors. Not all PCBs are Aroclors, but most Aroclors are mixtures of PCBs. Each Aroclor (e.g. 1016, 1221, 1232, ect.) contains a general mixture and the major congener composition has been used to estimate the type of Aroclor (s) present in the environmental samples.[16,17] However, it has been shown that Aroclors extracted from environmental samples show significantly different congener compositions than those present in the original Aroclor (s).[18,19] It is likely that there is a selective microbial degradation/dechlorination,[20,21] chemical/physical partitioning process [18,19]

and reactions of congeners. Thus to effectively evaluate the relative importance of congener-specific partitioning processes, accurate values of water-octanol partition coefficients must be measured or predicted for each congener.

8.1 Theoretical background

The Poct value is defined as the ratio of the equilibrium of concentration of a dissolved substance in a two-phase system consisting of the two largely immiscible solvents, octanol and water. Mallhot and Peters [22] studied the empirical relationships between water-octanol partition coefficient and nine physicochemical properties. They found that the property that predicts the partition coefficient most precisely is aqueous solubility. Recently, Isnard and Lambert[23] discussed the eighteen aqueous solubility and water-octanol partition coefficient correlations available in the literature. They concluded that there is a need to re-examine the theoretical approach. In part, published values of water solubility can vary greatly for the same compound and relatively little experimental data exists for many of the PCBs, an important class of organic chemicals. Estimating log Poct from aqueous solubility introduces an additional error into any correlation equation. Therefore, it is highly desirable to have a reliable method to calculate water-octanol partition coefficients only from information already present in the structural formulas of the compounds. Predicting log Poct from chemical structure has advantages over methods based on aqueous solubility. Warne et al.[24] predicted aqueous solubility and water-octanol partition coefficient for lipophilic compounds using molecular descriptors and physicochemical properties. The best simple linear regressions they incorporated are with either connectivity indices or some measure of molecular surface area or volume. The molecular surface area has been previously shown to be highly correlated with

log Poct for different chemicals[25] and for PCBs.[26] For semi-volatile organic compounds (SOCs) the air-octanol partitioning coefficient (L_{OA}) had been used with considerable success in describing the partitioning of SOCs between the gas phase and atmospheric particles[27] and for the terrestrial environment as a whole.[28]

L_{oA} (v / v) is defined as $L_{oA} = C_o / C_A$

Here C_o (mol/L) is the concentration of the compound in octanol and C_A (mol/L) is the gaseous concentration in the air at equilibrium. Equilibrium partitioning of a chemical between two compartments can be expressed as follows [29]

$$\Delta G_{OA} = -RT \ln L_{oA} \qquad (8.1)$$

Here L_{OA} is the air-octanol partition coefficient, ΔG_{OA} is the Gibbs free energy of the transfer from air to octanol, R is the gas constant and T is the absolute temperature (K). The Gibbs free energy is given by [29]

$$\Delta G_{OA} = \Delta H_{OA} - \Delta T_{OA} \qquad (8.2)$$

From these equations it is clear that L_{OA} can be a strong function of temperature.

8.2 The techniques used to measure log Poct for PCBs

The original method used is the so-called 'shake-flask' method, in which a solute is partitioned between water and octanol. The concentration of the solute is measured in each phase by some particular method of analysis, such as UV/visible spectroscopy

or chromatographic analysis. This method does not work very well for solutes with high values of log Poct, such as the PCBs. In these cases, the quantity of solute in the aqueous layer is too small to measure accurately. Additionally, very hydrophobic solutes may be adsorbed onto the walls of the glass vessels, or be entrapped in a sort of emulsion at the water- octanol interface.

Other, rather indirect, methods have therefore been used for hydrophobic solutes such as the highly chlorinated PCBs. Correlations between HPLC retention data and log Poct for a series of training compounds is often used as a method for the estimation of log Poct. Another HPLC method uses a stationary phase that is coated with octanol. The determined capacity factors (as log k') with an aqueous mobile phase are then supposed to be linearly correlated with log Poct. A generator column has also been used to determine air-octanol partitions. In this method, air is drawn through a column of octanol attached to a support in order to achieve partition of a compound between the air and octanol.

8.3 Results

The air-octanol partition coefficients which were measured for several PCBs,[31] using the generator column method are listed in listed in Table (8.1). Also given is the IUPAC number. In the last column are given calculated values for log L_{OA}, as obtained in this work, as described in previous chapters.

Table (8.1) PCBs, their IUPAC number, log L_{OA} exp, and log L_{OA} calc

Name	IUPAC	$LogL_{OA}$ exp	Log L_{OA} Calc (b)
4-Monochloro	3	6.78	6.43
4,4'-Dichloro	15	7.67	7.44
2,4,5-Trichloro	29	7.96	7.51

2,3,4,5-Tetrachloro	61	8.74	8.31
2,2',4,4',6,6'-Hexachloro	155	8.99	8.84

b Calculated values, this work.

Plots of log L_{OA} exp and log L_{OA} calc (b) versus the number of chlorine atoms in the PCB are shown in Figure (8.1).

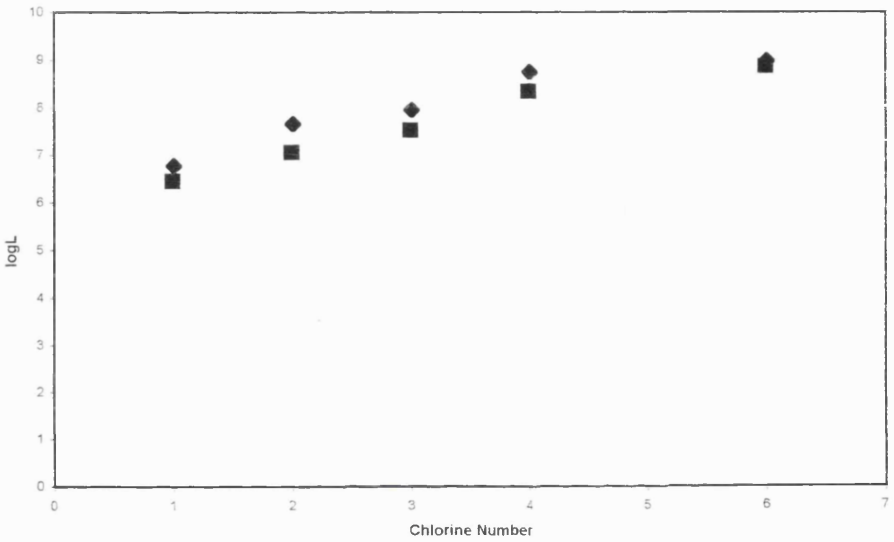

Figure (8.1) Plots of log L vs chlorine number (◆) log L measured and (■) calculated

8.3.1 The fugacity meter

Measurements of the partitioning of polychlorinated biphenyls between air and octanol have also been made using a fugacity meter.[30] Air was passed through a column packed with glass wool coated with an octanol solution of PCBs of known concentration. The PCBs in the air were allowed to come into equilibrium with the PCBs in the octanol. Upon leaving the column the PCBs in air were trapped on a Florisil cartridge. The extraction and analysis of this cartridge allowed the

determination of the air concentration. The air-octanol partition coefficient L_{OA} was calculated from the quotient of the volume-based octanol and air concentration. The PCBs which were used were not employed as single compounds but as technical mixtures, as this greatly increased the information yield of the experiments and the comparability of the results for the different congeners.

The octanol solution was prepared before the measurements in such a way that a wide range of PCBs congeners could be detected in the Florisil trap after short periods of fugacity meter operation.

8.4 Discussion of the L_{OA} values

In the literature there is a lack of experimentally determined L_{OA} values. There are only two papers [31,32] reporting measured values, and they are limited to several organochlorine pesticides and a number of PCBs congeners. It is possible to obtain L_{OA} values by an indirect calculation using water-octanol and air-water partition coefficients:

$$L_{OA} = P_{OW} * L_{WA} \tag{8.3}$$

However, this method gives the partition between air and water-saturated octanol, because Poct refers to mutually saturated systems. Care must therefore be taken not to confuse the directly determined L_{OA} value for partition between air and dry octanol with the indirectly determined values for partition between air and wet octanol, as obtained through equation 8.3. It has to be said that there is still a difficulty over equation 8.3 because air-water partition coefficients are themselves very difficult to determine for hydrophobic compounds.

However, because of the lack of directly determined values, environmental chemists are still dependent on the indirect calculated L_{OA} values. It is therefore

particularly interesting to evaluate the validity of this approach by comparing the measured values with calculated ones. In Figure (8.2) the directly measured log L_{OA} values[33] are plotted against log L_{OA} calculated from equation (8.3); values of L_{OW} and L_{WA} were taken from the literature.[26, 34]

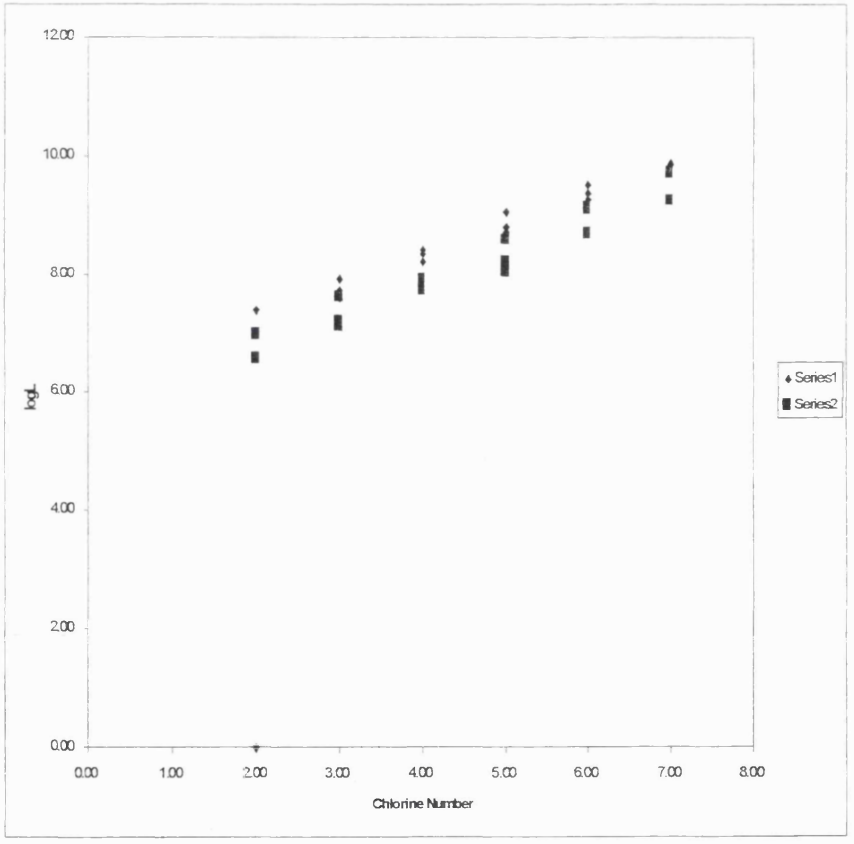

Figure (8.2) Plots of log L exp (◆) and log L calc (■) vs chlorine No.

The calculated and the direct experimental L_{OA} values are given in Table 8.2. As can seen, the experimental values are consistently higher than the calculated ones. This

indicates that the calculated L_{OA} systematically under predicts the true value. Harner and Mackay[31] suggested that this may be because the L_{OW} value represents the chemicals' partitioning between octanol saturated with water and water saturated with octanol, not between pure octanol and pure water. There is very good agreement, however, between the directly determined experimental values [33] and those calculated in this work, from the descriptors that have been obtained.

Table (8.2) IUPAC No. exp. Log L_{OA}[33(A)], calc. Log L_{OA}[33(B)], and our calc. LogL_{OA}[(C)]

PCB Substitution	IUPAC (D)	LogL exp A	LogL calc B	LogL calc C
(2,2');(2,6)	4+10	7.18	6.56	6.95
(2,4')(2,3)	8+5	7.40	6.98	6.98
(2,2',5)	18	7.60	7.12	7.58
(2,2',3);(2,4',6)	16+32	7.72	7.18	7.57
(2,4'5);(2,4,4')	31+28	7.92	7.61	7.61
(2,2',5,5')	52	8.22	7.73	8.22
(2,2',3,5')	44	8.36	7.78	8.22
(2,3,4',6)	64	8.41	7.91	8.32
(2,2',3,5',6)	95	8.71	8.04	8.64
(2,2',3,3',6); (2,2',4,5,5')	84+101	8.80	8.20	8.75
(2,3,3',4',6)	110	9.06	8.58	8.98
(2,2',3,4',5',6)	149	9.27	8.68	9.25
(2,2',4,4',5,5')	153	9.37	9.09	9.52
(2,2',3,4,4',5'); (2,3,3',4,4',6)	138+158	9.51	9.12	9.58
(2,2',3,4',5,5',6)	187	9.87	9.25	9.85
(2,2',3,4,4',5,5')	180	9.88	9.72	10.17

A- Experimental direct values.[33] B-Calculated values using eq. (8.3). C – Calculated values (this work). D-where two values are given, the results refer to both the indicated PCBs.

In Figure (8.3) are compared the calculated values of log L_{OA} which were shown in Table 8.2, with the experimental values. There is good agreement between the measured and the calculated values, which means that L_{OW} can now be calculated for any PCB.

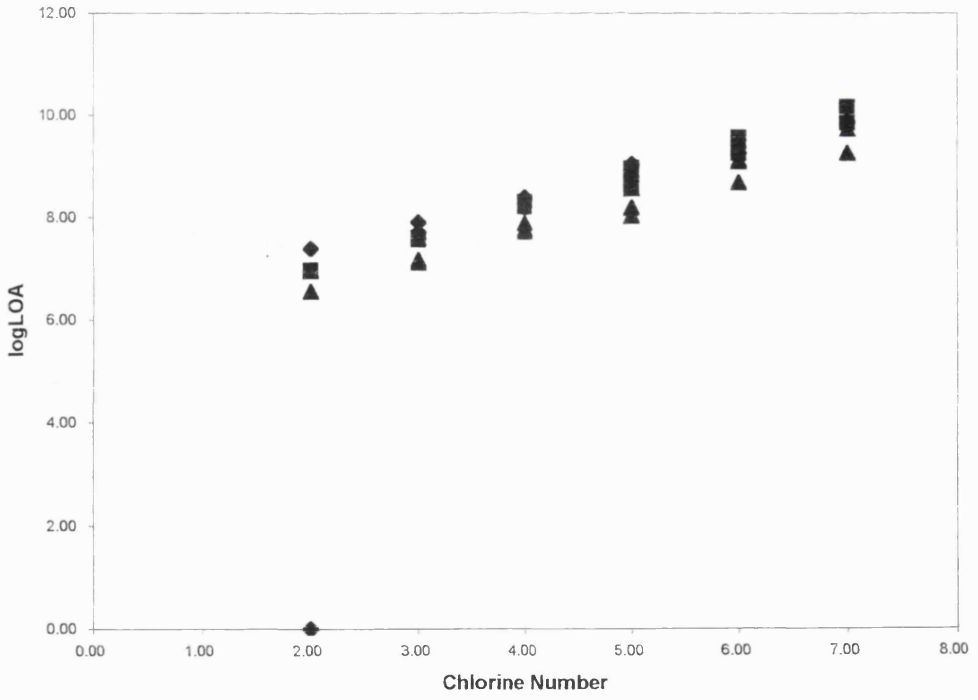

Figure (8.3) Plots of log L_{OA} exp (◆) our log L_{OA} calc. (■) and log L_{OA} cal (▲) using eq. (8.3) vs chlorine number.

8.5 The Final Comparison for Octanol/Water Partitioning of PCBs

Because the PCBs are quite hydrophobic compounds, with large values of logPoct, it is very difficult to obtain directly measured values. Thus, most quoted values are those that have been predicted by some calculation method, and only few measured values are known.

One of the most useful studies is that of Hawker[26] who measured 13 PCB congeners by the generator column method. The series of 13 PCBs was selected so as to contain a great deal of structural variation and cover a wide rang of lipophilicity. It included seven terachlorobiphenyls with from zero (3,3',4,4'-) to four (2,2',6,6'-) ortho-substitued chlorine atoms, two congeners substituted on one ring only, and others with five, six, eight, and nine chlorine substituents. The determined log Poct values had been used by Hansen[35] to compare his calculated log Poct for the same PCBs, as shown in Table (8.3). Another well known program for the calculation of log Poct values is the Clog P program of Leo. Values of Clog P are also given in Table (8.3). The most recent and accurate measured values for log P were the ones listed in MedChem [36] program; in this program more than one value for each PCBs may be found, the most reliable one is log P*. In Table (8.3) the calculated values (this work) were compared with the experimental and other calculated ones.

Table (8.3) Comparison of calculated values, this work, with experimental and other calculated values of log Poct for PCBs

		Callog Poct			Exp log Poct		
Name	**IUPAC**	**This work**	**Hansen**	**Clog P**	**Log P***	**MedChem**	**Hawker**
2,2',3,3'-Tetachlorobiphenyl	40	6.18	5.71	6.26	6.18	5.15	5.55
2,2',5,6'-Tetrachlorobiphenyl	53	6.06	5.67	6.13		5.54	5.46
2,2',6,6'-Tetrachlorobiphenyl	54	5.96	5.32	5.94	5.94		5.48
2,3,4,5-Tetrachlorobiphenyl	61	6.34	5.87	6.51	6.41		6.18
2,3,5,6-Tetrachlorobiphenyl	65	5.96	5.71	6.38	5.94		5.94
2,3',4,4'-Tetrachlorobiphenyl	66	6.25			6.31		6.31
3,3',4,4'-Tetrachlorobiphenyl	77	6.63	6.14	6.19	6.63	6.10	6.21
2,2',4,6,6'-Pentachlorobiphenyl	104	5.93	5.83	5.81	5.81	5.37	5.37
2,3,3',4,4'-Pentachlorobiphenyl	105	6.68	6.39	7.10		6.23	5.82
2,2',3,3',6,6'-Hexacchlorobiphenyl	136	7.16	6.19	5.92	7.12	6.44	5.76
2,2'3,3',4,4,5,5'-Octachlorobiphenyl	194	8.61	7.55	8.99	8.68	8.27	7.67
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	201	8.17	7.03			7.24	7.21
2,2',3,3',4,4',5,6,6'-Nonchlorobiphenyl	207	8.34	7.49	9.45		7.63	7.52

The last comparison for the calculated log Poct values in this work for all 209 PCBs, was obtained by comparing 209 PCBs with values from the MedChem data base. As mentioned before, in this data base there may be more than one value for any PCB. The average of the given values was taken and also the minimum and maximum for each PCB. For some of the PCBs, a value of log P* was given; this indicates the most reliable value. All these details are shown in Table (8.4) with the IUPAC number for each one. From these Table (8.4) it is clear that the calculated log Poct values in this work are in excellent agreement with observed values. Therefore, where there are no observed values, the calculated ones obtained in this work could be used quite reliably.

Table (8.4) IUPAC No, Calculated log Poct values from this work, and observed log Poct values from the Med Chem data base.

Name	IUPAC	Calc	Med Chem Obs value			
		This work	Log P*	Average	Min	Max
Biphenyl	-	4.04	4.01	3.70	3.16	4.29
2-Monochloro	1	4.54	4.53	4.46	4.10	4.60
3-Monochloro	2	4.60	4.71	4.67	4.42	4.95
4-Monochloro	3	4.58	4.61	4.53	4.26	4.90
2,2'-Dichlloro	4	5.07		4.97		
2,3-Dichloro	5	5.15		4.97		
2,3'-Dichloro	6	5.08	5.02	5.06		
2,4-Dichloro	7	5.13	5.30	5.07		
2,4'-Dichloro	8	5.13	5.10	4.88	4.00	5.14
2,5-Dichloro	9	5.15	5.16	5.17	5.06	5.30
2,6-Dichloro	10	5.14	4.98	5.02	4.84	5.31
3,3-Dichloro	11	5.20	5.30	5.28		
3,4-Dichloro	12	5.23	5.29	5.22		
3,4'-Dichloro	13	5.18		5.29		
3,5-Dichloro	14	5.23	5.37	5.28		
4,4'-Dichloro	15	5.30	5.58	5.33	4.65	6.00
2,2',3-Trichloro	16	5.62	5.60	5.02	4.60	5.31
2,2',4-Trichloro	17	5.69	5.76	5.43	5.25	5.60
2,2',5-Trichloro	18	5.62	5.60	5.02	4.79	5.55
2,2',6-Trichloro	19	5.48	5.47	5.02		
2,3,3'-Trichloro	20	5.63	5.57	5.57		
2,3,4-Trichloro	21	5.69	5.86	5.51		
2,3,4'-Trichloro	22	5.61	5.42	5.58		
2,3,5-Trichloro	23	5.69				
2,3,6-Trichloro	24	5.66	5.67	5.35		
2,3',4-Trichloro	25	5.69		5.67		
2,3',5-Trichloro	26	5.71	5.76	5.66		
2,3',6-Trichloro	27	5.68		5.44		
2,4,4'-Trichloro	28	5.62	5.62	5.49	5.25	5.60
2,4,5-Trichloro	29	5.69	5.90	5.81	5.51	6.25
2,4,6-Trichloro	30	5.71	5.71			
2,4',5-Trichloro	31	5.69	5.79	5.68	5.67	5.69
2,4',6-Trichloro	32	5.75	5.75	5.44		
2',3,4-Trichloro	33	5.69				
2',3,5-Trichloro	34	5.71				
3,3',4-Trichloro	35	5.84		5.82		
3,3',5-Trichloro	36	5.73		5.02	4.15	5.88
3,4,4'-Trichloro	37	5.73	5.90	5.44	4.49	5.83
3,4,5-Trichloro	38	5.75		5.76		
3,4',5-Trichloro	39	5.75		5.89		

Table 8.4 cont.

2,2',3,3'-Tetachloro	40	6.18	6.18	5.15	4.63	5.66
2,2',3,4-Tetrachloro	41	6.16	6.11	5.69		
2,2',3,4'-Tetrachloro	42	6.18		5.76		
2,2',3,5-Tetrachloro	43	6.20		5.75		
2,2',3,5'-Tetachloro	44	5.74	5.81	4.80		
2,2',3,6-Tetrachloro	45	6.06		5.53		
2,2',3,6'-Tetrachloro	46	6.06		5.53		
2,2',4,4'-Tetachloro	47	6.19	6.29	5.93	5.68	6.17
2,2',4,5-Tetrachloro	48	5.96	5.78			
2,2',4,5'-Tetachloro	49	6.21	6.36	5.98	5.73	6.22
2,2',4,6-Tetrachloro	50	6.04		5.63		
2,2',4,6'-Tetrachloro	51	6.04		5.63		
2,2',5,5'-Tetrachloro	52	6.23	6.26	5.20	4.30	6.09
2,2',5,6'-Tetrachloro	53	6.06		5.54	5.46	5.62
2,2',6,6'-Tetrachloro	54	5.96	5.94			
2,3,3',4-Tetrachloro	55	6.27				
2,3,3',4'-Tetrachloro	56	6.27		6.11		
2,3,3',5-Tetrachloro	57	6.29				
2,3,3',5'-Tetrachloro	58	6.17	6.17			
2,3,3',6-Tetrachloro	59	6.25		5.95		
2,3,4,4'-Tetrachloro	60	6.25		5.98	5.84	6.11
2,3,4,5-Tetrachloro	61	6.34	6.41			
2,3,4,6-Tetrachloro	62	6.22		5.89		
2,3,4',5-Tetrachloro	63	6.15		6.17		
2,3,4',6-Tetrachloro	64	6.22		5.95		
2,3,5,6-Tetrachloro	65	6.09	5.94			
2,3',4,4'-Tetrachloro	66	6.25	6.31			
2,3',4,5-Tetrachloro	67	6.27		6.20		
2,3',4,5'-Tetrachloro	68	6.27				
2,3',4,6-Tetrachloro	69	6.22		6.04		
2,3',4',5-Tetrachloro	70	6.28	6.39	6.17	5.95	6.30
2,3',4',6-Tetrachloro	71	6.16		5.98		
2,3',5,5'-Tetrachloro	72	6.29		6.26		
2,3',5',6-Tetrachloro	73	6.23		6.04		
2,4,4',5-Tetrachloro	74	6.53	6.67	6.20		
2,4,4',6-Tetrachloro	75	6.20				
2',3,4,5-Tetrachloro	76	6.25				
3,3',4,4'-Tetrachloro	77	6.63	6.63	6.10	5.45	6.77
3,3',4,5-Tetrachloro	78	6.33		6.35		
3,3',4,5'-Tetrachloro	79	6.33		6.42		
3,3',5,5'-Tetrachloro	80	6.77	6.85	6.53	6.48	6.58
3,4,4',5-Tetrachloro	81	6.31		6.36		
2,2',3,3',4-Pentachloro	82	6.68		6.20		
2,2',3,3',5-Pentachloro	83	6.70				
2,2',3,3',6-Pentachloro	84	6.20	6.04	6.04		
2,2',3,4,4'-Pentachloro	85	6.66	6.61	6.30		
2,2',3,4,5-Pentachloro	86	6.68		6.23		
2,2',3,4,5'-Pentachloro	87	6.81	6.85	6.32	6.29	6.37

Table 8.4 cont.

2,2',3,4,6-Pentachloro	88	6.56		6.07		
2,2',3,4,6'-Pentachloro	89	6.56		6.07		
2,2',3,4',5-Pentachloro	90	6.73		6.36		
2,2',3,4',6-Pentachloro	91	6.25	6.31			
2,2',3,5,5'-Pentachloro	92	6.86	6.97	6.35		
2,2',3,5,6-Pentachloro	93	6.58				
2,2',3,5,6'-Pentachloro	94	6.58		6.13		
2,2',3,5',6-Pentachloro	95	6.58	6.55			
2,2',3,6,6'-Pentachloro	96	6.65		5.71		
2,2',3',4,5-Pentachloro	97	6.66	6.67	6.29		
2,2',3',4,6-Pentachloro	98	6.56		6.07		
2,2',4,4',5-Pentachloro	99	6.79	7.21	6.39		
2,2'4,4'6-Pentachloro	100	6.54		6.23		
2,2',4,5,5'-Pentachloro	101	6.81	6.85	6.51	5.92	7.07
2,2',4,5,6'-Pentachloro	102	6.56		6.16		
2,2',4,5',6-Pentachloro	103	6.56		6.22		
2,2',4,6,6'-Pentachloro	104	5.93	5.81	5.37		
2,3,3',4,4'-Pentachloro	105	6.68		6.23	5.82	6.65
2,3,3',4,5-Pentachloro	106	6.74				
2,3,3',4',5-Pentachloro	107	6.74		6.71		
2,3,3',4,5'-Pentachloro	108	6.68		6.71		
2,3,3',4,6-Pentachloro	109	6.68		6.48		
2,3,3',4',6-Pentachloro	110	6.68		6.48		
2,3,3',5,5'-Pentachloro	111	6.76				
2,3,3',5,6-Pentachloro	112	6.72		6.45		
2,3,3',5',6-Pentachloro	113	6.70		6.54		
2,3,4,4',5-Pentachloro	114	6.72		6.65		
2,3,4,4',6-Pentachloro	115	6.66		6.49		
2,3,4,5,6-Pentachloro	116	6.72	6.74	6.49	6.30	6.85
2,3,4',5,6-Pentachloro	117	6.68		6.46		
2,3',4,4',5-Pentachloro	118	7.10	7.12	6.65		
2,3',4,4',6-Pentachloro	119	6.66		6.58		
2,3',4,5,5'-Pentachloro	120	6.74		6.24	5.68	6.79
2,3',4,5',6-Pentachloro	121	6.68		6.64		
2',3,3',4,5-Pentachloro	122	6.74		6.64		
2',3,4,4',5-Pentachloro	123	6.78		6.74		
2',3,4,5,5'-Pentachloro	124	6.74				
2',3,4,5,6'-Pentachloro	125	6.68				
3,3',4,5,5'-Pentachloro	127	6.48		6.96		
3,3',4,5,5'-Pentachloro	127	6.80		6.95		
2,2',3,3',4,4'-Hexachloro	128	7.29	7.32	7.09	6.74	7.44
2,2',3,3',4,5-Hexachloro	129	7.31	7.32	6.98	6.73	7.22
2,2',3,3',4,5'-Hexachloro	130	7.31	7.39	7.00	6.80	7.20
2,2',3,3',4,6-Hexachloro	131	6.93	6.82	6.58		
2,2',3,3',5,5'-Hexachloro	133	7.09	7.07	6.86		
2,2',3,3',5,6-Hexachloro	134	6.91	6.81	6.55		
2,2',3,3',5,6-Hexachloro	134	6.95	6.81			
2,2',3,3',6,6'-Hexachloro	136	7.16	7.12	6.44	5.76	6.81

Table 8.4 cont.

2,2',3,4,4',5-Hexachloro	137	7.33	7.43	7.24	6.83	7.46
2,2',3,4,4',5'-Hexachloro	138	7.29	7.25	7.37	6.83	7.90
2,2',3,4,4',6-Hexachloro	139	6.97	6.93			
2,2',3,4,4',6'-Hexachloro	140	6.96	6.97	6.67		
2,2',3,4,5,5'-Hexachloro	141	7.24	7.19	6.82		
2,2',3,4,5,6-Hexachloro	142	6.99	6.97	6.51		
2,2',3,4,56'-Hexachloro	143	6.99	6.92	6.60		
2,2',3,4,5',6-Hexachloro	144	6.95	6.79	6.67		
2,2',3,4,6,6'-Hexachloro	145	6.88	6.75	6.25		
2,2',3,4',5,6'-Hexachloro	148	6.93	6.87	6.73		
2,2',3,4',5,6'-Hexachloro	148	6.93	6.87	6.73		
2,2',3,4',5',6-Hexachloro	149	6.93	6.86	6.69	6.67	6.70
2,2',3,4',6,6'-Hexachloro	150	6.88	6.75	6.32		
2,2',3,5,5',6-Hexachloro	151	6.77	6.85	6.64		
2,2',3,5,6,6'-Hexachloro	152	6.63	6.51	6.22		
2,2'4,4,5,5'-Hexachloro	153	7.35	7.44	7.10	6.34	7.75
2,2',4,4',5,6'-Hexachloro	154	6.91	6.89	6.76		
2,2',4,4'6,6'-Hexachloro	155	7.12	7.29	6.99	6.41	7.55
2,3,3',4,4',5-Hexacchloro	156	7.50	7.57	7.18		
2,3,3',4,4',6-Hexachloro	158	7.23	7.25	7.02		
2,3,3',4,5,5'-Hexachloro	159	7.32	7.47	7.26		
2,3,3',4,5,6-Hexachloro	160	7.30	7.30	6.93		
2,3,3',4,5',6-Hexachloro	161	7.18	7.10	7.08		
2,3,3',4',5,5'-Hexachloro	162	7.32	7.47	7.24		
2,3,3',4',5,6-Hexachloro	163	7.27	7.25	6.99		
2,3,3',4',5',6-Hexachloro	164	7.22	7.20	7.02		
2,3,3',5,5',6-Hexachloro	165	7.32	7.37	7.08	7.05	7.11
2,3,4,4',5,6-Hexachloro	166	7.28	7.31	6.93		
2,3',4,4',5,5'-Hexachloro	167	7.34	7.50	7.27		
2,3',4,4',5',6-Hexachloro	168	7.18	7.17	7.11		
3,3',4,4',5,5'-Hexachloro	169	7.34	7.41	7.64	7.42	7.87
2,2',3,3',4,4',5-Hetachloro	170	7.78		7.27		
2,2',3,3',4,4',6-Hetachloro	171	7.70		6.90	6.68	7.11
2,2',3,3',4,5,5'-Hetachloro	172	7.74		7.33		
2,2',3,3',4,5,6-Heptachloro	173	7.72		7.02		
2,2',3,3',4,5,6'-Heptachloro	174	7.72		7.11		
2,2',3,3',4,5',6-Heptachloro	175	7.72		7.17		
2,2',3,3',4,6,6'-Heptachloro	176	7.71		6.76		
2,2',3,3',4',5,6-Heptachloro	177	7.66				
2,2',3,3',5,5',6-Heptachloro	178	7.72		7.14		
2,2',3,3',5,6,6'-Heptachloro	179	7.73		7.43	6.73	8.13
2,2',3,4,4',5,5'-Hetachloro	180	7.64		7.36		
2,2',3,4,4',5,6-Heptachloro	181	7.70		7.11		
2,2',3,4,4',5,6'-Heptachloro	182	7.70		7.02		
2,2',3,4,4',5',6-Heptachloro	183	7.70		7.20		
2,2',3,4,4',6,6'-Heptachloro	184	7.64		6.86		
2,2',3,4,5,5',6-Heptachloro	185	7.72	7.93	7.11		
2,2',3,4,5,6,6'-Heptachloro	186	7.66		6.69		

Table 8.4 cont.

2,2',3,4',5,5',6-Heptachloro	187	7.72		7.17		
2,2',3,4',5,6',6-Heptachloro	188	7.66		6.82		
2,3,3',4,4',5,5'-Hexachloro	189	7.72		7.71		
2,3,3',4,4',5,6-Heptachloro	190	7.66		7.46		
2,3,3',4,4',5',6-Heptachloro	191	7.66		7.55		
2,3,3',4,5,5',6-Heptachloro	192	7.68		7.52		
2,3,3',4',5,5',6-Heptachloro	193	7.68		7.52		
2,2',3,3',4,4',5,5'-Octachloro	194	8.61	8.68	8.27	7.67	9.35
2,2',3,3',4,4',5,6-Octachloro	195	8.16		8.41	7.56	9.25
2,2',3,3',4,4',5,6'-Ocachloro	196	8.23		7.65		
2,2',3,3',4,4',6,6'-Octachloro	197	8.15		7.30		
2,2',3,3',4,5,5',6'-Octachloro	198	8.25		7.62		
2,2',3,3',4,5,5',6-Octachloro	199	8.16		7.62		
2,2',3,3',4,5,6,6'-Octachloro	200	8.17	8.16	7.20		
2,2',3,3',4,5',6,6'-Octachloro	201	8.17		7.24	7.21	7.27
2,2',3,3',5,5',6,6'-Octachloro	202	7.99	7.73	7.77	7.11	8.42
2,2',3,4,4',5,5',6-Octachloro	203	8.29		7.65		
2,2',3,4,4',5,6,6'-Octachloro	204	8.15		7.30		
2,3,3',4,4',5,5',6-Octachloro	205	8.15		8.00		
2,2',3,3',4,4',5,5',6-Nonachloro	206	8.92	9.14	8.09		
2 ,2,,3,3',4,4',5,6,6-Nonachloro	207	8.34		7.63	7.52	7.74
2,2',3,3',4,5,5',6,6'Nonachloro	208	8.13	8.16	7.71		
Decachlorobiphenyl	209	8.30	8.27	9.09	8.18	10.00

8.6 Discussion

Many of the persistent, semi-volatile hydrophobic organic chemicals that are of interest are difficult to handle experimentally because they sorbs strongly to surfaces, especially from aqueous solution. Measurements of L_{AW} and Poct are thus difficult to make, and are subject to error, and the reported values often vary considerably, as is apparent from examination of compilations of data.[37,38]

Calculation of L_{OA} from Poct and L_{AW} thus combines these errors and introduces considerable uncertainty. It is also possible that the presence of octanol in the water layer, and, especially, water in the octanol layer, leads to the indirect value of L_{AW} being not the same as the direct value using dry octanol. The possibility of calculating L_{AW} for partition from air to dry octanol is therefore of considerable importance. In this work, such a calculation for all 209 PCBs has been achieved for the first time.

The calculation of log Poct for all 209 PCBs in this work, is not the first such calculation at all, but does seem to be more reliable than any other calculation of log Poct.

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Chapter 9 Calculation and Comparison of Aqueous Solubility for PCBs Using the Obtained Descriptors

9.0 Introduction

Aqueous solubility is a very important molecular property which plays an integral role in many different biological and physical processes. As a property involving water as the solvent, it is important in a diverse array of situations including pharmaceutical, environmental, and industrial applications. The rate and extent of biodegradation are also affected by the aqueous solubility of organic compounds in the environment.[1,2] Obtaining experimental values of aqueous solubility is not a difficult task for compounds that are reasonably soluble, but determination of very low solubilities can be very difficult indeed. There is therefore sample justification for creating methods that can predict this property. Being able to predict the aqueous solubility of compound would greatly assist drug development, because a solubility could be estimated before the compound was synthesized, which would eliminate the need to synthesize many unsuitable compounds. The ability to predict aqueous solubility would also be useful in environmental impact studies, because the solubility could be estimated without handling compounds that are highly toxic, carcinogenic, or undesirable for some other reason. There is no question that the ability to predict the aqueous solubility of compounds is useful. Many different methods have been developed for the estimation of aqueous solubility with varying success and applicability. [3,4] Some recent developments include a neural network model relating aqueous solubility to topological descriptors, [3] the use of mobile order solubility

models [5,6] a clustering approach, [7] group contribution approaches [1,8,9,10] and linear and neural network models based on semi-empirical quantum chemical descriptors. [11,12]

There is not only a correlation of aqueous solubility (Sw) with n-octanol/water partition coefficients (Kow)[13] but also with bioconcentration factors (BCF).[14] Therefore, a prediction of Sw is also useful as regards the prediction of bioconcentration, and also other environmental processes. Prediction of Sw or of log Sw for polychorinated biphenyl (PCBs) would be important, because these compounds have serious ecologically harmful effects and are implicated as carcinogens.[15] For the aqueous solubility of PCBs congeners, it has been found that there is high correlation with various physiochemical properties, including total surface area, molecular volume,[16] boiling point,[17] melting point,[18] third shadow area,[19] polarizability parameter,[20] mobile order of PCBs,[21] connectivity indexes [20,22,23] and the degree of ortho-chlorine substitution in the biphenyl skeleton. [24] Especially, linear solvation energy relationships (LSER), [25] are regarded as being useful in the prediction of partitioning and solubility. In addition, the substitution constant (π) derived from partition coefficients of compounds has also been reported as a useful descriptor to predict log Sw. [26,27]

9.1 Results

This method [28] starts with the general solvation equation, [29]

$$\log SP = c + r R_2 + s \pi_2^H + a \Sigma \alpha_2^H + b \Sigma\beta_2^H + v Vx \qquad (9.1)$$

Here, the dependent variable, log SP, is a property of a series of solutes in a given system, such as log Poct or log Sw, and the independent variables are solute descriptors as

follows, [29] R_2 is an excess molar refraction in units of (cm^3 mol^{-1}) /10, π_2^H is the dipolarity /polarizability, $\Sigma\alpha_2^H$ is the overall or summation hydrogen-bond acidity, $\Sigma\beta_2^H$ is the overall or summation hydrogen-bond basicity, and Vx is the McGowan characteristic volume [30] in units of (cm^3 mol^{-1})/100. There are numerous applications of equation 9.1 to physicochemical properties. [31]

Equation 9.1, has previously been applied to the aqueous solubility of non-electrolytes at 298 K, with Sw in units of mol dm^{-3}. Application of equation 9.1 to a training set of 594 compounds yielded equations 9.2, and 9.3, with sd values of 0.56 and 0.63 log units, respectively; note that fewer compounds were used in equation 9.2, because of lack of melting points (mps).

$$\text{Log Sw} = 0.579 - 0.576R_2 + 0.980\pi_2^H + 3.389\Sigma\beta_2^H + 1.233\Sigma\alpha_2^H + 3.389\Sigma\beta_2^H - 4.079\,V_x - 0.010(mp-25)$$

$$n = 411, \quad sd = 0.569, \quad r^2 = 0.915, \quad F = 724 \quad AAE = 0.389 \qquad (9.2)$$

$$\log Sw = 0.849 - 1.061R_2 + 0.851\pi_2^H + 0.646\,\Sigma\alpha_2^H + 3.279\,\Sigma\beta_2^H - 4.050\,Vx$$

$$n = 594, \quad sd = 0.630, \quad r^2 = 0.895, \quad F = 1004, \quad AAE = 0.470 \qquad (9.3)$$

Here AAE = Σ(log Sw obs – log Sw calc)/ n

It is somewhat surprising that equation 9.1 has led to the reasonable equations 9.2 and 9.3, because 9.1 was not set up at all to correlate quantities such as log Sw. There is a fundamental difference between processes such as water-solvent partition, to which equation 9.1 has previously been applied, and solubility in water which involves the pure liquid or solid compound.

Equation 9.1 could be amended to incorporate terms that reflect interactions in the pure liquid or solid. A term in $\Sigma\alpha_2^H * \Sigma\beta_2^H$ will deal with hydrogen-bond interactions between acid and basic sites in the solid or liquid, and a term in $\pi_2^H * \pi_2^H$ with dipole/dipole interactions. The best equations that were constructed on these lines are,

$$\log Sw = 0.403 - 0.484R_2 + 0.814\pi_2^H + 4.018S\beta_2^H - 1.130\Sigma\alpha_2^H * \Sigma\beta_2^H - 4.067V_x - 0.010(mp-25)$$

$$n = 411, \quad sd = 0.496, \quad r^2 = 0.934, \quad F = 819, \quad AAE = 0.245 \qquad (9.4)$$

$$\log Sw = 0.510 - 1.020R_2 + 0.813\pi_2^H + 2.124\Sigma\alpha_2^H + 4.187\Sigma\beta_2^H - 3.337\Sigma\alpha_2^H * \Sigma\beta_2^H - 3.986V_x$$

$$n = 594, \quad sd = 0.562, \quad r^2 = 0.918, \quad F = 1089, \quad AAE = 0.409 \qquad (9.5)$$

Considering these equations, those with a cross-term are significantly better and equation (9.5) is the best because it cover a wide range of compound type. On incorporating more solutes, the final equation 9.6 was obtained.

13.3.2 The Water-Bromobenzene system

The data for the Water-Bromobenzene system are given in Table, 13.4 and were entered into the standard multiple linear regression program.

Table (13.4) Solutes, their descriptors and values of log P(obs) and log P(calc) for the Water-Bromobenzene system

Compound Name	R_2	π_2^H	α_2^H	β_2^H	V_x	Log P obs	Log P calc
Butan-1-ol	0.224	0.420	0.370	0.480	0.730900	-0.470	-0.251
4-Chlorophenol	0.915	1.080	0.670	0.200	0.897500	0.960	0.843
2-Naphthol	1.520	1.080	0.610	0.400	1.144100	1.710	1.547
2-Ethoxyethanol	0.237	0.500	0.300	0.830	0.789600	-1.300	-1.340
Methyl 2-hydroxybenzoate	0.850	0.840	0.040	0.460	1.131300	2.630	2.934
Propyl acetate	0.092	0.600	0.000	0.450	0.887500	1.520	1.739
2-Methoxyphenol	0.837	0.910	0.220	0.520	0.974700	1.390	1.309
2-Fluorophenol	0.660	0.690	0.610	0.260	0.792800	0.450	0.312
Pentan-1-ol	0.219	0.420	0.370	0.480	0.871800	0.340	0.388
2-Iodophenol	1.360	1.000	0.400	0.350	1.033300	1.870	1.936
Hexan-1-ol	0.210	0.420	0.370	0.480	1.012700	1.140	1.026
Ethanol	0.246	0.420	0.370	0.480	0.449100	-1.550	-1.525
2-Butoxyethanol	0.201	0.500	0.300	0.830	1.071400	-0.070	-0.072
Aniline	0.955	0.960	0.260	0.410	0.816200	0.860	0.982
2-Bromophenol	1.037	0.900	0.350	0.310	0.950100	1.660	1.793
Methyl acetate	0.142	0.640	0.000	0.450	0.605700	0.400	0.464
3-Nitrophenol	1.050	1.570	0.790	0.230	0.949300	0.400	0.436
Phenol	0.805	0.890	0.600	0.300	0.775100	0.180	0.086
Propylamine	0.225	0.350	0.160	0.610	0.631100	-0.600	-0.552

$$\text{Log Sw} = a_0 + a_1 .M + a_2 .SAS + a_3 .\Delta H_f + a_4 . (-I) + a_5 . A + a_6 . \mu \qquad (9.8)$$

where:

M is the molecular weight;

SAS is the solvent accessible surface area;

ΔH_f is the heat of formation;

I is the ionization potential;

A is the electron affinity;

μ is dipole moment;

and a_i ($i = 0 \sim 6$) are correlation coefficients.

Both I and μ showed low correlation with the observed log Sw, and were therefore discarded. A multlinear regression analysis was again performed with four descriptors to yield,

$$\text{Log Sw} = 20.092 + 0.01473.M - 0.21764 .SAS - 0.03895 .\Delta H_f + 0.34852 .A$$

$$n = 136, \quad r^2 = 0.960, \quad sd = 0.227, \quad F = 0.816 \qquad (9.9)$$

In spite of removing two parameters, the decrease in all factors (R_2, s, and F) was small. Therefore, it seems that M, SAS, ΔH_f, and A can be regarded as essential descriptors to predict the observed log Sw. Patil found that this multilinear regression analysis, coupled

with the descriptors of M, SAS, ΔH_f and A, was an excellent way to predict the log Sw of 136 PCBs congeners. However, it should be noted that equation 9.9 is not a prediction at all, but is a correlation of already known log Sw values.

A comparison of the calculated values in this work using equation 9.7, with the experimental data obtained from the literature by Patil , and the correlated values based on equation 9.9 was therefore made. The sd between our values and the experimental values is 0.173 and between our values and the correlated ones is 0.171, which are more or less the same, as shown in Table 9.1.

Table 9.1. Comparison of our calc. Log S (a), predicted log S (b), with exp.log S (c) and the values of the sd.

Name	IUPAC	R_2	π_2^H	β_2^H	Vx	Calc.log S(a)	Calc.log S(b)	Obs.log S(c)	Sd (a-c)	Sd (b-c)
3-Monochlorobiphenyl	2	1.51	1.00	0.21	1.447	-5.10625	-5.0762	-5.39	0.080515	0.098470
4-Monochloro	3	1.50	1.00	0.20	1.447	-5.13859	-5.0361	-5.33	0.036638	0.086377
2,2'-Dichloro	4	1.60	1.24	0.19	1.569	-5.58274	-5.5390	-5.72	0.018839	0.032761
2,3-Dichloro	5	1.63	1.25	0.22	1.569	-5.47801	-5.5645	-5.35	0.016387	0.046010
2,3'-Dichloro	6	1.63	1.25	0.22	1.569	-5.47801	-5.6937	-5.26	0.047530	0.188096
2,4-Dichloro	7	1.62	1.15	0.18	1.569	-5.71459	-5.7971	-5.56	0.023899	0.056216
2,4'-Dichloro	8	1.62	1.18	0.19	1.569	-5.64908	-5.6393	-5.46	0.035752	0.032148
3,3'-Dichloro	11	1.66	1.13	0.17	1.569	-5.81255	-5.7762	-6.45	0.406339	0.454006
3,4-Dichloro	12	1.65	1.00	0.17	1.569	-5.90274	-5.6095	-6.39	0.237419	0.609180
3,4'-Dichloro	13	1.65	1.00	0.17	1.569	-5.90274	-5.7354	-6.40	0.247265	0.441693
4,4'-Dichloro	15	1.64	1.00	0.14	1.569	-6.01984	-5.7021	-6.37	0.122610	0.446090
2,2',3-Trichloro	16	1.75	1.31	0.17	1.691	-6.25055	-6.1252	-6.10	0.022664	0.000635
2,2',4-Trichloro	17	1.74	1.28	0.15	1.691	-6.34840	-6.3661	-6.49	0.020051	0.015351
2,2',5-Trichloro	18	1.75	1.31	0.16	1.691	-6.29293	-6.3321	-6.35	0.003257	0.000320
2,2',6-Trichloro	19	1.72	1.37	0.17	1.691	-6.17417	-5.9300	-5.90	0.075168	0.000900
2,3,4-Trichloro	21	1.77	1.32	0.17	1.691	-6.26292	-6.2698	-6.18	0.006875	0.008064
2,3,4'-Tirchloro	22	1.77	1.33	0.17	1.691	-6.25521	-6.1968	-5.80	0.207213	0.157450
2,3,6-Tirchloro	24	1.75	1.30	0.14	1.691	-6.38540	-6.4478	-6.49	0.010942	0.001781
2,3',4-Tirchloro	25	1.77	1.33	0.16	1.691	-6.29759	-6.4900	-6.11	0.035189	0.144400
2,3',5-Tirchloro	26	1.78	1.33	0.16	1.691	-6.30763	-6.4648	-6.14	0.028099	0.105495
2,4,4'-Tirchloro	28	1.76	1.32	0.15	1.691	-6.33764	-6.4256	-6.22	0.013838	0.042271
2,4',5-Tirchloro	31	1.77	1.32	0.16	1.691	-6.30530	-6.4316	-6.18	0.015699	0.063303
2,4',6-Tirchloro	32	1.74	1.32	0.16	1.691	-6.27518	-6.2607	-6.21	0.004248	0.002570

Table 9.1 continues

2,3',4'-Tirchloro	33	1.77	1.33	0.16	1.691	-6.29759	-6.2543	-6.21	0.007671	0.001962
2,3',5'-Tirchloro	34	1.78	1.30	0.15	1.691	-6.37314	-6.5126	-6.30	0.005349	0.045199
2,2',3,3'-Tetrachloro	40	1.90	1.44	0.13	1.814	-6.96084	-6.5924	-6.83	0.017119	0.056454
2,2',3,4-Tetrachloro	41	1.89	1.44	0.13	1.814	-6.95080	-6.8669	-7.00	0.002421	0.017716
2,2',3,5'-Tetrachloro	44	1.90	1.43	0.13	1.814	-6.96855	-6.8383	-6.91	0.003428	0.005141
2,2',3,6-Tetrachloro	45	1.87	1.54	0.17	1.814	-6.68410	-6.6696	-6.30	0.147531	0.136604
2,2',3,6-Tetrachloro	46	1.87	1.54	0.17	1.814	-6.68410	-6.4470	-6.30	0.147531	0.021609
2,2',4,4'-Tetrachloro	47	1.88	1.40	0.11	1.814	-7.05636	-7.0606	-7.23	0.030152	0.028696
2,2'4,5-Tetrachloro	48	1.89	1.50	0.17	1.814	-6.73502	-7.0886	-6.86	0.015621	0.052258
2,2',4,5'-Tetrachloro	49	1.89	1.40	0.11	1.814	-7.06640	-7.0226	-7.12	0.002873	0.009487
2,2',4,6-Tetrachloro	50	1.86	1.50	0.14	1.814	-6.83204	-6.9025	-6.94	0.011656	0.001406
2,2'4,6'-Tetrachloro	51	1.86	1.54	0.16	1.814	-6.71644	-6.7133	-6.65	0.004414	0.004007
2,2',5,5'-Tetrachloro	52	1.90	1.40	0.11	1.814	-7.07644	-7.0533	-7.00	0.005843	0.002841
2,2',5,6'-Tetrachloro	53	1.87	1.50	0.15	1.814	-6.79970	-6.6636	-6.65	0.022409	0.000185
2,2'6,6'-Tetrachloro	54	1.84	1.65	0.18	1.814	-6.52679	-6.2167	-6.20	0.106790	0.000279
2,3,3',4-Tetrachloro	55	1.92	1.50	0.15	1.814	-6.84990	-6.9593	-6.77	0.006384	0.035834
2,3,4,4'-Tetrachloro	60	1.91	1.42	0.15	1.814	-6.90154	-6.9017	-6.86	0.001725	0.001739
2,3,4',5-Tetrachloro	63	1.92	1.50	0.15	1.814	-6.84990	-7.0962	-6.77	0.006384	0.106406
2,3,4',6-Tetachloro	64	1.89	1.42	0.14	1.814	-6.92384	-6.9963	-7.02	0.009247	0.000562
2,3,5,6Tetrachloro	65	1.89	1.40	0.10	1.814	-7.10878	-7.2527	-7.25	0.019944	0.000006
2,3',4,4'-Tetrachloro	66	1.91	1.50	0.15	1.814	-6.83986	-7.0040	-6.63	0.044040	0.139876
2,3',4,5-Tetrachloto	67	1.92	1.40	0.10	1.814	-7.13890	-7.1838	-7.13	7.92E-05	0.002894
2,3'4,6-Tetrachloro	69	1.89	1.40	0.10	1.814	-7.10878	-7.3137	-7.26	0.022868	0.002884
2,3',4'5-Tetrachloro	70	1.89	1.50	0.15	1.814	-6.81978	-6.9797	-6.69	0.016842	0.083926
2,3',4',6-Tetrachloro	71	1.89	1.40	0.11	1.814	-7.06640	-6.9054	-7.02	0.002153	0.013133
2,4,4',5-Tetrachloro	74	1.91	1.50	0.15	1.814	-6.83986	-7.1181	-6.77	0.004880	0.121174
2,4,4',6-Tetrachloro	75	1.88	1.40	0.09	1.814	-7.14112	-7.2531	-7.26	0.014133	0.000045
2,3',4',5-Tetrachloro	76	1.91	1.52	0.15	1.814	-6.82444	-7.0365	-6.71	0.013096	0.106602
2,2',3,3'6-Pentachloro	84	2.02	1.75	0.17	1.936	-7.1592	-7.1384	-6.78	0.143794	0.128451

Table 9.1 continues

2,2',3,4,4'-Pentachloro	85	2.03	1.62	0.09	1.936	-7.60851	-7.5353	-7.62	0.000132	0.007174
2,2',3,4,5-Pentachloro	86	2.04	1.62	0.08	1.936	-7.66093	-7.7054	-7.87	0.043709	0.027093
2,2',3,4,5'-Pentachloro	87	2.04	1.62	0.08	1.936	-7.66093	-7.5016	-7.66	8.69E-07	0.025091
2,2',3,4,6-Pentachloro	88	2.01	1.62	0.08	1.936	-7.63081	-7.5142	-7.92	0.083630	0.164674
2,2',3,4,6-Pentachloro	89	2.01	1.75	0.17	1.936	-7.14916	-7.1926	-6.78	0.136281	0.170239
2,2',3,4',5-Pentachloro	90	2.04	1.62	0.08	1.936	-7.66093	-7.7204	-7.82	0.025303	0.009920
2,2',3,4',6-Pentachloro	91	2.01	1.74	0.14	1.936	-7.28401	-7.3246	-7.17	0.012999	0.023901
2,2',3,5,5'-Pentachloro	92	2.05	1.60	0.08	1.936	-7.68639	-7.6694	-7.82	0.017851	0.022680
2,2',3,5.6-Pentachloro	93	2.02	1.70	0.12	1.936	-7.40965	-7.4553	-7.40	9.32E-05	0.003058
2,2',3,5',6-Pentachloro	95	2.02	1.70	0.17	1.936	-7.19775	-7.3056	-7.19	6.01E-05	0.013363
2,2',3,4',5'-Pentachloro	97	2.04	1.58	0.09	1.936	-7.64939	-7.5735	-7.76	0.012234	0.034782
2,2',3,4',6'-Pentachloro	98	2.01	1.70	0.10	1.936	-7.48437	-7.4112	-7.40	0.007119	0.000125
2,2',4,4',5-Pentachloro	99	2.03	1.62	0.08	1.936	-7.65089	-7.7769	-7.95	0.089466	0.029964
2,2',4,4',6-Pentachloro	100	2.00	1.70	0.10	1.936	-7.47433	-7.5901	-7.66	0.034473	0.004886
2,2',4'5,6-Pentachloro	103	2.01	1.70	0.10	1.936	-7.48437	-7.5633	-7.47	0.000207	0.008705
2,3,3',4,4'-Pentachloro	105	2.04	1.70	0.10	1.936	-7.51449	-7.4775	-7.52	3.03E-05	0.001806
2,3,3',4,5-Pentachloro	106	2.07	1.70	0.08	1.936	-7.62937	-7.8317	-7.68	0.002563	0.023013
2,3,3',4,6-Pentachloro	110	2.04	1.65	0.10	1.936	-7.55304	-7.5113	-7.65	0.009401	0.019238
2,3,3',5,6-Pentachloro	112	2.05	1.65	0.09	1.936	-7.60546	-7.8593	-7.76	0.023882	0.009860
2,3,3',5',6-Pentachloro	113	2.05	1.65	0.09	1.936	-7.60546	-7.7172	-7.95	0.118706	0.054196
2,3,4,4',5-Pentachloro	114	2.06	1.58	0.08	1.936	-7.71185	-7.7500	-7.50	0.044881	0.062500
2,3,4,4',6-Pentachloro	115	2.03	1.65	0.08	1.936	-7.62776	-7.8701	-7.96	0.110382	0.008082
2,3,4',5,6-Pentachloro	117	2.04	1.58	0.08	1.936	-7.69177	-7.8021	-7.88	0.035430	0.006068
2,3',4,4',5-Pentachloro	118	2.06	1.58	0.08	1.936	-7.71185	-7.7000	-7.33	0.145811	0.136900
2,3',4,4',5-Pentachloro	119	2.03	1.63	0.08	1.936	-7.64318	-7.7753	-7.91	0.071192	0.018144
2,3',4,5',6-Pentachloro	121	2.04	1.58	0.07	1.936	-7.73415	-8.0149	-7.92	0.034539	0.009006
2,3,4,4',5'-Pentachloro	123	2.09	1.60	0.10	1.936	-7.64179	-7.4689	-7.42	0.049192	0.002391
2,2',3,3',4,4'-Hexachloro	128	2.18	1.65	0.04	2.059	-8.43828	-8.0402	-8.33	0.011725	0.083984
2,2',3,3',4,5-Hexachloro	129	2.19	1.65	0.04	2.059	-8.44832	-8.1899	-8.42	0.000802	0.052946

Table 9.1 continues

2,2',3,3',4,6-Hexachloro	131	2.16	1.77	0.13	2.059	-7.94426	-8.0103	-8.48	0.287014	0.220618
2,2',3,3',4,6'-Hexachloro	132	2.16	1.77	0.13	2.059	-7.94426	-7.7413	-7.65	0.086591	0.008336
2,2',3,3',5,6-Hexachloro	134	2.17	1.78	0.13	2.059	-7.94659	-7.9141	-7.65	0.087967	0.069749
2,2',3,3'5,6'-Hexachloro	135	2.17	1.78	0.13	2.059	-7.94659	-7.9431	-7.82	0.015523	0.014665
2,2,3,4,4',5-Hexachloro	137	2.18	1.60	0.04	2.059	-8.47683	-8.4062	-8.52	0.001863	0.012950
2,2,3,4,4',5'-Hexachloro	138	2.18	1.65	0.06	2.059	-8.35352	-8.1728	-8.38	0.000701	0.042932
2,2,3,4,4',6'-Hexachloro	140	2.18	1.76	0.10	2.059	-8.09919	-8.0438	-8.24	0.019827	0.038494
2,2',3,4,5,5'-Hexachloro	141	2.19	1.68	0.08	2.059	-8.25567	-8.3499	-8.42	0.027003	0.004914
2,2',3,4,5,6'-Hexachloro	143	2.16	1.75	0.11	2.059	-8.04444	-8.0651	-8.13	0.007320	0.004212
2,2,3,4,5',6-Hexachloro	144	2.16	1.78	0.13	2.059	-7.93655	-8.1667	-8.01	0.005394	0.024555
2,2',3,4',5,5'-Hexachloro	146	2.19	1.65	0.04	2.059	-8.44832	-8.3538	-8.58	0.017339	0.051166
2,2',3,4',5',6-Hexachloro	149	2.16	1.80	0.12	2.059	-7.96351	-8.0144	-7.94	0.000553	0.005535
2,2',3,5,5',6-Hexachloro	151	2.17	1.78	0.13	2.059	-7.94659	-8.1229	-7.93	0.000275	0.037210
2,2',4,4',5,5'-Hexachloro	153	2.18	1.60	0.04	2.059	-8.47683	-8.4047	-8.49	0.000173	0.007276
2,2',4,4',5,5'-Hexachloro	154	2.15	1.77	0.12	2.059	-7.9766	-8.2354	-8.12	0.020563	0.013317
2,2',4,4',6,6'-Hexachloro	155	2.12	1.65	0.05	2.059	-8.33566	-8.1089	-8.12	0.046511	0.000123
2,3,3',4,4',5-Hexachloro	156	2.21	1.60	0.06	2.059	-8.42219	-8.3394	-8.31	0.012587	0.000864
2,3,3',4,4',6-Hexachloro	158	2.18	1.65	0.05	2.059	-8.3959	-8.4114	-8.48	0.007072	0.004706
2,3,3',4'5,6Hexachloro	163	2.19	1.65	0.05	2.059	-8.40594	-8.3483	-8.48	0.005484	0.017345
2,3,3',4',5',6-Hexachloro	164	2.19	1.67	0.06	2.059	-8.34814	-8.2239	-8.27	0.006106	0.002125
2,3',4,4',5,5'-Hexachloro	167	2.21	1.65	0.06	2.059	-8.38364	-8.4216	-8.21	0.030152	0.044775
3,3',4,4',5,5'-Hexachloro	169	2.21	1.60	0.04	2.059	-8.50695	-8.3802	-8.85	0.117681	0.220712
2,2',3,3'4,4',5-Hexachloro	170	2.33	1.87	0.00	2.181	-9.07520	-8.8439	-8.90	0.030694	0.003147
2,2',3,3',4,5,5'-Heptachloro	172	2.34	1.85	0.00	2.181	-9.10066	-8.9644	-9.10	4.32E-07	0.018387
2,2',3,3',4,5,6'-Hexachloro	174	2.31	1.90	0.06	2.181	-8.77771	-8.6284	-8.59	0.035234	0.001475
2,2',3,3',4,5',6-Hexachloro	175	2.31	1.90	0.06	2.181	-8.77771	-8.7943	-8.68	0.009547	0.013064
2,2',3,3',4,6,6'-Hexachloro	176	2.31	1.95	0.12	2.181	-8.48488	-8.2893	-8.15	0.112143	0.019404
2,2',3,3',4,5',6'-Hexachloro	177	2.28	1.90	0.12	2.181	-8.49331	-8.5210	-8.42	0.005374	0.010201
2,2'3,3',5,5',6-Hexachloro	178	2.31	1.90	0.12	2.181	-8.52343	-8.6962	-8.59	0.004432	0.011278

Table 9.1 continues

2,2',3,3',5,6,6'-Hexachloro	179	2.32	1.95	0.12	2.181	-8.49492	-8.2248	-7.94	0.307933	0.081111
2,2',3,4,4',5,5'-Hexachloro	180	2.29	1.84	0.00	2.181	-9.05817	-8.9934	-9.10	0.001750	0.011364
2,2',3,4,4',5,6-Hexachloro	181	2.30	1.90	0.04	2.181	-8.85243	-8.8593	-8.97	0.013823	0.012254
2,2',3,4,4',5,6'-Hexachloro	182	2.30	1.90	0.06	2.181	-8.76767	-8.8672	-8.68	0.007686	0.035044
2,2',3,44',5',6-Heptachloro	183	2.30	1.90	0.04	2.181	-8.85243	-8.8050	-8.85	0.000106	0.002025
2,2',3,4,5,5',6-Heptachloro	185	2.31	1.90	0.04	2.181	-8.86247	-8.8208	-8.75	0.012649	0.005013
2,2',3,4',5,6,6'-Heptachloro	188	2.28	1.95	0.12	2.181	-8.45476	-8.4765	-8.49	0.001242	0.000182
2,3,3',4,4',5,5'-Heptachloro	189	2.36	1.87	0	2.181	-9.10532	-9.1040	-8.72	0.148469	0.147456
2,3,3',4,4',5,6-Heptachloro	190	2.33	1.89	0	2.181	-9.05978	-9.0829	-8.9.0	0.012306	0.001238
2,3,3',4,4',5',6-Heptachloro	191	2.33	1.85	0	2.181	-9.09062	-9.0920	-9.10	0.000005	6.000050
2,3,3',4,5,5',6-Heptachloro	192	2.34	1.85	0	2.181	-9.10066	-9.3078	-9.10	0.000100	0.043181
2,3,3',4',5,5',6-Heptachloro	193	2.34	1.85	0	2.181	-9.10066	-9.0200	-9.10	0.000040	0.006400
2,2',3,3',4,4',5,5'-Octachloro	194	2.48	1.75	0	2.303	-9.80473	-9.5810	-9.70	0.010969	0.014161
2,2',3,3',4,4',5,6-Octachloro	195	2.45	1.99	0	2.303	-9.58957	-9.3459	-9.29	0.089743	0.003125
2,2',3,3',4,4',5,6'-Octachloro	196	2.45	1.99	0	2.303	-9.58957	-9.4226	-9.42	0.028754	0.000076
2,2',3,3',4,4'6,6'-Octachloro	197	2.42	2.11	0	2.303	-9.46693	-9.1058	-9.10	0.134638	0.000030
2,2',3,3',4,5,5',6-Octachloro	198	2.46	1.99	0	2.303	-9.59961	-9.4485	-9.42	0.032260	0.000812
2,2',3,3',4,5,6,6'-Octachloro	199	2.46	2.20	0	2.303	-9.43770	-8.9608	-9.10	0.114042	0.019377
2,2',3,3',4,5',6,6'-Octachloro	200	2.43	2.20	0	2.303	-9.40758	-8.9550	-9.20	0.04309	0.060025
2,2',3,3',4,5,5',6-Octachloro	201	2.43	1.99	0	2.303	-9.56949	-9.2900	-9.29	0.078115	0
2,2',3,4,4',5,5',6-Octachloro	203	2.48	2.00	0	2.303	-9.61198	-9.4739	-9.5	0.01254	0.000681
2,2'3,4,4',5,6,6'-Octachloro	204	2.52	2.10	0	2.303	-9.57504	-9.2492	-9.48	0.009033	0.053269
2,3,3',4,4',5,5',6-Octachloro	205	2.48	1.99	0	2.303	-9.61969	-9.7792	-9.70	0.00645	0.006273
2,2',3,3',4,4',5,5',6-Nanochloro	206	2.60	2.11	0	2.426	-10.1381	-10.0286	-10.18	0.00176	0.022922
2,2',3,3',4,4',5,6,6'-Nanochlorobiphenyl	207	2.57	2.13	0	2.426	-10.0925	-9.7531	-10.07	0.000507	0.100426
									3.999493	3.899574

		0.029847	0.029101
	SD:	0.172763	0.17059

(a) Our calc. Log S using eqn. (9.7)
(b) Predicted log S based on eqn. (9.9)
(c) Exp. Log S data obtained from the literature by Patil [32]
Sd (a-c) our calc. Log S- exp. Log S
Sd (b-c) predicted log S – exp. Log S

The next step was to calculate log Sw for the rest of the 209 PCBs, but the sd between our values and those calculated by Patil, was about the same as that obtained before. Hence equation 9.7 is a good equation for the prediction of log Sw for the PCBs, possibly because the term $\Sigma\alpha_2^H$ is zero .

The second calculation that was carried out, uses equation 9.4 to calculate log Sw. Since the term in $\Sigma\alpha_2^H$ is zero, equation 9.4 becomes

$$\log Sw = 0.403 - 0.484\ R_2 + 4.018\ \Sigma\beta_2^H - 4.067\ Vx - 0.010\ (mp - 25) \qquad (9.10)$$

Where mp is the melting point for PCBs. [33] Values calculated through equation 9.10 were compared with the experimental and correlated values, as shown in Table 9.2. The sd value between those calculated through equation 9.10 and the experimental ones is 0.159 and between our calculated and Patil's correlated values is 0.171, which are nearly the same. Thus equation 9.10 seems a little better than equation 9.7 in that the sd between calculated and experimental is a little less. However, equation 9.10 requires the use of an experimental mp for the PCBs.

Table 9.2. Comparison of our calc. Log S (a), predicted log S(b), exp. Log S(c) and with the values of sd

Name	IUPAC	R2	π2	β2	Vx	mp	Calc.logS(a)	Calc.logS(b)	Exp.logS (c)	Sd (a-c)	Sd (b-c)
3-Monochlorobiphenyl	2	1.51	1.00	0.21	1.447	22	-6.24257	-5.0762	-5.39	0.726874	0.098470
4-Monochloro	3	1.50	1.00	0.20	1.447	25	-6.19755	-5.0361	-5.33	0.752641	0.086377
2,2'-Dichloro	4	1.60	1.24	0.19	1.569	77.9	-7.03558	-5.5390	-5.72	1.730759	0.032761
2,3-Dichloro	5	1.63	1.25	0.22	1.569		-6.38350	-5.5645	-5.35	1.068128	0.046010
2,3'-Dichloro	6	1.63	1.25	0.22	1.569		-6.38350	-5.6937	-5.26	1.262259	0.188096
2,4-Dichloro	7	1.62	1.15	0.18	1.569	24.4	-6.54334	-5.7971	-5.56	0.966963	0.056216
2,4'-Dichloro	8	1.62	1.18	0.19	1.569	43	-6.74510	-5.6393	-5.46	1.651490	0.032148
3,3'-Dichloro	11	1.66	1.13	0.17	1.569	29	-6.58480	-5.7762	-6.45	0.018172	0.454006
3,4-Dichloro	12	1.65	1.00	0.17	1.569	50	-6.89578	-5.6095	-6.39	0.255816	0.609180
3,4'-Dichloro	13	1.65	1.00	0.17	1.569	50	-6.39578	-5.7354	-6.40	0.000018	0.441693
4,4'-Dichloro	15	1.64	1.00	0.14	1.569	149	-7.76040	-5.7021	-6.37	1.933221	0.446090
2,2',3-Trichloro	16	1.75	1.31	0.17	1.691	28	-6.96802	-6.1252	-6.10	0.753454	0.000635
2,2',4-Trichloro	17	1.74	1.28	0.15	1.691		-6.62724	-6.3661	-6.49	0.018834	0.015351
2,2',5-Trichloro	18	1.75	1.31	0.16	1.691	44	-7.08784	-6.3321	-6.35	0.544403	0.000320
2,2',6-Trichloro	19	1.72	1.37	0.17	1.691		-6.62466	-5.9300	-5.90	0.525128	0.000900
2,3,4-Trichloro	21	1.77	1.32	0.17	1.691	60	-6.68956	-6.2698	-6.18	0.259648	0.008064
2,3,4'-Tirchloro	22	1.77	1.33	0.17	1.691	73	-7.41142	-6.1968	-5.80	2.596665	0.157450
2,3,6-Tirchloro	24	1.75	1.30	0.14	1.691	73	-6.57562	-6.4478	-6.49	0.007330	0.001781
2,3',4-Tirchloro	25	1.77	1.33	0.16	1.691	70	-6.64124	-6.4900	-6.11	0.282213	0.144400
2,3',5-Tirchloro	26	1.78	1.33	0.16	1.691	41	-6.64608	-6.4648	-6.14	0.256114	0.105495
2,4,4'-Tirchloro	28	1.76	1.32	0.15	1.691	57	-7.17436	-6.4256	-6.22	0.910797	0.042271
2,4',5-Tirchloro	31	1.77	1.32	0.16	1.691	67	-7.31938	-6.4316	-6.18	1.298180	0.063303
2,4',6-Tirchloro	32	1.74	1.32	0.16	1.691		-6.63486	-6.2607	-6.21	0.180503	0.002570
2,3',4'-Tirchloro	33	1.77	1.33	0.16	1.691	60	-7.24124	-6.2543	-6.21	1.063450	0.001962
2,3',5'-Tirchloro	34	1.78	1.30	0.15	1.691		-6.63032	-6.5126	-6.30	0.109109	0.045199
2,2',3,3'-Tetrachloro	40	1.90	1.44	0.13	1.814	21	-7.20432	-6.5924	-6.83	0.140114	0.056454

Table 9.2 continues

2,2',3,4-Tetrachloro	41	1.89	1.44	0.13	1.814		-6.98948	-6.8669	-7.00	0.000111	0.017716
2,2',3,5'-Tetrachloro	44	1.90	1.43	0.13	1.814	47	-7.47246	-6.8383	-6.91	0.316359	0.005141
2,2',3,6-Tetrachloro	45	1.87	1.54	0.17	1.814		-7.05912	-6.6696	-6.30	0.576260	0.136604
2,2',3,6-Tetrachloro	46	1.87	1.54	0.17	1.814		-7.05912	-6.4470	-6.30	0.576260	0.021609
2,2',4,4'-Tetrachloro	47	1.88	1.40	0.11	1.814	83	-7.76684	-7.0606	-7.23	0.288195	0.028696
2,2'4,5-Tetrachloro	48	1.89	1.50	0.17	1.814	66	-7.76136	-7.0886	-6.86	0.812446	0.052258
2,2',4,5'-Tetrachloro	49	1.89	1.40	0.11	1.814	64	-7.58168	-7.0226	-7.12	0.213147	0.009487
2,2',4,6-Tetrachloro	50	1.86	1.50	0.14	1.814		-6.96630	-6.9025	-6.94	0.000692	0.001406
2,2'4,6'-Tetrachloro	51	1.86	1.54	0.16	1.814		-7.01410	-6.7133	-6.65	0.132567	0.004007
2,2',5,5'-Tetrachloro	52	1.90	1.40	0.11	1.814		-6.94652	-7.0533	-7.00	0.002860	0.002841
2,2',5,6'-Tetrachloro	53	1.87	1.50	0.15	1.814		-7.01132	-6.6636	-6.65	0.130551	0.000185
2,2'6,6'-Tetrachloro	54	1.84	1.65	0.18	1.814		-6.99524	-6.2167	-6.20	0.632403	0.000279
2,3,3',4-Tetrachloro	55	1.92	1.50	0.15	1.814		-7.03552	-6.9593	-6.77	0.070500	0.035834
2,3,4,4'-Tetrachloro	60	1.91	1.42	0.15	1.814	142	-8.51580	-6.9017	-6.86	2.741667	0.001739
2,3,4',5-Tetrachloro	63	1.92	1.50	0.15	1.814	88	-7.91552	-7.0962	-6.77	1.312211	0.106406
2,3,4',6-Tetachloro	64	1.89	1.42	0.14	1.814	87	-7.91594	-6.9963	-7.02	0.802705	0.000562
2,3,5,6Tetrachloro	65	1.89	1.40	0.10	1.814	76	-7.66150	-7.2527	-7.25	0.169331	0.000007
2,3',4,4'-Tetrachloro	66	1.91	1.50	0.15	1.814	124	-8.27068	-7.0040	-6.63	2.691824	0.139876
2,3',4,5-Tetrachloto	67	1.92	1.40	0.10	1.814	62	-7.53602	-7.1838	-7.13	0.164851	0.002894
2,3'4,6-Tetrachloro	69	1.89	1.40	0.10	1.814	52	-7.42150	-7.3137	-7.26	0.026082	0.002884
2,3',4'5-Tetrachloro	70	1.89	1.50	0.15	1.814	104	-8.06100	-6.9797	-6.69	1.879636	0.083926
2,3',4',6-Tetrachloro	71	1.89	1.40	0.11	1.814	36	-7.30168	-6.9054	-7.02	0.079342	0.013133
2,4,4',5-Tetrachloro	74	1.91	1.50	0.15	1.814	127	-8.30068	-7.1181	-6.77	2.342975	0.121174
2,4,4',6-Tetrachloro	75	1.88	1.40	0.09	1.814	62	-7.47648	-7.2531	-7.26	0.046863	0.000048
2,3',4',5-Tetrachloro	76	1.91	1.52	0.15	1.814	134	-8.35440	-7.0365	-6.71	2.704045	0.106602
2,2',3,3'6-Pentachloro	84	2.02	1.75	0.17	1.936	109	-8.54695	-7.1384	-6.78	3.122119	0.128451
2,2',3,4,4'-Pentachloro	85	2.03	1.62	0.09	1.936	47	-7.71617	-7.5353	-7.62	0.009249	0.007174
2,2',3,4,5-Pentachloro	86	2.04	1.62	0.08	1.936	85	-8.06083	-7.7054	-7.87	0.036417	0.027093
2,2',3,4,5'-Pentachloro	87	2.04	1.62	0.08	1.936	110	-8.31083	-7.5016	-7.66	0.423582	0.025091

Table 9.2 continues

2,2',3,4,6-Pentachloro	88	2.01	1.62	0.08	1.936	66	-7.85631	-7.5142	-7.92	0.004056	0.164674
2,2',3,4,6-Pentachloro	89	2.01	1.75	0.17	1.936	85	-8.30211	-7.1926	-6.78	2.316825	0.170239
2,2',3,4',5-Pentachloro	90	2.04	1.62	0.08	1.936	51	-7.72083	-7.7204	-7.82	0.009834	0.009920
2,2',3,4',6-Pentachloro	91	2.01	1.74	0.14	1.936	62	-7.95971	-7.3246	-7.17	0.623645	0.023901
2,2',3,5,5'-Pentachloro	92	2.05	1.60	0.08	1.936	60	-7.83195	-7.6694	-7.82	0.000143	0.022680
2,2',3,5.6-Pentachloro	93	2.02	1.70	0.12	1.936	96	-8.25675	-7.4553	-7.40	0.734024	0.003058
2,2',3,5',6-Pentachloro	95	2.02	1.70	0.17	1.936	93	-8.42765	-7.3056	-7.19	1.531782	0.013363
2,2',3,4',5'-Pentachloro	97	2.04	1.58	0.09	1.936	78	-8.06357	-7.5735	-7.76	0.092156	0.034782
2,2',3,4',6'-Pentachloro	98	2.01	1.70	0.10	1.936	94	-8.15155	-7.4112	-7.40	0.564830	0.000125
2,2',4,4',5-Pentachloro	99	2.03	1.62	0.08	1.936	59	-7.79599	-7.7769	-7.95	0.023718	0.029964
2,2',4,4',6-Pentachloro	100	2.00	1.70	0.10	1.936		-7.20671	-7.5901	-7.66	0.205470	0.004886
2,2',4'5,6-Pentachloro	103	2.01	1.70	0.10	1.936	69	-7.90155	-7.5633	-7.47	0.186237	0.008705
2,3,3',4,4'-Pentachloro	105	2.04	1.70	0.10	1.936	116	-8.38607	-7.4775	-7.52	0.750081	0.001806
2,3,3',4,5-Pentachloro	106	2.07	1.70	0.08	1.936	85	-8.01023	-7.8317	-7.68	0.109053	0.023013
2,3,3',4,6-Pentachloro	110	2.04	1.65	0.10	1.936	53	-7.79677	-7.5113	-7.65	0.021542	0.019238
2,3,3',5,6-Pentachloro	112	2.05	1.65	0.09	1.936	91	-8.14143	-7.8593	-7.76	0.145490	0.009860
2,3,3',5',6-Pentachloro	113	2.05	1.65	0.09	1.936	56	-7.79143	-7.7172	-7.95	0.025144	0.054196
2,3,4,4',5-Pentachloro	114	2.06	1.58	0.08	1.936	98	-8.23307	-7.7500	-7.50	0.537395	0.062500
2,3,4,4',6-Pentachloro	115	2.03	1.65	0.08	1.936	65	-7.83157	-7.8701	-7.96	0.016494	0.008082
2,3,4',5,6-Pentachloro	117	2.04	1.58	0.08	1.936	167	-8.91339	-7.8021	-7.88	1.067899	0.006068
2,3',4,4',5-Pentachloro	118	2.06	1.58	0.08	1.936	111	-8.36307	-7.7000	-7.33	1.067238	0.136900
2,3',4,4',5-Pentachloro	119	2.03	1.63	0.08	1.936	75	-7.94785	-7.7753	-7.91	0.001433	0.018144
2,3',4,5',6-Pentachloro	121	2.04	1.58	0.07	1.936	93	-8.13321	-8.0149	-7.92	0.045459	0.009006
2,3,4,4',5'-Pentachloro	123	2.09	1.60	0.10	1.936	134	-8.67167	-7.4689	-7.42	1.566683	0.002391
2,2',3,3',4,4'-Hexachloro	128	2.18	1.65	0.04	2.059	150	-9.09369	-8.0402	-8.33	0.583227	0.083984
2,2',3,3',4,5-Hexachloro	129	2.19	1.65	0.04	2.059	102	-8.61853	-8.1899	-8.42	0.039415	0.052946
2,2',3,3',4,6-Hexachloro	131	2.16	1.77	0.13	2.059	135	-9.19795	-8.0103	-8.48	0.515457	0.220618
2,2',3,3',4,6'-Hexachloro	132	2.16	1.77	0.13	2.059	116	-9.00795	-7.7413	-7.65	1.844036	0.008336

Table 9.2 continues

2,2',3,3',5,6-Hexachloro	134	2.17	1.78	0.13	2.059	132	-9.16465	-7.9141	-7.65	2.294174	0.069749
2,2',3,3'5,6'-Hexachloro	135	2.17	1.78	0.13	2.059	102	-8.86465	-7.9431	-7.82	1.087125	0.014665
2,2,3,4,4',5-Hexachloro	137	2.18	1.60	0.04	2.059	81	-8.44439	-8.4062	-8.52	0.005716	0.012950
2,2,3,4,4',5'-Hexachloro	138	2.18	1.65	0.06	2.059	79	-8.46405	-8.1728	-8.38	0.007065	0.042932
2,2,3,4,4',6'-Hexachloro	140	2.18	1.76	0.10	2.059	68	-8.42523	-8.0438	-8.24	0.034311	0.038494
2,2',3,4,5,5'-Hexachloro	141	2.19	1.68	0.08	2.059	88	-8.61483	-8.3499	-8.42	0.037960	0.004914
2,2',3,4,5,6'-Hexachloro	143	2.16	1.75	0.11	2.059	89	-8.67387	-8.0651	-8.13	0.295798	0.004212
2,2,3,4,5',6-Hexachloro	144	2.16	1.78	0.13	2.059	72	-8.55981	-8.1667	-8.01	0.302294	0.024555
2,2',3,4',5,5'-Hexachloro	146	2.19	1.65	0.04	2.059	88	-8.47853	-8.3538	-8.58	0.010296	0.051166
2,2',3,4',5',6-Hexachloro	149	2.16	1.80	0.12	2.059	78	-8.56335	-8.0144	-7.94	0.388569	0.005535
2,2',3,5,5',6-Hexachloro	151	2.17	1.78	0.13	2.059	98	-8.82465	-8.1229	-7.93	0.800404	0.037210
2,2',4,4',5,5'-Hexachloro	153	2.18	1.60	0.04	2.059	102	-8.65439	-8.4047	-8.49	0.027025	0.007276
2,2',4,4',5,5'-Hexachloro	154	2.15	1.77	0.12	2.059	68	-8.48293	-8.2354	-8.12	0.131720	0.013317
2,2',4,4',6,6'-Hexachloro	155	2.12	1.65	0.05	2.059	111	-8.71483	-8.1089	-8.12	0.353826	0.000123
2,3,3',4,4',5-Hexachloro	156	2.21	1.60	0.06	2.059	129	-9.01927	-8.3394	-8.31	0.503068	0.000864
2,3,3',4,4',6-Hexachloro	158	2.18	1.65	0.05	2.059	110	-8.73387	-8.4114	-8.48	0.064452	0.004706
2,3,3',4'5,6Hexachloro	163	2.19	1.65	0.05	2.059	121	-8.84871	-8.3483	-8.48	0.135949	0.017345
2,3,3',4',5',6-Hexachloro	164	2.19	1.67	0.06	2.059	92	-8.58261	-8.2239	-8.27	0.097727	0.002125
2,3',4,4',5,5'-Hexachloro	167	2.21	1.65	0.06	2.059	125	-8.93857	-8.4216	-8.21	0.530819	0.044775
3,3',4,4',5,5'-Hexachloro	169	2.21	1.60	0.04	2.059	208	-9.72891	-8.3802	-8.85	0.772488	0.220712
2,2',3,3'4,4',5-Hexachloro	170	2.33	1.87	0.00	2.181	136	-9.18267	-8.8439	-8.90	0.079901	0.003147
2,2',3,3',4,5,5'-Heptachloro	172	2.34	1.85	0.00	2.181	135	-9.19379	-8.9644	-9.10	0.008796	0.018387
2,2',3,3',4,5,6'-Hexachloro	174	2.31	1.90	0.06	2.181	124	-9.26965	-8.6284	-8.59	0.461920	0.001475
2,2',3,3',4,5',6-Hexachloro	175	2.31	1.90	0.06	2.181	121	-9.23965	-8.7943	-8.68	0.313205	0.013064
2,2',3,3',4,6,6'-Hexachloro	176	2.31	1.95	0.12	2.181	102	-9.25003	-8.2893	-8.15	1.210059	0.019404
2,2',3,3',4,5',6'-Hexachloro	177	2.28	1.90	0.12	2.181	152	-9.77621	-8.5210	-8.42	1.839297	0.010201
2,2'3,3',5,5',6-Hexachloro	178	2.31	1.90	0.12	2.181	110	-9.37073	-8.6962	-8.59	0.609535	0.011278
2,2',3,3',5,6,6'-Hexachloro	179	2.32	1.95	0.12	2.181	129	-9.52487	-8.2248	-7.94	2.511803	0.081111

Table 9.2 continues

2,2',3,4,4',5,5'-Hexachloro	180	2.29	1.84	0.00	2.181	112	-8.94773	-8.9934	-9.10	0.023187	0.011364
2,2',3,4,4',5,6-Hexachloro	181	2.30	1.90	0.04	2.181	125	-9.19445	-8.8593	-8.97	0.050376	0.012254
2,2',3,4,4',5,6'-Hexachloro	182	2.30	1.90	0.06	2.181	107	-9.09481	-8.8672	-8.68	0.172065	0.035044
2,2',3,44',5',6-Heptachloro	183	2.30	1.90	0.04	2.181	93	-8.87445	-8.8050	-8.85	0.000598	0.002025
2,2',3,4,5,5',6-Heptachloro	185	2.31	1.90	0.04	2.181	148	-9.42929	-8.8208	-8.75	0.461431	0.005013
2,2',3,4',5,6,6'-Heptachloro	188	2.28	1.95	0.12	2.181	134	-9.55551	-8.4765	-8.49	1.135305	0.000182
2,3,3',4,4',5,5'-Heptachloro	189	2.36	1.87	0.00	2.181	162	-9.45719	-9.1040	-8.72	0.543445	0.147456
2,3,3',4,4',5,6-Heptachloro	190	2.33	1.89	0.00	2.181	122	-9.02639	-9.0829	-8.90	0.015740	0.033452
2,3,3',4,4',5',6-Heptachloro	191	2.33	1.85	0.00	2.181	112	-8.95895	-9.0920	-9.10	0.019896	0.000064
2,3,3',4,5,5',6-Heptachloro	192	2.34	1.85	0.00	2.181	171	-9.55379	-9.3078	-9.10	0.205923	0.043181
2,3,3',4',5,5',6-Heptachloro	193	2.34	1.85	0.00	2.181	138	-9.22379	-9.0200	-9.10	0.015323	0.006400
2,2',3,3',4,4',5,5'-Octachloro	194	2.48	1.75	0.00	2.303	155	-10.03912	-9.5810	-9.70	0.115003	0.014161
2,2',3,3',4,4',5,6-Octachloro	195	2.45	1.99	0.00	2.303	170	-9.97924	-9.3459	-9.29	0.475053	0.003125
2,2',3,3',4,4',5,6'-Octachloro	196	2.45	1.99	0.00	2.303	127	-9.54924	-9.4226	-9.42	0.016703	0.000007
2,2',3,3',4,4'6,6'-Octachloro	197	2.42	2.11	0.00	2.303	137	-9.53704	-9.1058	-9.10	0.191005	0.000034
2,2',3,3',4,5,5',6-Octachloro	198	2.46	1.99	0.00	2.303	195	-10.23408	-9.4485	-9.42	0.662728	0.000812
2,2',3,3',4,5,6,6'-Octachloro	199	2.46	2.20	0.00	2.303	175	-9.86314	-8.9608	-9.10	0.582384	0.019377
2,2',3,3',4,5',6,6'-Octachloro	200	2.43	2.20	0.00	2.303	141	-9.50862	-8.9550	-9.20	0.095247	0.060025
2,2',3,3',4,5,5',6-Octachloro	201	2.43	1.99	0.00	2.303	157	-9.83956	-9.2900	-9.29	0.302017	0.000000
2,2',3,4,4',5,5',6-Octachloro	203	2.48	2.00	0.00	2.303	111	-9.39562	-9.4739	-9.50	0.010895	0.000681
2,2'3,4,4',5,6,6'-Octachloro	204	2.52	2.10	0.00	2.303	175	-9.97358	-9.2492	-9.48	0.243622	0.053269
2,3,3',4,4',5,5',6-Octachloro	205	2.48	1.99	0.00	2.303	197	-10.26376	-9.7792	-9.70	0.317826	0.006273
2,2',3,3',4,4',5,5',6-Nanochloro	206	2.60	2.11	0.00	2.426	202	-10.77440	-10.0286	-10.18	0.353314	0.022922
2,2',3,3',4,4',5,6,6'-Nanochlorobiphenyl	207	2.57	2.13	0.00	2.426	213	-10.85360	-9.7531	-10.07	0.614032	0.100426
										3.3859679	3.8995744
										0.0252684	0.0291013
									Sd	0.1589591	0.1705902

(a) Our cacl. LogS using eqn. (9.10)
(b) Predicted log S based on eqn. (9.9)
(c) Exp. Log S data obtained from the literature by Patil [32]
Sd (a - c) our cacl. Log S- exp. Log S
Sd (b- c) predicted log S – exp log S

9.2 Discussion

In general the factors that influence aqueous solubility are hydrogen-bond acidity and hydrogen-bond basicity; these properties no doubt reflect the strong hydrogen-bond acidity of water as a bulk solvent.[31] However, if the compound is itself both a hydrogen - bond acid and a hydrogen -bond base, then intermolecular hydrogen -bond interactions will lead to an increase in mp and to a decrease in solubility. In Table 9.3 are values for some representative compounds that have both hydrogen bond acidic and basic sites.

Table 9. 3. Hydrogen–bond effects on solubility, as log Sw

Compound	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	$\Sigma\alpha_2 * \Sigma\beta_2^H$	Resultant
acetic acid	1.30	1.84	-0.90	2.24
trichloroacetic acid	2.02	1.17	-0.89	2.30
benzoic acid	1.25	1.67	-0.79	2.14
phenol	1.27	1.26	-0.60	1.93
4-nitrophenol	1.75	1.09	-0.71	2.12
ethanol	0.79	2.01	-0.59	2.20
2,2,2-trifluoroethanol	1.21	1.05	-0.48	1.78
estrstriol	2.97	5.11	-5.70	2.38
aniline	0.55	1.72	-0.36	1.91
benzamide	1.04	2.81	-1.10	2.75
pyrazole	1.15	1.88	-0.81	2.22
morpholine	0.13	3.81	-0.18	3.76
progesterone	0.00	4.77	0.00	4.77
trichloromethane	0.32	0.08	-0.01	0.39

The intermolecular acid base interaction in a solid or liquid, given by the $\Sigma\alpha_2^H * \Sigma\beta_2^H$ term, reduces the hydrogen bond effect but still leaves a negative resultant. For the large number of compounds that are hydrogen-bond bases, but not acids, there is a straight

forward effect of increased solubility (also shown in Table 9.3).There are but few compounds that are hydrogen-bond acids and yet have no or very little hydrogen bond basicity. The term in s. π_2^H leads also to an increase in solubility. The two other terms in equation 9.5, that affect the solubility are r.R_2 and v.Vx both of which result in a decrease in solubility; the r - and v- coefficients in equation 9.5, are markedly more negative than in the solvation equation for gaseous solubility. The R_2 descriptor refers to the propensity of solute to interact with surrounding σ and π electrons, the negative r-coefficient suggesting that such interaction within the solid or liquid is much larger than the corresponding interaction between the solute and bulk water.

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Chapter 10 The Conformation of the PCBs

It has been shown that, in addition to gas chromatography, high-performance liquid chromatography (HPLC) has great potential for the analysis of halogenated aromatics. A considerable amount of data on the retention behavior of polychlorinatednbiphenyls (PCBs), polybrominated biphenyls (PBBs) and polychlorinated naphthalenes (PCNs) has been published.[1-4] Chromatograms have been recorded for the complete series of Aroclor-5 mixtures; details of retention times and the capacity factor, k' have been mentioned before in chapter 4. Values of k', see equation (4.2) of the PCBs generally decrease with increasing chlorine content, but vary widely with both the number and position of the chlorine atoms in the biphenyl nucleus, as shown in Table 10.1.

Table 10.1. HPLC capacity factors (k') of PCBs

Cl Substitution	k'	Cl Substitution	k'
Biphenyl	9.25	2,3,2',3'	3.50
2	6.35	2,4,2',4'	1.65
3	4.60	2,5,2',5'	2.00
4	5.05	2,6,2',6'	3.75
2,2'	2.50	3,4,3',4'	2.35
3,3'	2.65	3,5,3',5'	0.95
4,4'	2.90	2,3,2',4'	2.35
2,3	5.25	2,4,6,3'	1.70
2,4	3.80	2,4,6,4'	1.55
2,5	3.55	2,5,3',4'	1.85

2,6	5.40	2,3,4,2',3',4'	2.15
3,4	4.00	2,3,6,2',3',6'	2.25
3,5	2.60	2,4,5,2',4',5'	1,15
2,5,2'	3.20	2,4,6,2',4',6'	0.75
2,5,3'	2.15	3,4,5,3',4',5'	1.50
2,5,4'	2.05	Deca	0.45

From the results in Table 10.1 and from other previously published compilations of retention time data on PCBs,[1,2] several conclusions can be drawn;

1- Although, in general, retention decreases when an increasing number of chlorine atoms are introduced into the biphenyl nucleus, the introduction of chlorine atoms ortho to the phenyl-phenyl bond (2-and 6- positions) increases retention.

2- The order of elution of homogenate biphenyls bearing one to four halogen atoms in a single ring as a rule is the same as that of the symmetrically substituted compounds having from two to eight constituents.

3- Although there is a general tendency for the k' values to decrease with increase in the number of substitutions, the positions of the halogen atoms are seen to exert a marked influence. For instance, the chlorobiphenyls, having substituents ortho to the phenyl-phenyl bond, display markedly lower k' values than do their non-ortho-substituted isomers. For the remainder, substitution meta to the central C-C bond affects retention only slightly, whereas substituted para to this bond strongly promotes retention, as shown

by the high k', values observed for e.g.,4-mono-, 4,4- and 3,4,3',4'- tetra-substituted chlorobiphenyls

Similar effects are observed with respect to values of log Poct (chapter 8, Table 8.4). These differ for chlorobiphenyls with the same number of substituents in different positions. Thus for tetrachlorobiphenyls, log Poct varies from 5.96 to 6.63, as shown for the calculated values obtained in this work, seen Table 10.2

Table 10.2. IUPAC no. and calculated values (this work) of log Poct for some PCBs

Name	IUPAC	Calclog P
2-Monochlorobiphenyl	1	4.54
3-Monochlorobiphenyl	2	4.60
4-Monochlorobiphenyl	3	4.58
2,2'-Dichlorobiphenyl	4	5.07
3,3-Dichlorobiphenyl	11	5.20
3,4-Dichlorobiphenyl	12	5.23
2,2',6-Trichlorobiphenyl	19	5.48
2,2',3-Trichlorobiphenyl	16	5.62
3,3',4-Trichlorobiphenyl	35	5.84
2,2',6,6'-Tetrachlorobiphenyl	54	5.96
2,3,3',4-Tetrachlorobiphenyl	55	6.27
3,3',4,4'-Tetrachlorpbiphenyl	77	6.63
3,3',4,5-Tetrachlorobiphenyl	78	6.33
2,2',3,6,6'-Pentachlorobiphenyl	96	6.65
2,3,3',5,5'-Pentachlorobiphenyl	111	6.76
3,3',4,5,5'-Pentachlorobiphenyl	127	6.80
2,2',3,5,6,6'-Hexachlorobiphenyl	152	6.63
2,2',3,4',5,6'-Hexachlorobiphenyl	148	6.93
3,3',4,4',5,5'-Hexachlorobiphenyl	169	7.34
2,2',3,3',4,6,6'-Heptachlorobiphenyl	176	7.71
2,2',3,3',4',5,6-Heptachlorobiphenyl	177	7.66
2,2',3,3',5,5',6-Heptachlorobiphenyl	178	7.72
2,2',3,3',4,4',6,6'-Octavhlorobiphenyl	197	8.15
2,2',3,3',4,5,5',6'-Octachlorobiphenyl	198	8.25
2,3,3',4,4',5,5',6-Octachlorobiphenyl	205	8.15
2,2',3,3',4,4',5,5',6-Nonchlorobiphenyl	206	8.92
2,2,,3,3',4,4',5,6,6-Nonchlorobiphyl	207	8.34
2,2',3,3',4,5,5',6,6'-Nonchlorobiphenyl	208	8.13
Decachlorobiphenyl	209	8.30

Looking closely at Table 10.2 there are differences between log Poct values for each groups of PCBs, as regards the number of substituents. With few substituents, the differences are greater, and as the molecule becomes bigger (ie with more substituents), the differences become smaller. The PCBs with 2,6 or 2,2',6,6'-substution always have smallest values of log Poct, as mentioned before in chapter (7). The ortho-substitution effect which increases the polarity of the PCB was noted especially for the 2,2',6 and 2,2',6,6'-congeners as compared to other PCBs, with the same chlorine number.

All these results on HPLC capacity factors and log Poct values, suggests that the rotational energy in the PCBs could be important, and so a study was made to obtain the energy barrier to rotation about the C-C bond for a number of ortho-substituted PCBs. The modeling software program PC Model was used to construct the PCBs and to obtain the rotational energy as function of rotational angle (in Figure 10.1, the rotational angle is defined, looking down the molecule along the C-C central bond). This work started with biphenyl, then with the ortho substituted PCBs with 2,2'-, 3,3'-, 4,4'- and 2, 2', 6, 6'- substituents as shown in Table 10.3; graphs of the rotational energy are shown below in Figures 10.3 and 10.4 as two examples. From the PC Model results, the rotational energy maximum for all the PCBs studied were more or less the same, except for the 2,2', 6,6'-PCB where the energy maximum was much larger. This helps to explain the substitutent effect on descriptors. For example the value of π_2^H for the 2,2',6,6'-substituted tetrachlorobiphenyl was larger than those of the other tetrachlorobiphenyls. This can be seen also in Figure (7.2) chapter 7. The presence of ortho-substitution increases the polarity, decreases the contact area and makes the molecules non-planar. [3] These conclusions agree with those of Brinkman et al. [5]

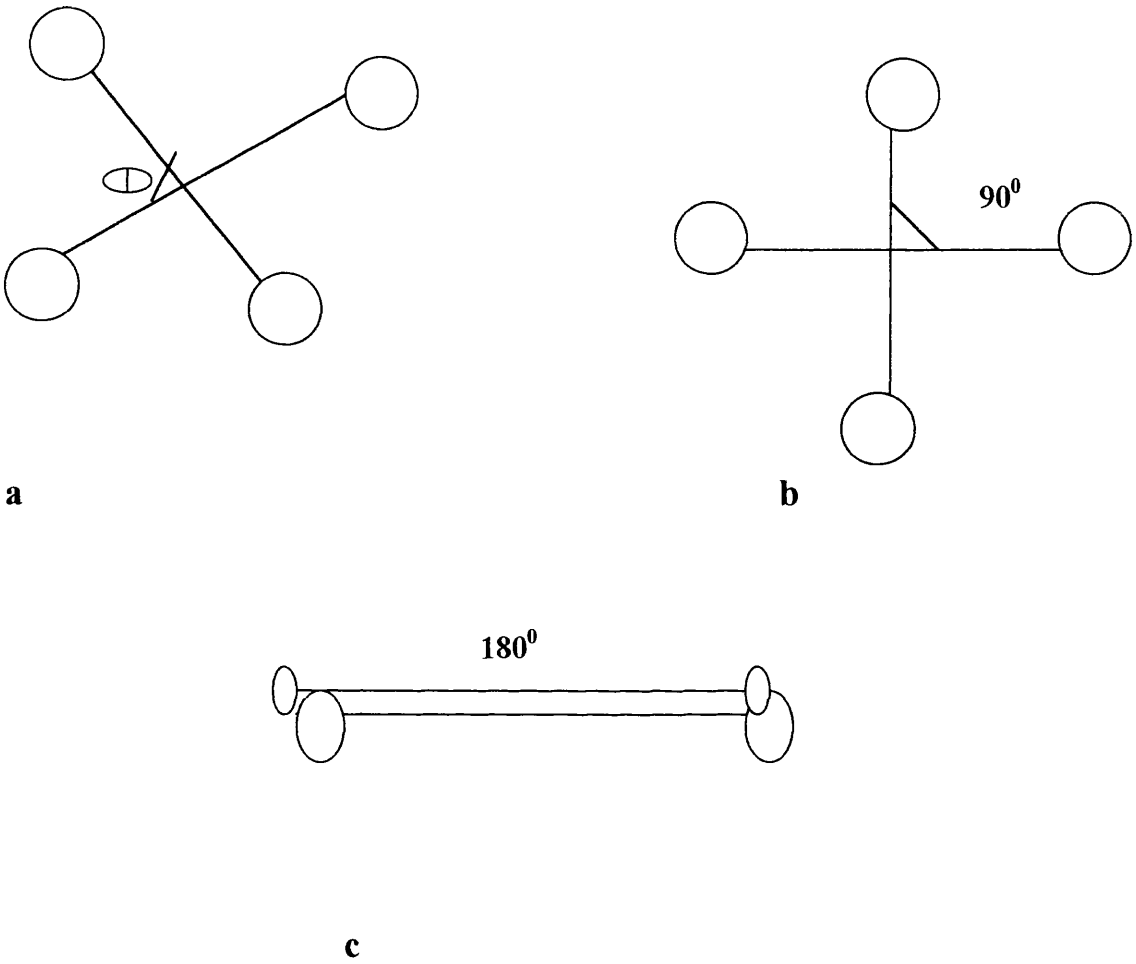
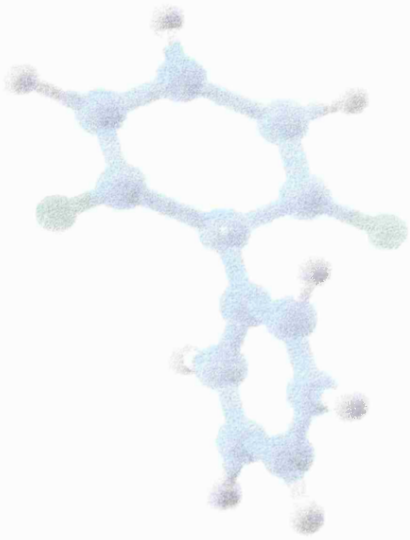


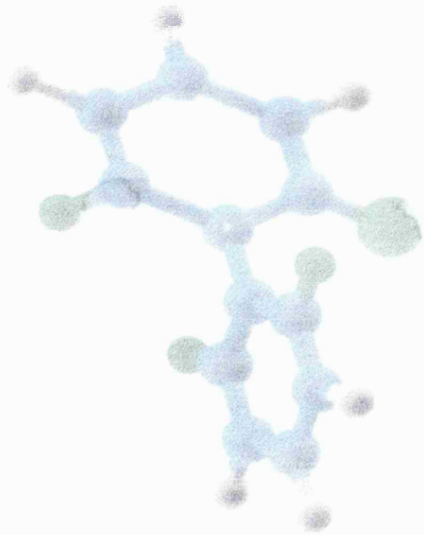
Figure. 10.1. The rotation angle about the central C-C bond

Table 10.3. The rotational energy maximum, in Kcal/ mol, for some PCBs

Name	Rotational Energy
Biphenyl	46.4
4,4'-Dichlorobiphenyl	450.4
3,3'-Dichlorobiphenyl	670.3
2,2'-Dichlorobiphenyl	809.6
2,6-Dichlorobiphenyl	1038.5
2,2',6,6'-Tetrachlorobiphenyl	1776.9



A



B

Figure 10.2. The PC Model for constructing the PCBs. A for 2,6- B for 2,2',6,6-orth-subs.PCBs

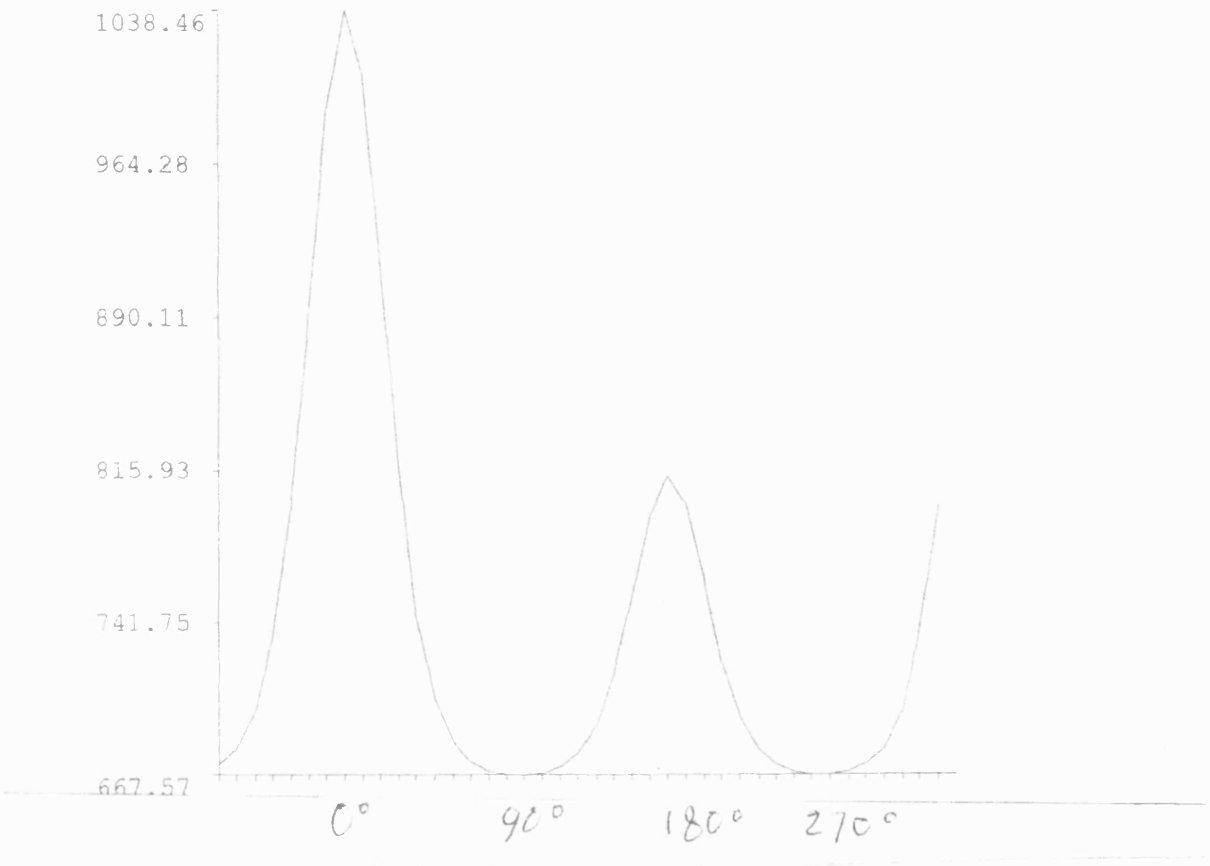


Figure 10.3. Rotation energy about the c-c bond for 2,6–ortho-substituted PCBs,

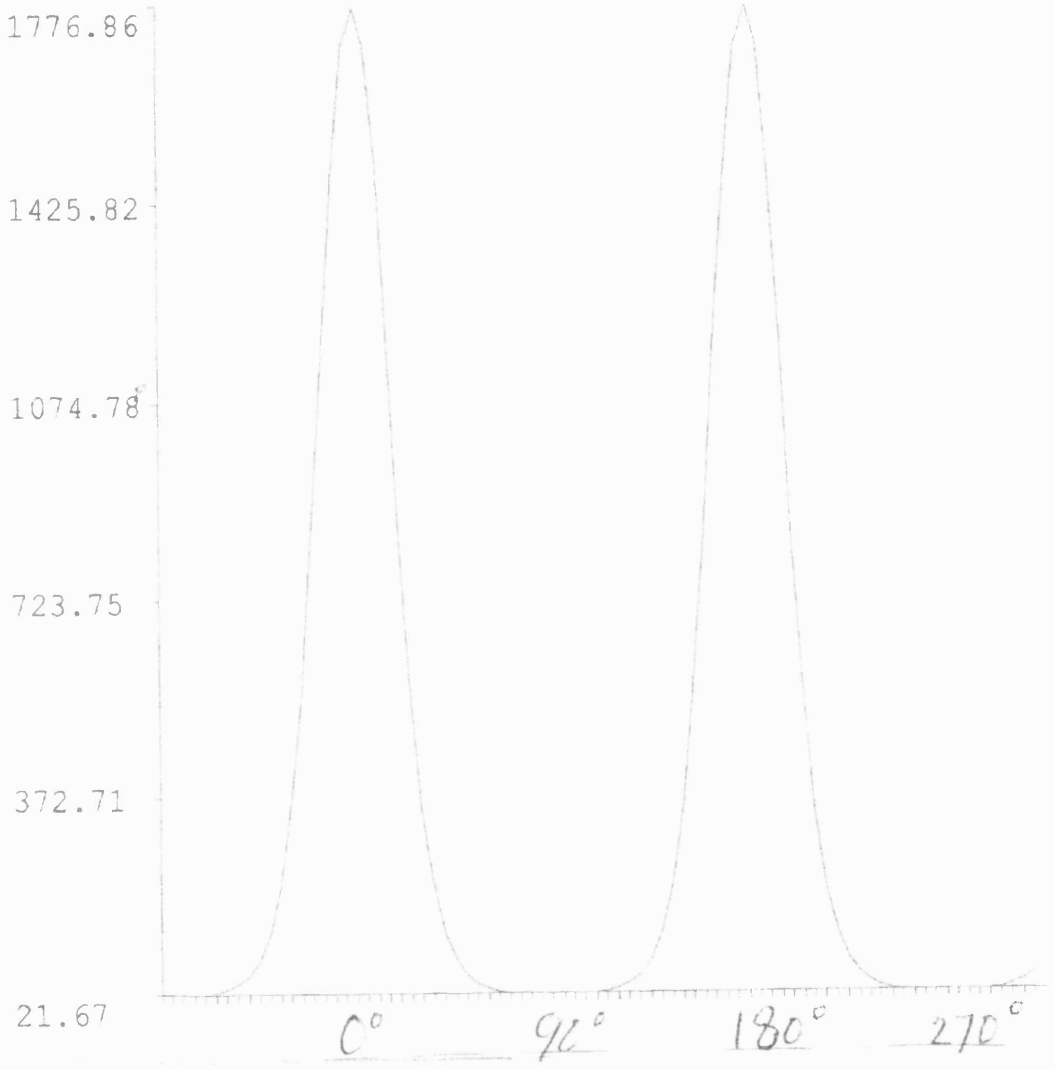


Figure 10.4. Rotation energy about the c-c bond for 2,2',6,6'-ortho-substituted PCBs

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Chapter 11 Calculation of the Descriptors for Polychloro-naphthalenes, PCNs

11.0 Introduction

Polychlorinated naphthalenes (PCNs), written as $C_{10}H_{8-x}Cl_x$, are a group of compounds composed of two fused benzene rings (naphthalene) with one to eight chlorine substitutions (Figure 1). There are a total of 75 possible PCN congeners. In general, they are hydrophobic waxy solids with thermal stability and inertness. [1,2] PCNs are structurally similar to PCBs and exhibit similar physical and chemical properties. [1,2,3] Technical mixtures of the 75 possible PCN congeners have been used in dielectric fluids, engine oil additives, electroplating masking compounds, wood preservatives, lubricants and dye production.[1,3] Technical PCN mixtures with chlorine contents ranging from 22 to 70 wt %, known as Halowaxes, have been produced by Koppers Company in the United States since the 1920s. PCNs have also been manufactured in other countries as Nibren waxes (Bayer Germany), Seekay waxes (ICI, U.K.) and Cerifal materials (Caffaro, Italy). The exact amount of production of technical PCN mixtures is not known, but it has been estimated to be approximately 150 000 tons, which is 10 % of the total global production of PCBs. [4,5] Although the industrial production of technical PCN formulations has declined in the United States since the early 1980s, products containing these formulations are still present in the environment. [6] Furthermore, the secondary formation of PCNs in thermal processing such as municipal solid waste incineration (MWI) suggests sustaining environmental sources of PCNs. Similar to PCBs, PCNs are persistent and lipophilic compounds that tend to bioaccumulate. PCNs are wide spread in the biosphere on global scale.[7,8] PCNs have been found in a wide variety of environmental matrices including Arctic and urban air, [9,10] wildlife, [7, 8,11,12]

and human tissues [13,14] including breast milk. [15] Consumption of contaminated fish is considered to be an important route of exposure of humans to PCNs. High concentrations of penta-and hexachloronaphthalenes in human blood plasma have been correlated with fish consumption.[16]

Distribution, bioaccumulation, and fate of PCBs, polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) in various environmental media near a chlor-alkali plant have been described. [17-18] Little is know about the fate, transport, and biological effects of individual PCN congeners. This is due in part, to a deficiency of standards of individual congeners and a lack of sensitive, congener specific analytical methods. Now that many standards have been developed, such as capillary gas chromatography and high–resolution mass spectrometry (HRGC/HRMS), PCN congeners have been detected in environmental samples. [7, 10, 11, 19, 20, 21] Recently, the composition of PCN congeners in technical Halowax mixtures has been reported.[3] The characteristic properties of PCNs are hydrophobicity or lipophilicity, relatively low vapour pressure and extreme resistance to chemical reaction, and high chemical and thermal stability. Many of the PCNs are toxic [2,22,23] and in view of their tendency to bioaccumulate and their widespread distribution[21, 24, 25, 26] are now acknowledged to be important environmental contaminants.[5]

Polychloronaphthlenes (PCNs) have similar structural functionalities, but a number of analytical methods have been used to separate the congeners. The corresponding data can then be used to obtain physicochemical properties of PCNs. Such analytical methods include normal phase HPLC capacity factors, [27] reversed-phase HPLC capacity factors [28] and gas liquid chromatographic (GLC) retention data on DB-5, Rtx-5 and TC-1701/OV-1701. [2, 3, 24, 29, 30] Water-octanol partition coefficients, as log Poct, have been determined for a number of PCNs [28,31] and values of log Poct can be estimated for all the 75 PCNs through the CLOGP program.[32] Gas-dry

octanol partition coefficients for 24 PCNs have been determined at several temperatures.[33]

However, key environmental quantities such as gas-water partition coefficients and aqueous solubilities are unknown, except for a few aqueous solubilities.[28] There are enormous practical difficulties in the experimental determination of these quantities for very lipophilic compounds, and so resort is often had to some form of estimation. It is the aim of this work to obtain from the available physicochemical data, solvation descriptors that can then be used to estimate all kinds of other physicochemical data, and especially those of use in environmental analyses.

Although there is a numbering scheme for the 75 PCNs [5] we prefer to use abbreviations that relate to the PCN structure. We therefore denote 1,2-dichloronaphthalene as PCN12, and 1,2,3,5-tetrachloronaphthalene as PCN1235, etc.

11.1 Methodology

We start with two general solvation equations: [34]

$$\text{Log SP} = c + r.\, R_2 + s.\, \pi_2{}^{H} + a.\, \Sigma\, \alpha_2{}^{H} + b.\, \Sigma\, \beta_2{}^{H} + v.\, V_x \qquad (11.1)$$

$$\text{Log SP} = c + r.\, R_2 + s.\, \pi_2{}^{H} + a.\, \Sigma\, \alpha_2{}^{H} + b.\, \Sigma\, \beta_2{}^{H} + \log L^{16} \qquad (11.2)$$

The dependent variable, SP, is a set of solute properties in a given system. Eqn.(11.1) is used for processes in condensed systems; for example SP might then be log Poct where Poct is the water-octanol partition coefficient for a series of compounds. Eqn.(11.2) is used for gas-condensed phase processes, such as gas liquid chromatography where SP can be a relative retention time, as log t, or the Kovats retention index, I, can be used instead of log SP. The independent variables in

eqn.(11.1) and eqn.(11.2) are solute descriptors as follows.[34] R_2 is the solute excess molar refractivity, in units of (mol dm^{-3})/10, defined as the solute molar refractivity less the molar refractivity of an alkane of the same McGowan volume. R_2 represents the tendency of a solute to take part in intermolecular interactions through σ and π electrons. The reason why an 'excess' molar refraction is used instead of the molar refraction itself, is that the latter is too closely related to solute volume to be incorporated in the any linear equation that includes volume as a descriptor. π_2^H is the solute dipolarity/polarizability and $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ are the overall or summation hydrogen bond acidity and basicity. Vx is the McGowan characteristic volume in units of (mol dm^{-3})/100. This volume is calculated through addition of atomic fragments, and can very simply be calculated just from the solute molecular formula and the number of rings in the molecule, using the algorithm of Abraham. [34] Log L^{16} is the logarithm of the gas-hexadecane partition coefficient at 298 K. [35] Both Vx and $\log L^{16}$ encode two particular types of interaction, that may be explained as follows. The dissolution of a gaseous solute in a solvent can conceptually take place in two stages, (a) a hole or cavity has to be formed in the solvent, and (b) the solute is then inserted into the cavity and then takes part in various solute/solvent interactions. The work required to form a cavity is roughly proportional to the size of the cavity, and since both Vx and log L^{16} are related to size, this cavity work will depend on Vx or log L^{16}. The solute/solvent interactions can mostly be modeled by the descriptors R_2, $\Sigma\alpha_2^H$, and $\Sigma\beta_2^H$, but there will be interactions of the London dispersion force type that are not thus modeled. These interactions depend also on solute size, and so the Vx and $\log L^{16}$ descriptors include not only the cavity size effect, but also the propensity of a solute to undergo London dispersion interactions. Thus the descriptors in eqn.(11.1) and eqn.(11.2) all refer to how a solute might interact with a solvent phase, and the Vx and $\log L^{16}$ descriptors also include the cavity effect. Although the

processes listed in Table 11.1 appear to be quite different, they have in common the various solute/ solvent interactions to which our descriptors refer. This is why the R_2 -descriptor, for example, seems relevant in all sorts of different processes.

The coefficients in eqn. (11.1) and eqn. (11.2) are evaluated through multiple linear regression analysis, MLRA, using standard mathematical software packages or our own in-house software. Some examples of eqn. (11.1) and eqn. (11.2) are in Table 11.1, where the obtained coefficients and statistics are summarized.

The general method for the determination of solute descriptors has been given previously.[35] We start with values of SP for a given compound in a number of systems that have been characterized through eqn. (11.1) or eqn. (11.2). The R_2 descriptor can be obtained from the liquid refractive index at 293K, or can easily be estimated, Vx can readily be calculated from structure,[34] and so we have four descriptors π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and log L^{16} that remain to be evaluated. Various combinations of π_2^H,$\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and log L^{16} are used to calculate the known SP values, and the combination that best reproduces the observed values is then selected. It is important to note that $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ refer to hydrogen bond acidity and basicity, and not to proton acidity and basicity. The PCNs have no hydrogen bond acidity ($\alpha_2^H = 0$), but they are potentially hydrogen bond bases, and so there are the three descriptors, π_2^H, $\Sigma\beta_2^H$ and log L^{16} to be evaluated. In this respect, the PCNs resemble the chlorobenzenes that have zero hydrogen bond acidity, but some hydrogen bond basicity.[34]

11.2 Calculation of the descriptors

Preliminary estimates of descriptors are used to start with, as follows. The R_2 descriptor can easily be estimated by analogy with previous work on the polychlorinated benzenes. We started

with R_2 = 1.45 for PCN2 and added 0.12 units for each additional chlorine atom. Thus PCN12 has R_2 = 1.57, etc. Initial work indicated that the π_2^H-descriptor was almost additive (like the R_2-descriptor) except for compounds that had adjacent chorine atoms. Starting with π_2^H = 1.00 for PCN2, each extra chlorine atom increases π_2^H by 0.06 units, with an extra increase of 0.06 units for adjacent chlorine atoms. Thus the dichloronaphthalenes have π_2^H = 1.06 except for PCNs 12, 23, and 18 that have π_2^H = 1.12 ; it is interesting that PCN18 behaves as though it had adjacent chlorine atoms. In this way, values of R_2 and π_2^H for all the 75 PCNs were assigned as a preliminary. Eqn.(11.1) had been applied [37] to values of log Poct , see Table 11.1, so that with R_2, π_2^H and $\Sigma\alpha_2^H$ available, an estimate of log Poct through the CLOG P program [32] was all that was necessary to obtain first, preliminary, values of $\Sigma\beta_2^H$.

The π_2^H, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ descriptors thus estimated, together with Vx, allow the further estimation of the gas/water partition coefficient (or Ostwald solubility coefficient), K^W, and the water-hexadecane partition coefficient, P_{16}, from the following known equations: [37,38]

$$\log K^W = -0.994 + 0.577 R_2 + 2.549 \pi_2^H + 3.813 \Sigma\alpha_2^H + 4.841 \Sigma\beta_2^H - 0.869 Vx \quad (11.3)$$

$$\log P_{16} = 0.087 + 0.667R2 - 1.617 \pi_2^H - 3.587 \Sigma\alpha_2^H - 4.869 \Sigma\beta_2^H + 4.433 Vx \quad (11.4)$$

Then an estimate of the final descriptor, log L^{16} (i.e. log K^{16}), can be obtained through eqn. (11.5):

$$\log P_{16} = \log L^{16} - \log K^W \quad (11..5)$$

Once the initial estimates of all four descriptors had been accomplished, it was then possible to characterize the various sets of GLC retention data through eqn.(11.2). The resulting equations were then used to adjust the initial estimates to give a second set of π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and log L^{16} descriptors; use was also made of known [33] gas-dry octanol partition coefficients, as log K^{OCT} because the correlation equation for log L^{OCT} involves the logL^{16}-descriptor. The second set of log L^{16} values were again used to characterize the sets of GLC retention data that were then used to obtain a third (final) set of descriptors. The final GLC equations are summarized in Table 11.1, together with details of the other equations that were have used. [37-39] The statistics of the GLC equations are only notional, because the equations are a result of an iterative procedure. In order to weight the equations satisfactorily, Kovats retention indices were correlated as I/100, and t and log t were correlated as 10t and 10log t so that the equation coefficients were then of the same order as those for the log P equations. The following statistics of the regressions are in Table 11.1: n is the number of data points (compounds), sd is the standard deviation, and r^2 is the variance. Note that for the retention data of Falandysz et al.[3] the given relative retention times, t, were used, that gave a better regression than the normally-used log t values.

Table 11.1. Details of the regression equations used

System	c	e	s	a	b	v/l	n	sd	r^2
Water/wet octanol	0.088	0.562	-1.054	0.034	-3.460	3.814 [a]	613	0.12	0.995
Water/CH_2Cl_2	0.314	0.001	0.022	-3.328	-4.137	4.259	38	0.14	0.991
Water/$CHCl_3$	0.327	0.157	-0.391	-3.191	-3.437	4.191	335	0.25	0.971
Water/CCl_4	0.260	0.573	-1.254	-3.558	-4.588	4.589	210	0.11	0.996

Water/C6	0.361	0.579	-1.723	-3.599	-4.764	4.344	200	0.21	0.996
Water/C16	0.087	0.667	-1.647	-3.587	-4.869	4.433	370	0.12	0.996
Gas/water	-0.994	0.577	2.549	3.813	4.841	-0.869	408	0.15	0.995
Gas/dry octanol	-0.120	-0.204	0.562	3.582	0.694	0.939 [b]	156	0.13	0.997
Gas/CH_2Cl_2	0.107	-0.429	1.671	0.380	0.821	0.942	34	0.12	0.991
Gas/$CHCl_3$	0.168	-0.595	1.256	0.280	1.370	0.981	150	0.23	0.985
Gas/CCl_4	0.282	-0.303	0.460	0.000	0.000	1.047	173	0.12	0.996
Gas/C16	0.000	0.000	0.000	0.000	0.000	1.000	-	-	-
Gas/water	-1.271	0.822	2.743	3.904	4.814	-0.213	392	0.19	0.992
GLC, 10t [c]	-2.721	0.660	1.177	0.000	0.000	0.734	63	0.02	0.999
GLC, 10log t [d]	1.165	2.197	0.575	0.000	0.000	1.111	58	0.08	0.996
GLC, I/100 [e]	-1.759	- 0.907	3.591	0.000	0.000	2.213	80	0.23	0.995
GLC, I/100 [f]	-1.029	-2.563	6.755	0.000	0.000	2.146	70	0.21	0.995

[a] The v-coefficient. [b] The l-coefficient. [c] The relative retention time on phase DB-5.[3] [d] Log of the relative retention time on DB-5, not used for the hexa-PCNs and above.[29] [e] I is the Kovats retention index on phase DB-5.[2,30] [f] I is the Kovats retention index on TC-1701/OV-1701.[2]

Results for PCN1 are in Table 11.2, where the observed experimental values are summarized.

The value of 1.98 for log K^W was obtained from the aqueous solubility, log S_W = -3.93, [40] and the gaseous concentration, log C_G = -5.91 [41] where S_W and C_G are both in units of mol dm^{-3}. There are two equations for log K^W, see Table 11.1, based on eqn.(11.1) and eqn.(11.2). In Table 11.2 are the seven systems for which the equation coefficients were available, together with the seven corresponding experimental observations. A set of descriptors is then chosen, and from the system coefficients, calculated values for the seven can be obtained. This is repeated with different sets of descriptors until the best agreement between calculated and experimental observations is achieved, as indicated by the minimum standard deviation of calculated and experimental values. It is clear from Table 11.2, that solute descriptors can be assigned that reproduce the observed physicochemical properties. The same procedure was repeated for the rest of the 74 PCNs as shown below.

Table 11.2. Analysis of physicochemical data for PCN1 (1-chloronaphthalene) at 298 K; with $R_2 = 1.417$, $\pi_2^H = 1.00$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.14$, $\log L^{16} = 5.8556$, $Vx = 1.2078$

System	Quantity	Obs	Calc
Water/wet octanol	$\log P_{OCT}$	4.00	3.95
Gas/water	$\log K^W$	1.98	2.00
Gas/wet octanol	$\log K^{OCT}$	5.98	5.74
Gas/water	$\log K^W$	1.98	2.06
GLC (c)	10t	3.756	3.688
GLC (d)	10log t	11.072	11.010
GLC (e)	I/100	13.350	13.506

Table 11.3. Analysis of physicochemical data for PCN2 (2-chloronaphthalene) at 298 K;

with $R_2 = 1.450$, $\pi_2^H = 1.00$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.14$, $\log L^{16} = 5.8343$, $Vx = 1.2078$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.06	3.97
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	3.727	3.696
GLC (d)	10log t	11.047	11.048
GLC (e)	I/100	13.280	13.408

Table 11.4. Analysis of physicochemical data for PCN12 (12-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.09$, $\log L^{16} = 6.8067$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.50	4.55
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.680	4.630
GLC (d)	10log t	12.510	12.419
GLC (e)	I/100	15.902	15.902

Table 11.5. Analysis of physicochemical data for PCN13 (13-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.06$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.08$, $\log L^{16} = 6.6747$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.65	4.65
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.506	4.462
GLC (d)	10log t	12.235	12.235
GLC (e)	I/100	15.380	15.395

Table 11.6. Analysis of physicochemical data for PCN14 (14-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.06$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.09$, $\log L^{16} = 6.7569$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.66	4.62
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.572	4.522
GLC (d)	10log t	12.345	12.325
GLC (e)	I/100	15.560	15.576

Table 11.7. Analysis of physicochemical data for PCN15 (15-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.06$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.09$, $\log L^{16} = 6.7801$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.67	4.62
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.593	4.539
GLC (d)	10log t	12.378	12.351
GLC (e)	I/100	15.610	15.628

Table 11.8. Analysis of physicochemical data for PCN16 (16-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.06$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.08$, $\log L^{16} = 6.7683$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.65	4.65
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.572	4.531
GLC (d)	10log t	12.354	12.338
GLC (e)	I/100	15.580	15.602

Table 11.9. Analysis of physicochemical data for PCN17 (17-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.06$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.10$, $\log L^{16} = 6.8346$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.56	4.58
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.623	4.623
GLC (d)	10log t	12.479	12.411
GLC (e)	I/100	15.700	15.748

Table 11.10. Analysis of physicochemical data for PCN18 (18-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.11$, $\log L^{16} = 7.1519$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.50	4.48
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.949	4.883
GLC (d)	10log t	12.949	12.800
GLC (e)	I/100	16.570	16.666

Table 11.11. Analysis of physicochemical data for PCN23 (23-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.09$, $\log L^{16} = 6.9322$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.51	4.55
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t		
GLC (d)	10log t	12.558	12.557
GLC (e)	I/100		

Table 11.12. Analysis of physicochemical data for PCN26 (26-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.08$, $\log L^{16} = 6.7403$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.60	4.59
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.623	4.581
GLC (d)	10log t	12.428	12.346
GLC (e)	I/100	15.700	15.755

Table 11.13. Analysis of physicochemical data for PCN27 (27-chloronaphthalene) at 298 K;

with $R_2 = 1.570$, $\pi_2^H = 1.06$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.08$, $\log L^{16} = 6.7846$, $Vx = 1.3302$

System	Quantity	Obs	Calc
Water/w-octanol	$\log P_{OCT}$	4.60	4.65
Gas/w-octanol	$\log K^{OCT}$		
Gas/water	$\log K^{W}$		
GLC (c)	10t	4.593	4.543
GLC (d)	10log t	12.378	12.356
GLC (e)	I/100	15.610	15.638

Table 11.14. Analysis of physicochemical data for PCN123 (123-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.01$, $\log L^{16} = 7.6652$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.22	5.24
GLC (c)	10t	5.552	5.480
GLC (d)	10log t		
GLC (e)	I/100	18.272	18.124
GLC (f)	I/100	19.290	19.465

Table 11.15. Analysis of physicochemical data for PCN124 (124-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.18$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.5365$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.34	5.33
GLC (c)	10t	5.353	5.315
GLC (d)	10log t	13.621	13.484
GLC (e)	I/100	17.760	17.624
GLC (f)	I/100	18.560	18.784

Table 11.16. Analysis of physicochemical data for PCN125 (125-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.18$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.6438$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.34	5.33
GLC (c)	10t	5.430	5.394
GLC (d)	10log t	13.719	13.602
GLC (e)	I/100	17.960	17.861
GLC (f)	I/100	18.840	19.014

Table 11.17. Analysis of physicochemical data for PCN126 (126-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.7029$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.34	5.33
GLC (c)	10t	5.455	5.437
GLC (d)	10log t	13.777	13.668
GLC (e)	I/100	18.020	17.992
GLC (f)	I/100	19.050	19.141

Table 11.18. Analysis of physicochemical data for PCN127 (127-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.18$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.7566$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.34	5.33
GLC (c)	10t	5.495	5.477
GLC (d)	10log t	13.825	13.727
GLC (e)	I/100	18.121	18.111
GLC (f)	I/100	19.190	19.256

Table 11.19. Analysis of physicochemical data for PCN128 (128-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.18$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.2064$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.34	5.33
GLC (c)	10t	5.836	5.807
GLC (d)	10log t	14.344	14.223
GLC (e)	I/100	18.960	18.106
GLC (f)	I/100	20.300	20.221

Table 11.20. Analysis of physicochemical data for PCN135 (135-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.5853$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t	5.283	5.280
GLC (d)	10log t	13.510	13.499
GLC (e)	I/100	17.610	17.516
GLC (f)	I/100	18.380	18.483

Table 11.21. Analysis of physicochemical data for PCN136 (136-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.18$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.5948$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t	5.283	5.287
GLC (d)	10log t	13.472	13.509
GLC (e)	I/100	17.590	17.537
GLC (f)	I/100	18.470	18.504

Table 11.22. Analysis of physicochemical data for PCN137 (137-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.6492$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t	5.330	5.327
GLC (d)	10log t	13.543	13.570
GLC (e)	I/100	17.960	17.658
GLC (f)	I/100	18.600	18.620

Table 11.23. Analysis of physicochemical data for PCN138 (138-chloronaphthalene) at 298 K; with $R_2 = 1.690$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.0412$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t	5.616	5.615
GLC (d)	10log t	14.021	14.002
GLC (e)	I/100	18.420	18.525
GLC (f)	I/100	19.560	19.461

Table 11.24. Analysis of physicochemical data for PCN145 (145-chloronaphthalene) at 298 K; with $R_2 = 1.690$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.0696$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t	5.658	5.636
GLC (d)	10log t	14.082	14.034
GLC (e)	I/100	18.520	18.588
GLC (f)	I/100	19.560	19.522

Table 11.25. Analysis of physicochemical data for PCN146 (146-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.12$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.6511$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t	5.330	5.329
GLC (d)	10log t	13.579	13.572
GLC (e)	I/100	17.720	17.662
GLC (f)	I/100	18.560	18.624

Table 11.26. Analysis of physicochemical data for PCN167 (167-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.18$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.7568$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t		
GLC (d)	10log t	13.911	13.789
GLC (e)	I/100	18.120	18.111
GLC (f)	I/100	19.160	19.256

Table 11.27. Analysis of physicochemical data for PCN236 (236-chloronaphthalene) at 298 K;

with $R_2 = 1.690$, $\pi_2^H = 1.18$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 7.8127$, $Vx = 1.4526$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.46	5.40
GLC (c)	10t		
GLC (d)	10log t	13.911	13.789
GLC (e)	I/100	18.190	18.235
GLC (f)	I/100	19.360	19.376

Table 11.28. Analysis of physicochemical data for PCN1234 (1234-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.6212$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.80	5.81
GLC (c)	10t	6.310	6.261
GLC (d)	10log t	15.022	14.940
GLC (e)	I/100	20.180	20.131
GLC (f)	I/100	21.100	21.209

Table 11.29. Analysis of physicochemical data for PCN1235 (1235-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.5406$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.239	6.202
GLC (d)	10log t	14.958	14.851
GLC (e)	I/100	20.000	19.953
GLC (f)	I/100	20.920	21.036

Table 11.30. Analysis of physicochemical data for PCN1236 (1236-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.5913$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.05	5.81
GLC (c)	10t		
GLC (d)	10log t		
GLC (e)	I/100	20.060	20.065
GLC (f)	I/100	21.150	21.145

Table 11.31. Analysis of physicochemical data for PCN1237 (1237-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.6502$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.50	5.81
GLC (c)	10t		
GLC (d)	10log t	15.007	14.972
GLC (e)	I/100	20.170	20.195
GLC (f)	I/100	21.280	21.272

Table 11.32. Analysis of physicochemical data for PCN1245 (1245-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.6742$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.05	5.81
GLC (c)	10t	6.042	6.006
GLC (d)	10log t	14.666	14.556
GLC (e)	I/100	20.290	20.248
GLC (f)	I/100	20.250	20.462

Table 11.33. Analysis of physicochemical data for PCN1246 (1246-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.2732$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.042	6.006
GLC (d)	10log t	14.666	14.556
GLC (e)	I/100	19.500	19.361
GLC (f)	I/100	20.250	20.462

Table 11.34. Analysis of physicochemical data for PCN1247 (1247-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.2732$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.042	6.006
GLC (d)	10log t	14.666	14.556
GLC (e)	I/100	19.500	19.361
GLC (f)	I/100	20.250	20.462

Table 11.35. Analysis of physicochemical data for PCN1248 (1248-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.7362$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.383	6.345
GLC (d)	10log t	15.143	15.067
GLC (e)	I/100	20.380	20.385
GLC (f)	I/100	21.410	21.456

Table 11.36. Analysis of physicochemical data for PCN1256 (1256-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.5215$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.213	6.188
GLC (d)	10log t	14.921	14.830
GLC (e)	I/100	19.930	19.910
GLC (f)	I/100	20.920	20.995

Table 11.37. Analysis of physicochemical data for PCN1257 (1257-chloronaphthalene) at 298 K; with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.2808$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.042	6.011
GLC (d)	10log t	14.666	14.565
GLC (e)	I/100	19.500	19.378
GLC (f)	I/100	20.290	20.479

Table 11.38. Analysis of physicochemical data for PCN1257 (1257-chloronaphthalene) at 298 K; with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.2808$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.042	6.011
GLC (d)	10log t	14.666	14.565
GLC (e)	I/100	19.500	19.378
GLC (f)	I/100	20.290	20.479

Table 11.39. Analysis of physicochemical data for PCN1258 (1258-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.8189$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.438	6.406
GLC (d)	10log t	15.202	15.159
GLC (e)	I/100	20.520	20.568
GLC (f)	I/100	21.650	21.633

Table 11.40. Analysis of physicochemical data for PCN1267 (1267-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.6740$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.310	6.300
GLC (d)	10log t	15.055	14.999
GLC (e)	I/100	20.180	20.248
GLC (f)	I/100	21.360	21.323

Table 11.41. Analysis of physicochemical data for PCN1268 (1268-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.8550$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.81
GLC (c)	10t	6.438	6.433
GLC (d)	10log t	15.240	15.198
GLC (e)	I/100	20.520	20.648
GLC (f)	I/100	21.820	21.711

Table 11.42. Analysis of physicochemical data for PCN1278 (1278-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.6243$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.05	5.74
GLC (c)	10t	6.670	6.650
GLC (d)	10log t	15.540	15.471
GLC (e)	I/100	21.140	21.361
GLC (f)	I/100	22.680	22.539

Table 11.43. Analysis of physicochemical data for PCN1357 (1357-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.1891$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.91	5.87
GLC (c)	10t	5.889	5.873
GLC (d)	10log t	14.417	14.425
GLC (e)	I/100	19.110	18.959
GLC (f)	I/100	19.720	19.877

Table 11.44. Analysis of physicochemical data for PCN1358 (1358-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.6686$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.18	5.87
GLC (c)	10t	6.239	6.225
GLC (d)	10log t	14.958	14.954
GLC (e)	I/100	20.000	20.020
GLC (f)	I/100	20.920	20.906

Table 11.45. Analysis of physicochemical data for PCN1367 (1367-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.5446$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.05	5.87
GLC (c)	10t		
GLC (d)	10log t	14.812	14.817
GLC (e)	I/100	19.700	19.746
GLC (f)	I/100	20.690	20.640

Table 11.46. Analysis of physicochemical data for PCN1368 (1368-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.6618$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.05	5.87
GLC (c)	10t		
GLC (d)	10log t	14.983	14.947
GLC (e)	I/100	19.930	20.005
GLC (f)	I/100	20.950	20.891

Table 11.47. Analysis of physicochemical data for PCN1458 (1458-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.5446$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.05	5.87
GLC (c)	10t	6.571	6.568
GLC (d)	10log t	15.441	15.469
GLC (e)	I/100	20.860	21.053
GLC (f)	I/100	22.120	21.907

Table 11.48. Analysis of physicochemical data for PCN1467 (1467-chloronaphthalene) at 298 K;

with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.5446$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	5.93	5.87
GLC (c)	10t	6.138	6.126
GLC (d)	10log t	14.803	14.804
GLC (e)	I/100	19.740	19.720
GLC (f)	I/100	20.590	20.614

Table 11.49. Analysis of physicochemical data for PCN2367 (2367-chloronaphthalene) at 298 K; with $R_2 = 1.810$, $\pi_2^H = 1.24$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.7990$, $Vx = 1.5750$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.05	5.81
GLC (c)	10t	6.383	6.392
GLC (d)	10log t	15.202	15.137
GLC (e)	I/100	20.430	20.524
GLC (f)	I/100	21.750	21.591

Table 11.50. Analysis of physicochemical data for PCN12345 (12345-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.6562$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	7.247	7.241
GLC (d)	10log t	16.245	16.381
GLC (e)	I/100	22.750	22.743
GLC (f)	I/100	23.990	23.993

Table 11.51. Analysis of physicochemical data for PCN12346 (12346-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.1955$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	6.972	6.903
GLC (d)	10log t	15.865	15.872
GLC (e)	I/100	21.860	21.742
GLC (f)	I/100	22.800	22.945

Table 11.52. Analysis of physicochemical data for PCN12356 (12356-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.2223$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	6.942	6.923
GLC (d)	10log t	15.892	15.902
GLC (e)	I/100	21.900	21.783
GLC (f)	I/100	22.880	23.002

Table 11.53. Analysis of physicochemical data for PCN12357 (12357-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 8.9836$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	6.776	6.747
GLC (d)	10log t	15.676	15.638
GLC (e)	I/100	21.450	21.255
GLC (f)	I/100	22.260	22.490

Table 11.54. Analysis of physicochemical data for PCN12358 (12358-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.4955$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	7.130	7.123
GLC (d)	10log t	16.131	16.203
GLC (e)	I/100	22.430	22.388
GLC (f)	I/100	23.580	23.589

Table 11.55. Analysis of physicochemical data for PCN12367 (12367-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.4037$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	7.033	7.056
GLC (d)	10log t	16.033	16.102
GLC (e)	I/100	22.170	22.185
GLC (f)	I/100	23.450	23.391

Table 11.56. Analysis of physicochemical data for PCN12368 (12368-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.5432$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	7.130	7.158
GLC (d)	10log t	16.131	16.256
GLC (e)	I/100	22.430	22.493
GLC (f)	I/100	23.830	23.691

Table 11.57. Analysis of physicochemical data for PCN12378 (12378-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.7920$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	7.367	7.414
GLC (d)	10log t	16.421	16.641
GLC (e)	I/100	23.090	23.265
GLC (f)	I/100	24.750	24.440

Table 11.58. Analysis of physicochemical data for PCN12456 (12456-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.4111$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	7.071	7.061
GLC (d)	10log t	16.058	16.110
GLC (e)	I/100	22.270	22.201
GLC (f)	I/100	23.360	23.408

Table 11.59. Analysis of physicochemical data for PCN12457 (12457-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.30$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.2247$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.76	6.28
GLC (c)	10t	6.836	6.854
GLC (d)	10log t	15.785	15.866
GLC (e)	I/100	21.680	21.573
GLC (f)	I/100	22.530	22.602

Table 11.60. Analysis of physicochemical data for PCN12458 (12458-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.5937$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.40	6.21
GLC (c)	10t	7.196	7.195
GLC (d)	10log t	16.222	16.312
GLC (e)	I/100	22.610	22.605
GLC (f)	I/100	23.840	23.799

Table 11.61. Analysis of physicochemical data for PCN12467 (12467-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.30$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.1115$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.76	6.28
GLC (c)	10t	6.776	6.771
GLC (d)	10log t	15.675	15.741
GLC (e)	I/100	21.450	21.323
GLC (f)	I/100	22.260	22.359

Table 11.62. Analysis of physicochemical data for PCN12468 (12468-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.30$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.2796$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.76	6.28
GLC (c)	10t	6.896	6.894
GLC (d)	10log t	15.833	15.926
GLC (e)	I/100	21.780	21.694
GLC (f)	I/100	22.680	22.720

Table 11.63. Analysis of physicochemical data for PCN12478 (12478-chloronaphthalene) at 298 K, with $R_2 = 1.930$, $\pi_2^H = 1.36$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 9.4620$, $Vx = 1.6974$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	6.64	6.21
GLC (c)	10t	7.106	7.099
GLC (d)	10log t	16.101	16.166
GLC (e)	I/100	22.350	22.314
GLC (f)	I/100	23.510	23.517

Table 11.64. Analysis of physicochemical data for PCN123456 (123456-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.5365$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.952	8.037
GLC (d)	10log t		
GLC (e)	I/100	24.720	24.798
GLC (f)	I/100	26.030	25.920

Table 11.65. Analysis of physicochemical data for PCN123457 (123457-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.1808$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.708	7.776
GLC (d)	10log t		
GLC (e)	I/100	24.050	24.011
GLC (f)	I/100	25.140	25.157

Table 11.66. Analysis of physicochemical data for PCN123458 (123458-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.6570$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	8.032	8.126
GLC (d)	10log t		
GLC (e)	I/100	24.930	25.065
GLC (f)	I/100	26.350	25.179

Table 11.67. Analysis of physicochemical data for PCN123467 (123467-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.0388$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.602	7.672
GLC (d)	10log t		
GLC (e)	I/100	23.780	23.697
GLC (f)	I/100	24.790	24.852

Table 11.68. Analysis of physicochemical data for PCN123567 (123567-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.0388$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.602	7.672
GLC (d)	10log t		
GLC (e)	I/100	23.780	23.697
GLC (f)	I/100	24.790	24.852

Table 11.69. Analysis of physicochemical data for PCN123568 (123568-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.1808$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.708	7.776
GLC (d)	10log t		
GLC (e)	I/100	24.050	24.011
GLC (f)	I/100	25.140	25.157

Table 11.70. Analysis of physicochemical data for PCN123578 (123578-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.2421$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.748	7.821
GLC (d)	10log t		
GLC (e)	I/100	24.150	24.147
GLC (f)	I/100	25.310	25.288

Table 11.71. Analysis of physicochemical data for PCN123678 (123678-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.7712$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t		
GLC (d)	10log t		
GLC (e)	I/100	25.050	25.318
GLC (f)	I/100	26.700	26.424

Table 11.72. Analysis of physicochemical data for PCN124568 (124568-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.2947$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.786	7.860
GLC (d)	10log t		
GLC (e)	I/100	24.250	24.263
GLC (f)	I/100	25.440	25.401

Table 11.73. Analysis of physicochemical data for PCN124578 (124578-chloronaphthalene) at 298 K, with $R_2 = 2.050$, $\pi_2^H = 1.42$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 10.2947$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.23	6.68
GLC (c)	10t	7.786	7.860
GLC (d)	10log t		
GLC (e)	I/100	24.250	24.263
GLC (f)	I/100	25.440	25.401

Table 11.74. Analysis of physicochemical data for PCN1234567 (1234567-chloronaphthalene) at 298 K, with $R_2 = 2.170$, $\pi_2^H = 1.48$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 11.3866$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.95	7.16
GLC (c)	10t	8.705	8.811
GLC (d)	10log t		
GLC (e)	I/100	26.940	26.786
GLC (f)	I/100	27.720	27.842

Table 11.75. Analysis of physicochemical data for PCN1234568 (1234568-chloronaphthalene) at 298 K, with $R_2 = 2.170$, $\pi_2^H = 1.48$, $\Sigma\alpha_2^H = 0$, $\Sigma\beta_2^H = 0.00$, $\log L^{16} = 11.3866$, $Vx = 1.8198$

System	Quantity	Obs	Calc
Water/octanol	CLOGP	7.95	7.16
GLC (c)	10t	8.705	8.811
GLC (d)	10log t		
GLC (e)	I/100	26.940	26.786
GLC (f)	I/100	27.720	27.842

A more representative PCN is PCN136, and a similar analysis is given in Table 11.21. No statistics of the fit of calculated and observed values is given, because the GLC equations are the result of an iterative procedure. However, from previous work,[36] the error in π_2^H, α_2^H, and $\Sigma\beta_2^H$ is likely to be around 0.03 units, and in $\log L^{16}$ about 0.025 units. In exactly the same way as shown in Tables 11.2 and 11.21, a final set of descriptors for all the 75 PCNs was constructed as given above.

There is an inherent difficulty in the procedure, based as it is on experimental values, in that faulty observations may lead to incorrect descriptors. However, because all the various experimental values are correlated at the same time, as shown in Table11.2, it is often possible to decide between two alternative experimental values, or to uncover an observation that is out of line. For PCN1234, values of log Poct are recorded as 5.75, 5.76, 5.93 (CLOGP) and 6.3 as shown in Table 11. 76. With log Poct taken as 5.8 a set of six equations (for six different processes) could be solved with an sd of 0.086 log units, but with log Poct as 6.3, the best

solution led to an sd of no less than 0.231 log units. Very clearly, the smaller log Poct value of 5.8 is more compatible with the other five experimental values.

11.3 Discussion

Although the descriptors change reasonably regularly with the number of chlorine atoms, there are a number of exceptions. PCNs with chlorine atoms in the 1,8-positions nearly always have larger log L^{16}- descriptors than the corresponding PCNs without the 8-substituent. In addition, the increase of 0.06 in π_2^H for adjacent chlorine atoms is never more than 0.12, no matter if there are more than two adjacent interactions. Structure-retention relationships have been developed for retention indices, I, of 62 PCNs on the DB-5 phase.[30] A four-parameter equation gave $r^2 = 0.995$ and sd = 17 I; the PCN descriptors were (1) the number of chlorine atoms, (2) a quantum chemical index obtained by subtracting the atomic heats of formation from the binding energy, (3) the spatial electronic distribution in a particular carbon atom, and (4) the minimum electronic orbital population. The correlation equation, Table 1.11 (e), gives $r^2 = 0.995$ and sd = 23 I using the standard descriptors in eqn. (11.2); note that n = 80 for the equation because values for the alkanes are included as well as the PCNs

What is more important is to compare physicochemical properties calculated from the solvation descriptors with what is known in the literature. In Table 11.76 is given a comparison of calculated log Poct values with the observed values that are available. Lei et al. [31] gave two sets of log Poct values, both obtained by an HPLC method. In the first procedure, the solute 1,3,5-trichlorobenzene was used as a reference, and the obtained log Poct values were denoted as 'experimental'; these are in Table 11.76 under heading (d). In the second procedure, the 'experimental' log Poct values were regressed against values for standard compounds and a set of

log Poct values, referred to [31] as 'calibrated' values, were deduced from the regression equation:

$$\log \text{Poct 'calibrated'} = -1.115 + 1.294 \log \text{Poct 'experimental'} \qquad (11.6)$$

These 'calibrated' values are in Table 11.76, under heading (e). Unfortunately, as was pointed out,[31] the fit to the regression line, eqn. (11.6) is very poor for 'experimental' values above about 4.5 (corresponding to 'calibrated' values above 4.7). Furthermore, eqn. ((11.6) has a very large intercept-if the regression line was forced through the origin, then the 'calibrated' values would be very close to the 'experimental' ones at high log Poct values. Interestingly, the calculated values are extraordinarily close to the 'experimental' ones. The calculated values using mobile order theory, MOD, [42] are also very close to the 'experimental' values, see Table 11.76. This difficulty over the 'calibrated' and 'experimental' values applies only to the more lipophilic PCNs. Up to and including the pentachloronaphthalenes, there is general agreement between all the log Poct values shown in Table 11.76.

There is also a recorded value [43] for the water-hexane partition coefficient for PCN12345678, 6.00 as log P_6, but this seems far too small to be realistic. The MOD method [42] also leads to a low value of 6.70 which is much lower than the predicted MOD value of 7.35 for log Poct. On the other hand, the descriptors for PCN12345678 can be used, together with the regression coefficients in Table 11.1, to predict a value of 8.00 for log P_6. This value is quite compatible with the value of 7.63 for log Poct.

Table 11.76. Comparison of calculated and observed values of log Poct

PCN	Calc [a]	Calc [b]	Calc [c]	Obs			
	CLOGP	**This work**	**Rouelle (29)**	**(d)**	**(e)**	**(f)**	
1	4.03	3.95	4.34	3.90	3.97	4.0	4.10 [g]
2	4.03	3.97	4.34	3.98	3.91	3.9	4.14 [g]
12	4.62	4.55	4.77	4.42	4.45	4.6	
14	4.74	4.62	4.77	4.66	4.57	4.8	
15	4.74	4.62	4.77	4.67			
17	4.74	4.58	4.77	4.56			
18	4.74	4.48	4.77	4.19			
23	4.74	4.55	4.77	4.51			
137	5.46	5.40	5.20	5.35			
236	5.34	5.33	5.20	5.12			
1234	5.93	5.80	5.63	5.75	5.76	6.3	
1235	6.05	5.80	5.63	5.77			
1357	6.17	5.87	5.63	6.19			
1358	6.17	5.87	5.63	5.76			
1467	6.05	5.87	5.63	5.81			
12346	6.64	6.21			6.27	7.0	
12358	6.64	6.21			6.13	6.8	
123578	7.23	6.68			6.69	7.5	
123467	7.23	6.68			6.79	7.7	
1234567	7.95	7.16			7.18	8.2	
12345678	8.54	7.63	7.35	7.80 [h]	7.46	8.5	6.42 [i]
12345678 [j]	---	8.00	6.70	6.00 [k]			

[a] From the CLOGP program.[32] [b] From the descriptors in Table 11.2-76 and the log Poct equation in Table 1.11. [c] Calculated using mobile order theory. [42] [d] By an HPLC method.[28] [e] By

an HPLC method.[31] [f] 'Calibrated values' by the HPLC method.[31] [g] Recommended values.[32] [h] A value derived from the given HPLC data in ref.c. [i] A 'shake-flask' value.[28] [j] Values in this row for water-hexane partitions. [k] Observed 'shake-flask' value.[43]

11.4 References

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Chapter 12 Estimation of some Physicochemical Properties for the Polychloronaphthalenes

12.0 Methodology

A number of aqueous solubility's for PCNs have been determined [1] and so it was of interest to obtain values of log S_W, with S_W in mol dm^{-3}, for the same PCNs using a published [2] equation. For compounds with $\Sigma\alpha_2^H = 0$ this becomes:

$$\text{Log } S_W = 0.518 - 1.00\ R_2 + 0.771\ \pi_2^H + 4.238\ \beta_2^H - 3.987\ Vx \qquad (12.1)$$

The solubilities obtained by application of the descriptors to eqn. (12.1) are actually predictions, because they are obtained without any knowledge of PCN solubilities. Results are in Table 12.1. All our values of log S_W are more positive than the observed values of Opperhuizen.[1] It makes little difference if we use the alternative [2] equation, eqn.(9 from ref 2), that includes a term in melting point. Other recorded observed values of log S_W for the monochloronaphthalenes[3] are also much more positive than those of Opperhuizen.[1] Given the possible rather large error in the determination of solubilities of very sparingly soluble compounds, the comparison in Table 12.1 is not unreasonable.

Table 12.1. Comparison of predicted (this work) and observed solubilities, as log S_W at 298 K

PCN	Pred [a]	Obs [b]
1	-4.35	-4.75 (-3.93) [c]
2	-4.39	-5.25 (-4.14) [c]
12	-5.12	-6.16
14	-5.16	-5.80
15	-5.16	-5.70
17	-5.12	-5.92
18	-5.03	-5.52
23	-5.12	-5.36
137	-6.11	-6.55
236	-6.06	-7.14
1234	-6.63	-7.80
1235	-6.63	-7.86
1357	-6.67	-7.82
1358	-6.67	-7.51
1467	-6.67	-7.52
12345678	-8.83	-9.70

[a] Predicted values from PCN descriptors and eqn.(12.1). [b] Observed values.[1]
[c] Observed values.[3]

It is also of interest to see if the descriptors in eqn. (11.2) that reproduce the various GLC retention data do also reproduce the observed gas-dry octanol partition coefficients.[4] Details are in Table 12.2; the agreement is excellent. Although this does not verify either our calculations or the accuracy of the data, it certainly indicates that there is an extraordinary self-consistency in the observed values.[4]

Table 12.2. Comparison of calculated (this work) and observed gas-dry octanol partition coefficients, as log K^{OCT}, at 298 K

PCN	Calc [a]	Obs [b]
14	6.56	6.93
124	7.28	7.27
135	7.29	7.32
145	7.74	7.56
146	7.35	7.27
1245	8.36	8.58
1246	7.98	8.08
1247	7.98	8.08
1248	8.41	8.41
1257	7.99	8.08
1258	8.49	8.40
1458	8.75	8.45
1467	8.19	8.13
12346	8.89	8.91
12357	8.69	8.73
12358	9.17	9.13
12457	8.88	8.86
12458	9.26	9.18
12467	8.77	8.73
12468	8.93	8.78
12478	9.14	9.06
123456	10.16	10.11
123457	9.82	9.80
123458	10.27	10.37
123467	9.69	9.70

123567	9.69	9.70
123568	9.82	9.80
123578	9.88	9.83
124568	9.93	9.89
124578	9.93	9.89

[a] From the descriptors in Tables (11.2-76) and the coefficients given in Table 11.1.
[b] Observed values.[4]

Finally, we can use our solvation descriptors together with already published equations, Table 11.1, to predict a number of environmentally important physicochemical properties of the PCNs, in the hope that they may be useful in cases where the experimental determination is difficult. Our predictions of gas-hexadecane partition coefficients are in Tables (11.2-11.75) because this is what the log L^{16} - descriptor refers to. We give in Table 12.3 predicted values for all 75 PCNs of water/octanol partition coefficients as log Poct, water/hexadecane partition coefficients as log P_{16}, gas/water partition coefficients as log K^{W}, gas/dry octanol partition coefficients as log K^{OCT} and molar solubilities in water as log S_W. It is a simple matter to predict numerous other properties using the coefficients for systems as shown in Table 11.1; a large number of other water-solvent and gas-solvent partitions can be predicted from the PCN descriptors and published equations.[5,6-8] Other properties of the PCNs can be predicted from the descriptors in Tables (11.2-11.75) and the various regression equations that have been published. For example, the rate of permeation of human skin from aqueous solution can easily be predicted,[9] and so can the partition of the PCNs between air and plant cuticular matrix and between water and plant cuticular matrix.[10]

Table 12.3. Predictions of some physicochemical properties of the PCNs, at 298 K

PCN	Log Poct	log P_{16} [a]	Log K^W	log K^{OCT} [b]	log S_W
1	3.95	4.09	2.00	6.89	-4.35
2	3.97	4.11	2.02	5.72	-4.39
12	4.55	4.78	2.05	5.65	-5.12
13	4.65	4.93	1.85	6.48	-5.20
14	4.62	4.88	1.89	6.56	-5.16
15	4.62	4.88	1.89	6.59	-5.16
16	4.65	4.93	1.85	6.57	-5.20
17	4.58	4.83	1.94	6.65	-5.12
18	4.48	4.68	2.14	6.98	-5.03
23	4.55	4.78	2.05	6.76	-5.12
26	4.59	4.83	2.00	6.58	-5.16
27	4.65	4.93	1.85	6.58	-5.20
123	5.24	5.60	1.93	7.44	-5.97
124	5.33	5.75	1.73	7.28	-6.06
125	5.33	5.75	1.73	7.38	-6.06
126	5.33	5.75	1.73	7.43	-6.06
127	5.33	5.75	1.73	7.48	-6.06
128	5.33	5.75	1.73	7.90	-6.06
135	5.40	5.83	1.57	7.29	-6.11
136	5.40	5.84	1.57	7.30	-6.11
137	5.40	5.84	1.57	7.35	-6.11
138	5.40	5.84	1.57	7.72	-6.11
145	5.40	5.84	1.57	7.74	-6.11
146	5.40	5.84	1.57	7.35	-6.11
167	5.33	5.75	1.73	7.48	-6.06
236	5.33	5.75	1.73	7.54	-6.06
1234	5.80	6.27	1.84	8.31	-6.63
1235	5.80	6.27	1.84	8.23	-6.63
1236	5.80	6.27	1.84	8.28	-6.63
1237	5.80	6.27	1.84	8.33	-6.63
1238	5.80	6.27	1.84	8.75	-6.63
1245	5.80	6.27	1.84	8.36	-6.63
1246	5.80	6.27	1.84	7.98	-6.63
1247	5.80	6.27	1.84	7.98	-6.63
1248	5.80	6.27	1.84	8.41	-6.63
1256	5.80	6.27	1.84	8.21	-6.63
1257	5.80	6.27	1.84	7.99	-6.63
1258	5.80	6.27	1.84	8.49	-6.63
1267	5.80	6.27	1.84	8.36	-6.63
1268	5.80	6.27	1.84	8.52	-6.63
1278	5.72	6.17	2.00	8.34	-6.58
1357	5.87	6.37	1.69	7.87	-6.67

1358	5.87	6.37	1.69	8.32	-6.67
1367	5.87	6.37	1.69	8.20	-6.67
1368	5.87	6.37	1.69	8.31	-6.67
1458	5.87	6.37	1.69	8.75	-6.67
1467	5.87	6.37	1.69	8.19	-6.67
2367	5.80	6.27	1.84	8.47	-6.63
12345	6.21	6.70	2.11	9.32	-7.14
12346	6.21	6.70	2.11	8.89	-7.14
12356	6.21	6.70	2.11	8.91	-7.14
12357	6.21	6.70	2.11	8.69	-7.14
12358	6.21	6.70	2.11	9.17	-7.14
12367	6.21	6.70	2.11	9.08	-7.14
12368	6.21	6.70	2.11	9.21	-7.14
12378	6.21	6.70	2.11	9.45	-7.14
12456	6.21	6.70	2.11	9.09	-7.14
12457	6.28	6.80	1.96	8.88	-7.19
12458	6.21	6.70	2.11	9.26	-7.14
12467	6.28	6.80	1.96	8.77	-7.19
12468	6.28	6.80	1.96	8.93	-7.19
12478	6.21	6.70	2.11	9.14	-7.14
123456	6.68	7.22	2.23	10.16	-7.70
123457	6.68	7.22	2.23	9.82	-7.70
123458	6.68	7.22	2.23	10.27	-7.70
123467	6.68	7.22	2.23	9.69	-7.70
123567	6.68	7.22	2.23	9.69	-7.70
123568	6.68	7.22	2.23	9.82	-7.70
123578	6.68	7.22	2.23	9.88	-7.70
123678	.68	7.22	2.23	10.38	-7.70
124568	6.68	7.22	2.23	9.93	-7.70
124578	6.68	7.22	2.23	9.93	-7.70
1234567	7.16	7.75	2.34	10.96	-8.27
1234568	7.16	7.75	2.34	10.99	-8.27
12345678	7.63	8.28	2.46	12.37	-8.83

[a] P_{16} is the water-hexadecane partition coefficient. [b] K^{OCT} is the gas – dry octanol partition coefficient.

Considering some of the values listed in Table 12.3, it might seem odd that log P_{16} is not very much larger than log Poct, even for the very lipophilic PCNs. However, if the coefficients in the latter equation are subtracted from the former, leaving out the a-coefficient that is irrelevant in the present case, it can be seen that:

$$\log P_{16} - \log Poct = -0.001 + 0.105\, R_2 - 0.563\, \pi_2^H - 1.409\, \Sigma\beta_2^H + 0.619\, Vx \qquad (12.2)$$

For the PCNs, $\Sigma\beta_2^H$ is quite small, never more than 0.14, and for the very lipophilic PCNs $\Sigma\beta_2^H$ is actually zero. There is partial cancellation of the ($e.R_2$ and $v.Vx$) terms by the $s.\pi_2^H$ term, to leave a positive resultant that is never very large.

The rather small values of the gas-water partition coefficient, as $\log K^W$, might suggest that this parameter is experimentally accessible. However, K^W is the ratio of two quantities, viz: the molar aqueous concentration and the molar concentration of the saturated vapor in the gas phase, both of which are so small as to render the experimental determination of K^W very difficult.

Hence the present work provides the wherewithal to estimate a number of physicochemical properties of the polychloronaphthalenes that are of environmental use and significance.

12.1 References

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Chapter 13 Calculation of the Descriptors for N-Nitrosodialkylamines

13.0 Introduction

N-Nitrosodialkylamines form a large class of genotoxic chemical carcinogens which occur in the human diet and environment. They can be also formed endogenously in human body, especially in-tragastrically. Much interest is therefore directed toward quantitation of the various N-nitroso-organic compounds (NOC) that occur in different matrices. Twenty-five years after the carcinogenicity of N-nitrosodimethylamine (NDMA) was first demonstrated,[1] scientific research in the field of N-nitroso compounds has virtually exploded. More than 1400 papers have been published annually on the analysis, formation, chemistry, biochemistry, metabolism and biological effects of N-nitroso compounds. There are many reasons for this development, the potent carcinogenicity of many N-nitroso compounds, the organ-specificity of this group of chemical carcinogens, the occurrence of certain N-nitroso compounds in the human environment and the possibility of an in vivo formation of such potent carcinogens from precursor amines and nitrosating agents.

Although N-nitroso compounds have mutagenic, [2,3,4,5] and teratogenic [6,7] activity, carcinogenicity clearly is the most important biological activity of this group of compounds. Data on carcinogenicity in experimental animals showed that about 300 different N-nitroso compounds have been tested for carcinogenicity, and about 90% of these compounds have shown carcinogenic activity.

N-nitroso compounds are important because they are often found in a large variety of food and consumer products such as meat, [8] beer, [9] cosmetics,[10] infant pacifiers, [11] and drug formulations. [12] Their widespread prevalence can be attributed to the relative ease of formation and the abundance of their amine precursors in the environment. The occurrence of N-nitroso compounds in these products is of great concern, owing to the carcinogenic properties that many of them exhibit. [13]

As was shown in the first chapter the term "correlation analysis" was first introduced in 1966. [14] Since then, interest in this type of study has grown remarkably among both basic and applied researchers. Today, research on quantitative structure-activity relationships (QSARs) is given priority by regulatory agencies and industry so that valuable and cost-effective predictions and environmental chemical.[15] N-nitroso compounds, in general, and nitrosoamines, in particular, attract a great deal of interest with regard to QSAR studies for several reasons. (1) They have carcinogenic,[16,17] mutagenic,[18] and teratogenic [19] potential in numerous animal species, including primates. (2) It is well-known [20, 21] that the incidence of cancer in humans is associated not so much with direct contact with these chemical species as with the formation mechanisms that occur prior to their action (therefore, this is a subject of utmost importance in food science and technology[22]). As a consequence, in addition to interest in kinetics, research on the mechanisms of formation of nitroso compounds [23-26] and their biochemical decomposition [27-28] is increasing. (3) It is a proven fact that nitosoamines are well suited as a subject for free energy correlations. [29]

A number of physicochemical properties of N-nitrosodialkylamines have been reported. The evaluation of the carcinogenicity of a large number of NOCs towards the

liver of the rat,[30] also the determination of aqueous solubility, and water–hexane partition coefficients. Mirvish et al [31] measured water-ether and air–water partition coefficients, and showed that many N-nitrosodialkylamines were volatilized from aqueous solution. The water-solvent partition coefficients for fourteen alpihatic N-nitrosodialklamines in six systems have been determined;[32] these values were given in terms of mol fraction, but were later converted [33] to the more usual standard state of mol dm^{-3}. It is the aim of this work to obtain, from the available physicochemical data, chemical properties or ' descriptors' that can then be used to estimate all kinds of other physicochemical data, and especially those employed in environmental analyses.

13.1 Using LFER to calculated the descriptors for N-Nitroso dialkylamines

The majority of the analytical methods for detection of N-nitrosodialkylamines, have employed gas chromatography (GC) or liquid chromatography (LC) in conjunction with detectors based on a thermal energy analyzer (TEA),[34] which relies on the pyrolytic break down of N-NO moieties to release the nitrosyl radical. The disadvantage of these techniques, however, is that a subsequent confirmation is needed to ensure that the method does not give rise to false-positive response. [34] These techniques however, are often unreliable and can suffer from a significant loss in sensitivity, [35] however, they do furnish quantitative data that can be used.

The LFER that will be used is the same as that previously introduced in chapter two:

$$\text{Log SP} = c + r.\, R_2 + s.\pi_2^{H} + \alpha.\, \Sigma\alpha_2^{H} + b.\, \Sigma\beta_2^{H} + v.\, V_x \qquad (13.1)$$

Here SP is a set of solute properties, such as relative biological activity (RBA) or a partition coefficient, P, in a given system. The main descriptors are: π_2^H the solute dipolarity/polarizability,[36] $\Sigma\alpha_2^H$ the solute hydrogen bond acidity,[37] $\Sigma\beta_2^H$ the solute hydrogen bond basicity,[38] and V_x the McGowan intrinsic volume [39] of the solute; all these have been mentioned in previous chapters.

The excess molar refraction, and the intrinsic volume can be easily calculated, and so for any solute, there remain three descriptors which need to be calculated, or estimated in some way. One method of estimating the parameters is through the use of partition coefficients. The partition coefficients of each of the compounds in each of at least three systems needs to be measured. Usually the partition coefficients of the systems water-octanol, water-trichloromethane, and water-cyclohexane are used because these provide a good spread of coefficients in equation (13.1). However, if more systems are available, they can all be used. Reference equations are given as shown in Table (13.1);

Table (13.1) The LFER coefficients for water-solvent partitions

Solvent	C	r	S	a	b	v	n	r^2	sd
Isobutanol	0.249	0.480	-0.639	-0.050	-2.284	2.758	35	0.9903	0.119
Octanol	0.081	0.585	-1.090	0.033	-3.401	3.810	584	0.9965	0.133
n-Butyl aceate	-0.468	0.712	-0.397	0.010	-3.743	3.865	47	0.9892	0.152
Diethyl ether	0.462	0.571	-1.035	-0.024	-5.508	4.346	84	0.9897	0.195
Nitrobenzene	-0.181	0.576	0.003	-2.356	-4.420	4.263	84	0.9913	0.172
Chlorobenzene	0.046	0.259	-0.466	-3.047	-4.819	4.660	93	0.9973	0.115
Benzene	0.017	0.490	-0.604	-3.301	-4.628	4.587	112	0.9953	0.119

Toluene	0.015	0.594	-0.781	-2.918	-4.517	4.533	87	0.9957	0.114
Olive oil	-0.086	0.575	-0.861	-1.447	-4.945	4.295	111	0.9972	0.129
Choroform	0.125	0.118	-0.372	-3.390	-3.467	4.521	112	0.9972	0.112
Teteachloromethane	0.223	0.564	-1.151	-3.510	-4.536	4.501	111	0.9980	0.102
Cyclohexane	0.124	0.844	-1.800	-3.727	-4.923	4.692	152	0.9955	0.155
Alkane	0.281	0.647	-1.687	-3.520	-4.848	4.326	173	0.9982	0.120
Hexadecane	0.103	0.686	-1.624	-3.566	-4.880	4.444	366	0.9983	0.123
Gasphase	1.003	-0.630	-2.469	-3.901	-4.843	0.852	353	0.9967	0.160
Diisopropylether	0.179	0.695	-1.220	-0.238	-4.921	4.388	27	0.9901	0.241

For example, the equation for partition in the system water-cyclohexane [40] is;

$$\text{Log P(cyc)} = 0.127 + 0.816\, R_2 - 1.731\, \pi_2^H - 3.77\, \Sigma\, \alpha_2^H - 4.905\, \Sigma\, \beta_2^H + 4.646\, V_x$$

n =170 r = 0.9968 sd = 0.121 F =5123 (13.3)

Here, n = number of data points, r = overall correlation coefficient, sd = overall standard deviation and F= Fisher F-statistic.

13.2 Methods for characterization of water-solvent systems

Although a large number of water-solvent partition systems had been characterized, it was thought useful to characterize some additional systems. The values of the partition coefficients, as log P, for a series of compounds in a given water-solvent system were obtained from the MedChem data base, and entered into a standard multiple linear regression program. The regression program produced a linear equation of the form of equation (13.1). It also produced a calculated log P value for each compound, together with the compound descriptors.

13.3 Characterization of some new water-solvent systems

13.3.1 The Water–Tributylphosphate system

Values of log P for a series of solutes in various given systems were obtained from the Medical Chemistry project of Pomona. The data is listed in Table 13.2

Table (13.2) Solutes, their descriptors and values of log P(obs) and log P(calc) for the Water-Tributylphosphate system.

Compound Name	R_2	π_2^H	α_2^H	β_2^H	V_x	Log P obs	Log Pcalc
Butan-1-ol	0.224	0.420	0.370	0.480	0.730900	1.140	1.134
Pentanoic acid	0.205	0.600	0.600	0.450	0.887500	1.950	2.069
2-Ethoxyethanol	0.237	0.500	0.300	0.830	0.789600	-0.300	-0.406
Formic acid	0.300	0.790	0.720	0.340	0.323900	0.470	0.332
3-Methylbutanoic acid	0.178	0.570	0.600	0.490	0.887500	1.890	1.887
Pentan-1-ol	0.219	0.420	0.370	0.480	0.871800	1.630	1.712
Acetic acid	0.265	0.650	0.610	0.440	0.464800	0.140	0.389
Methanol	0.278	0.440	0.430	0.470	0.308200	-0.670	-0.455
p-Toluidine	0.923	0.950	0.230	0.450	0.957100	1.970	2.118
Maleic acid	0.450	1.000	0.850	0.760	0.778000	0.330	0.376
Ethylamine	0.236	0.350	0.160	0.610	0.490200	-0.300	-0.686
Hexan-1-ol	0.210	0.420	0.370	0.480	1.012700	2.430	2.286
Succinic acid	0.370	1.360	0.850	0.700	0.821000	0.760	0.457
Chloroacetic acid	0.373	1.080	0.740	0.360	0.587000	1.150	1.162
Ethanol	0.246	0.420	0.370	0.480	0.449100	-0.250	-0.012
2-Butoxyethanol	0.201	0.500	0.300	0.830	1.071400	0.570	0.729
Propanoic acid	0.233	0.650	0.600	0.450	0.605700	0.920	0.885
Aniline	0.955	0.960	0.260	0.410	0.816200	1.550	1.780
Propylamine	0.225	0.350	0.160	0.610	0.631100	0.280	-0.113

Heptan-1-ol	0.211	0.420	0.370	0.480	1.153600	2.740	2.869
Propan-1-ol	0.236	0.420	0.370	0.480	0.590000	0.430	0.562
Butanoic acid	0.210	0.620	0.600	0.450	0.746600	1.410	1.474
2-Aminophenol	1.110	1.100	0.600	0.660	0.874900	1.530	1.337
Oxygen	0.000	0.000	0.000	0.000	0.183000	0.400	0.771
Butylamine	0.224	0.350	0.160	0.610	0.772000	0.580	0.468
2-Propoxyethanol	0.212	0.500	0.300	0.830	0.930500	0.000	0.156
Argon	0.000	0.000	0.000	0.000	0.190000	0.756	0.799
Carbon dioxide	0.000	0.280	0.050	0.100	0.280900	0.578	0.538
Methane	0.000	0.000	0.000	0.000	0.249500	1.096	1.045
Ethane	0.000	0.000	0.000	0.000	0.390400	1.740	1.627
Propane	0.000	0.000	0.000	0.000	0.531300	2.398	2.209
Butane	0.000	0.000	0.000	0.000	0.672200	2.935	2.790
Ethene	0.107	0.100	0.000	0.070	0.347400	1.317	1.124
Buta-1,3-diene	0.320	0.230	0.000	0.100	0.586200	2.132	2.029
Ammonia	0.139	0.350	0.140	0.620	0.208400	-2.297	-2.001
Phenol	0.805	0.890	0.600	0.300	0.775100	2.650	2.534
2-Methylphenol	0.840	0.860	0.520	0.300	0.916000	3.060	3.059
3-Methylphenol	0.822	0.880	0.570	0.340	0.916000	3.020	2.911
4-Methylphenol	0.820	0.870	0.570	0.310	0.916000	3.000	3.057
2,3-Dimethylphenol	0.850	0.810	0.530	0.360	1.056900	3.360	3.427
2,4-Dimethylphenol	0.843	0.800	0.530	0.390	1.056900	3.230	3.290
2,5-Dimethylphenol	0.840	0.790	0.540	0.370	1.056900	3.300	3.403
2,6-Dimethylphenol	0.860	0.790	0.390	0.390	1.056900	3.410	3.118
3,4-Dimethylphenol	0.830	0.860	0.560	0.390	1.056900	3.040	3.270
3,5-Dimethylphenol	0.820	0.840	0.570	0.360	1.056900	3.220	3.432
2-Ethylphenol	0.831	0.840	0.520	0.370	1.056900	3.450	3.325
3-Ethylphenol	0.810	0.910	0.550	0.370	1.056900	3.380	3.290
4-Ethylphenol	0.800	0.900	0.550	0.360	1.056900	3.200	3.337
4-Propylphenol	0.793	0.880	0.550	0.370	1.197800	3.600	3.884
4-Hydroxybenzoic acid	0.930	0.920	0.870	0.530	0.990400	3.260	2.804

The regression for the Water-Tributylphosphate system produced the following equation.

$$\text{Log } P = 0.015 + 0.804\, R_2 - 0.862\pi_2^H + 1.389\, \Sigma\, \alpha_2^H - 4.647 \Sigma\, \beta_2^H + 4.129\, V_x$$

n = 50 r = 0.9906 sd = 0.200 F = 460.5 (13.4)

For this regression, seven compound data sets were deleted. The compounds that were deleted were those whose standard deviations of log P calc-log P obs. were greater than two regression standard deviations. An output for the values of log P obs, log Pcalc, the coefficients and the statistics are shown in Tables (13.2) and (13.3). The values of the T-Test for all coefficients were between (0.99-1.0). It therefore seemed that the overall parameter relationship produced a good linear relationship.

Table (13.3) The regression output for the water-tributylphosphate system

VAR:	R_2	π_2^H	α_2^H	β_2^H	V_x
π_2^H	0.802				
α_2^H	0.559	0.859			
β_2^H	0.187	0.474	0.474		
V_x	0.681	0.620	0.518	0.404	
log Pobs	0.623	0.351	0.280	-0.335	0.704

VAR:	R_2	π_2^H	α_2^H	β_2^H	V_x	CONST
COEFFS	0.804	-0.862	1.389	-4.647	4.129	0.015
ST.DEV	0.191	0.273	0.248	0.169	0.147	0.085
T	4.200	3.155	5.593	27.492	28.005	0.175
TTEST	0.99987	0.99711	1.00000	1.00000	1.00000	0.82600

OVERALL.COR.COE FF	0.99060
ST.DEV.LOG POBS-LOG PCALC	0.200
DEGREES-FREEDOM	44.00
F-STATISTIC	460.500
NO.OF POINTS	50.00

A plot of log Pobs. vs log Pcalc. Is shown in Figure (13.1)

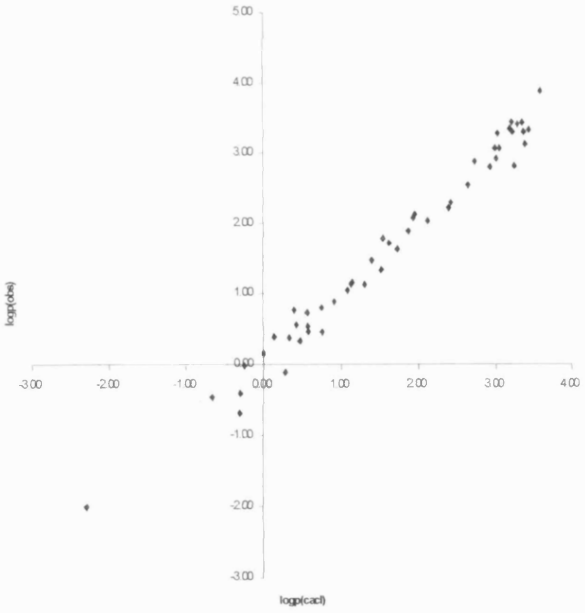

Figure 13.1 plot of log P(obs) versus log P(calc) for the Water-Tributylphosphate system

$$\log Sw = 0.518 - 1.004\ R_2 + 0.771\ \pi_2^H + 2.168\ \Sigma\ \alpha_2^H + 4.238\ \Sigma\ \beta_2^H - 3.362\ \Sigma\ \alpha_2^H * \Sigma\beta_2^H - 3.987\ V_x$$

$$n = 659, \quad sd = 0.557, \quad r^2 = 0.920, \quad F = 1256, \quad AAN = 0.408 \qquad (9.6)$$

Abraham and Le [28] considered that equation 9.6 was the best equation that had been constructed from the general solvation descriptors. They concluded that equation 9.6 which contains the extra $\Sigma\ \alpha_2^H * \Sigma\ \beta_2^H$ term, can correlate and predict log Sw values to 0.561 log units.

In the present calculations for log Sw, equation 9.6 will be used. However, since PCBs have no hydrogen bond acidity the two terms containing $\Sigma\alpha_2^H$ will be redundant. Then equation 9.6 becomes,

$$\text{Log } Sw = 0.518 - 1.004\ R_2 + 0.771\pi_2^H + 4.238\Sigma\ \beta_2^H - 3.987\ Vx \qquad (9.7)$$

The log Sw values for the 136 PCBs, were first calculated using the descriptors calculated in this work, and are compared with the experimental data obtained from the literature by Patil,[32] and with the predicted values also obtained by Patil. The latter were based on a multilinear regression analysis that was carried out on the observed log Sw values for 136 PCBs congeners.[32] The regression analysis gave the following equation,

4-Hydroxy-3-methoxybenzaldehyd	1.040	1.040	0.320	0.670	1.131300	0.810	1.057
Heptan-1-ol	0.211	0.420	0.370	0.480	1.153600	1.790	1.668
Propan-1-ol	0.236	0.420	0.370	0.480	0.590000	-0.800	-0.888
4-Nitroaniline	1.220	1.910	0.420	0.380	0.990400	1.510	1.175
2-Hydroxybenzoic acid	0.890	0.700	0.720	0.410	0.990400	0.100	0.264
4-Ethylphenol	0.800	0.900	0.550	0.360	1.056900	1.240	1.265
3-Chlorophenol	0.909	1.060	0.690	0.150	0.897500	0.930	1.003
4-Iodophenol	1.380	1.220	0.680	0.200	1.033300	1.550	1.593
Pentan-2,4-dione	0.412	0.560	0.000	0.790	0.844500	0.790	0.172
2-Furaldehyde	0.690	1.200	0.000	0.440	0.692900	0.770	0.973
5-Methylfurfural	0.744	1.100	0.000	0.550	0.833900	1.200	1.178
3,4-Dimethylphenol	0.830	0.860	0.560	0.390	1.056900	1.120	1.123
2,4-Dimethylphenol	0.843	0.800	0.530	0.390	1.056900	1.160	1.251
2,5-Dimethylphenol	0.840	0.790	0.540	0.370	1.056900	1.330	1.308
3,5-Dimethylphenol	0.820	0.840	0.570	0.360	1.056900	1.170	1.226
Ethyl acetate	0.106	0.620	0.000	0.450	0.746600	1.080	1.097
1-Naphthol	1.520	1.050	0.600	0.370	1.144100	1.800	1.725
Pentyl acetate	0.067	0.600	0.000	0.450	1.169300	2.860	3.011
2,4-Dichlorophenol	0.960	0.840	0.530	0.190	1.019900	1.900	2.022
Helium	0.000	0.000	0.000	0.000	0.068000	0.118	0.183
Neon	0.000	0.000	0.000	0.000	0.085000	0.218	0.261
Argon	0.000	0.000	0.000	0.000	0.190000	0.665	0.739
Krypton	0.000	0.000	0.000	0.000	0.246000	0.937	0.994
Xenon	0.000	0.000	0.000	0.000	0.329000	1.372	1.373
Hydrogen	0.000	0.000	0.000	0.000	0.108600	0.415	0.368
Deuterium	0.000	0.000	0.000	0.000	0.110000	0.442	0.375
Oxygen	0.000	0.000	0.000	0.000	0.183000	0.661	0.707
Nitrogen	0.000	0.000	0.000	0.000	0.222200	0.665	0.886
Carbon dioxide	0.000	0.280	0.050	0.100	0.280900	0.343	0.442
Methane	0.000	0.000	0.000	0.000	0.249500	1.035	1.010
Ethane	0.000	0.000	0.000	0.000	0.390400	1.788	1.652
Propane	0.000	0.000	0.000	0.000	0.531300	2.482	2.294

Octane	0.000	0.000	0.000	0.000	1.235800	5.846	5.504
Ethene	0.107	0.100	0.000	0.070	0.347400	1.318	1.158
Tetrafluoromethane	-0.280	-0.200	0.000	0.000	0.320300	1.141	1.271
Chloromethane	0.249	0.430	0.000	0.080	0.371900	1.187	1.181
Iodoethane	0.640	0.400	0.000	0.150	0.648600	2.551	2.314
Dimethylether	0.000	0.270	0.000	0.410	0.449100	0.138	-0.013
1,4-Dioxane	0.329	0.750	0.000	0.640	0.681000	0.122	0.002
Butanone	0.166	0.700	0.000	0.510	0.687900	0.498	0.560
Triethylamine	0.101	0.150	0.000	0.790	1.053800	0.902	1.119
Nitromethane	0.313	0.950	0.060	0.310	0.423700	0.089	0.037
Ethanol	0.246	0.420	0.370	0.480	0.449100	-1.434	-1.525
Sulfur hexafluoride	-0.600	-0.200	0.000	0.000	0.464300	1.741	1.782
Toluene	0.601	0.520	0.000	0.140	0.857300	3.136	3.253

For this system, the following equation was obtained.

$$\text{Log P} = -0.126 + 0.455\, R_2 - 0.327\, \pi_2^H - 3.407\Sigma\, \alpha_2^H - 4.497\Sigma\beta_2^H + 4.556\, V_x$$

n = 64 r = 0.9906 sd = 0.161 F= 611 (13.5)

Five data points were deleted form the regression to get a good value for correlation coefficient as shown in Table (13.5); the compounds that were deleted were those that had standard deviations greater than twice those of the regression equation. An output for the values of log Pobs, log Pcalc is shown in Table 13.4 and statistics are given in Table 13.5. A plot of log Pobs vs. log Pcalc. was made; see Figure (13.2).

Table (13.5) The regression output for the Water-Bromobenzene system

VAR:	R_2	π_2^H	α_2^H	β_2^H	V_x
π_2^H	0.862				
α_2^H	0.729	0.633			
β_2^H	0.282	0.453	0.227		
V_x	0.667	0.668	0.582	0.589	
Yobs	0.148	0.019	-0.149	-0.329	0.387

VAR	R_2	π_2^H	α_2^H	β_2^H	V_x	CONST
COEFFS	0.455	-0.33	-3.41	-4.497	4.556	0.126
ST.DEV	0.102	0.10	0.12	0.115	0.099	0.050
T	4.474	3.33	29.24	39.006	45.867	2.517
TTEST	0.9996	0.9980	1.0000	1.0000	1.0000	0.9857

OVERALL.COR.COEFF		0.9906
ST.DEV.LOGPOBS-LOG PCALC		0.161
DEGREES-FREEDOM	58.00	
F-STATISTIC	611.00	
NO.OF POINT	64.00	

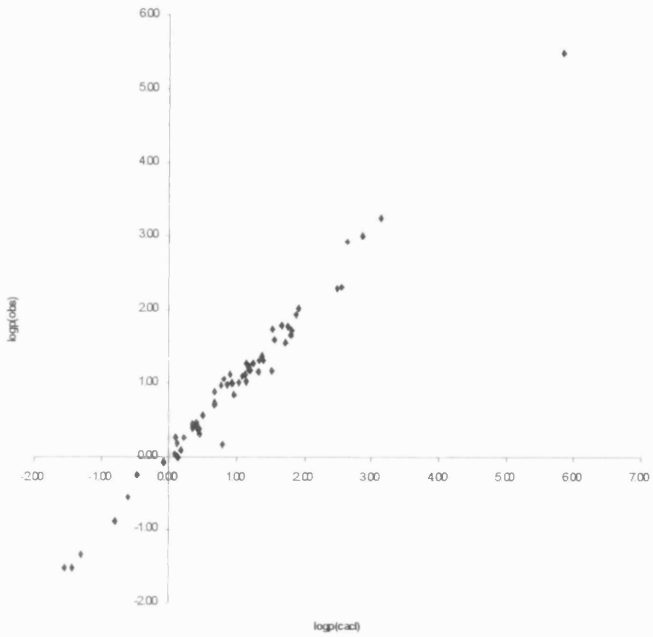

Figure 13.2 A plot of log P(obs) vs log P(calc) for the Water-Bromobenzene system

13.3.3 The Water-Iodobenzene system

The third regression was for the Water-Iodobenzene system. The data are in Table 13.6, where log P values were again from the MedChem data base.

Table (13.6) Solutes, their descriptors and the values of log Pobs and log Pcalc for the Water-Iodobenzene system

Compound Name	R_2	π_2^H	α_2^H	β_2^H	V_x	Log P obs	log P calc
Butan-1-ol	0.224	0.420	0.370	0.480	0.730900	-0.490	-0.335
4-Chlorophenol	0.915	1.080	0.670	0.200	0.897500	0.900	0.783

2-Naphthol	1.520	1.080	0.610	0.400	1.144100	1.510	1.451
Methyl 2-hydroxybenzoate	0.850	0.840	0.040	0.460	1.131300	2.690	2.776
5-Methylfurfural	0.744	1.100	0.000	0.550	0.833900	1.090	1.037
2-Methylphenol	0.840	0.860	0.520	0.300	0.916000	0.930	0.946
1-Naphthol	1.520	1.050	0.600	0.370	1.144100	1.730	1.630
3-Methylphenol	0.822	0.880	0.570	0.340	0.916000	0.400	0.585
2-Furaldehyde	0.690	1.200	0.000	0.440	0.692900	0.690	0.847
2-Fluorophenol	0.660	0.690	0.610	0.260	0.792800	0.400	0.255
Pentan-1-ol	0.219	0.420	0.370	0.480	0.871800	0.400	0.293
Ethyl 2-hydroxybenzoate	0.802	0.990	0.120	0.350	1.272200	3.400	3.569
2-Chlorophenol	0.853	0.880	0.320	0.310	0.897500	1.320	1.477
3,5-Dimethylphenol	0.820	0.840	0.570	0.360	1.056900	1.080	1.137
Butylamine	0.224	0.350	0.160	0.610	0.772000	-0.120	-0.025
Methanol	0.278	0.440	0.430	0.470	0.308200	-2.150	-2.359
4-Bromophenol	1.080	1.170	0.670	0.200	0.950100	0.970	1.063
2-Nitroaniline	1.180	1.370	0.300	0.360	0.990400	1.780	1.716
Ethylamine	0.236	0.350	0.160	0.610	0.490200	-1.300	-1.279
2-Iodophenol	1.360	1.000	0.400	0.350	1.033300	1.840	1.828
Hexan-1-ol	0.210	0.420	0.370	0.480	1.012700	0.990	0.918
Propyl 2-hydroxybenzoate	0.793	0.900	0.140	0.350	1.413100	4.100	4.159
2,4-Dichlorophenol	0.960	0.840	0.530	0.190	1.019900	1.830	1.937
2-Bromophenol	1.037	0.900	0.350	0.310	0.950100	1.640	1.689
3-Nitrophenol	1.050	1.570	0.790	0.230	0.949300	0.220	0.382
Phenol	0.805	0.890	0.600	0.300	0.775100	0.100	0.027
Propylamine	0.225	0.350	0.160	0.610	0.631100	-0.620	-0.654
Heptan-1-ol	0.211	0.420	0.370	0.480	1.153600	1.680	1.548
Propan-1-ol	0.236	0.420	0.370	0.480	0.590000	-0.960	-0.959
4-Nitroaniline	1.220	1.910	0.420	0.380	0.990400	1.350	1.069
3-Chlorophenol	0.909	1.060	0.690	0.150	0.897500	0.860	0.948
4-Iodophenol	1.380	1.220	0.680	0.200	1.033300	1.500	1.521
Butylamine	0.224	0.350	0.160	0.610	0.772000	-0.120	-0.025
3,5-Dimethylphenol	0.820	0.840	0.570	0.360	1.056900	1.080	1.137

Helium	0.000	0.000	0.000	0.000	0.068000	-0.065	0.135
Neon	0.000	0.000	0.000	0.000	0.085000	0.019	0.211
Argon	0.000	0.000	0.000	0.000	0.190000	0.506	0.680
Krypton	0.000	0.000	0.000	0.000	0.246000	0.781	0.931
Xenon	0.000	0.000	0.000	0.000	0.329000	1.257	1.302
Oxygen	0.000	0.000	0.000	0.000	0.183000	0.550	0.649
Methane	0.000	0.000	0.000	0.000	0.249500	0.845	0.946
Ethane	0.000	0.000	0.000	0.000	0.390400	1.785	1.576
Propane	0.000	0.000	0.000	0.000	0.531300	2.757	2.206
Chloromethane	0.249	0.430	0.000	0.080	0.371900	1.143	1.101
Iodoethane	0.640	0.400	0.000	0.150	0.648600	2.555	2.207
Dimethylether	0.000	0.270	0.000	0.410	0.449100	0.091	-0.109
1,4-Dioxane	0.329	0.750	0.000	0.640	0.681000	-0.078	-0.126
Butanone	0.166	0.700	0.000	0.510	0.687900	0.380	0.437
Triethylamine	0.101	0.150	0.000	0.790	1.053800	0.820	0.957
Nitromethane	0.313	0.950	0.060	0.310	0.423700	-0.020	-0.052
Ethanol	0.246	0.420	0.370	0.480	0.449100	-1.500	-1.584
Toluene	0.601	0.520	0.000	0.140	0.857300	3.140	3.127

An output for the values of log Pobs and log Pcalc is in Table 13.6. The regression equation was found as,

$$\text{Log P} = -0.169 + 0.453\, R_2 - 0.332\, \pi_2^H - 3.295\, \Sigma\, \alpha_2^H - 4.532\, \Sigma\beta_2^H + 4.469\, V_x$$

n = 52 r = 0.9922 sd = 0.150 F =584.6 (13.6)

For this regression, five compound data sets needed to be deleted to get a good value for the correlation coefficient, as shown in Table (13.7). From the value of the T-Test, all five descriptors were significant; it therefore seemed that the overall parameter relationship produced a good linear relationship. The statistics are in Table 13.7, and a plot of log Pobs. vs log Pcalc. Is shown in Figure (13.3).

Table (13.7) Regression output for the Water-Iodobenzene system

VAR:	R_2	π_2^H	α_2^H	β_2^H	V_x
π_2^H	0.871				
α_2^H	0.681	0.606			
β_2^H	0.099	0.250	0.098		
V_{Xx}	0.734	0.684	0.534	0.452	
Yobs	0.397	0.235	-0.094	-0.304	0.530

VAR:	R_2	π_2^H	α_2^H	β_2^H	V_x	CONST
COEFFS	0.453	-0.332	-3.295	-4.532	4.469	-0.169
ST.DEV	0.127	0.105	0.117	0.138	0.121	0.059
T	3.561	3.165	28.229	32.755	37.083	2.883
TTEST	0.99913	0.99725	1.00000	1.00000	1.00000	0.99403

OVERALL.COR.COEFF 0.9922
ST.DEV.LOGPOBS-LOG PCALC 0.158
DEGREES-FREE 46.00

F- STATISTIC 584.60
NO.OF POINTS 52

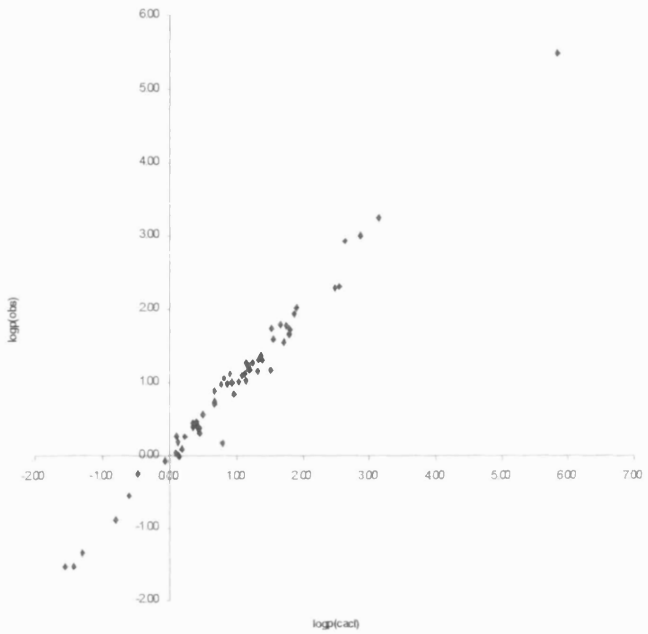

Figure 13.3 A plot of log P(obs) versus log P(calc) for the Water-Iodobezene system

13.3.4 The Water-Diisopropylether system

The last regression was for the Water-Diisopropylether system using data for 82 compounds as shown in Table 13.8

Table (13.8) solutes, their descriptors and values of log P(obs) and log P(calc) for the Water-Diisopropylether system

Compound Name	R_2	π_2^H	α_2^H	β_2^H	V_x	LogP obs	Log P calc
Catechol	0.970	1.0700	0.8500	0.5200	0.8338	0.6500	0.464
2-Naphthylamine	1.670	1.2800	0.2200	0.5500	1.1850	2.1500	2.238
Pentanoic acid	0.205	0.6000	0.6000	0.4500	0.8875	1.0500	1.145
5-Methylfurfural	0.744	1.1000	0.0000	0.5500	0.8339	0.6300	0.325
2-Furaldehyde	0.690	1.2000	0.0000	0.4400	0.6929	0.3000	0.088
Pyridine	0.631	0.8400	0.0000	0.5200	0.6753	0.1300	0.015
Diethylamine	0.154	0.3000	0.0800	0.6900	0.7720	-0.2100	-0.089
Formaldehyde	0.220	0.7000	0.0000	0.3300	0.2652	-1.2600	-0.964
Butylamine	0.224	0.3500	0.1600	0.6100	0.7720	-0.0400	0.273
1-Naphthylamine	1.670	1.2600	0.2000	0.5700	1.1850	2.1500	2.168
Formic acid	0.300	0.7900	0.7200	0.3400	0.3239	-0.8100	-0.981
1-Naphthol	1.520	1.0500	0.6000	0.3700	1.1441	3.3800	3.030
4-Hydroxybenzaldehyde	1.010	1.5400	0.7900	0.4000	0.9317	0.8400	0.952
Butanoic acid	0.210	0.6200	0.6000	0.4500	0.7466	0.3900	0.506
Hexanoic acid	0.174	0.6000	0.6000	0.4500	1.0284	1.4800	1.742
Hydroquinone	1.000	1.0000	1.1600	0.6000	0.8338	0.0700	0.103
5-Ethyl-5-(2-pentyl)barbital	1.030	1.1100	0.4700	1.2300	1.7966	1.6900	1.278
Naphthalene	1.340	0.9200	0.0000	0.2000	1.0854	3.5500	3.785
Acetic acid	0.265	0.6500	0.6100	0.4400	0.4648	-0.6100	-0.683
Trimethylamine	0.140	0.2000	0.0000	0.6700	0.6311	-0.3600	-0.477
Estrone	1.730	3.1000	0.5600	0.9100	2.1558	2.3000	2.466
Phenol	0.805	0.8900	0.6000	0.3000	0.7751	1.3200	1.453
Propanoic acid	0.233	0.6500	0.6000	0.4500	0.6057	-0.0600	-0.133
Cocaine	1.355	1.9200	0.0000	1.5000	2.2977	1.1900	1.498
Estradiol	1.800	3.3000	0.8800	0.9500	2.1988	2.3000	2.187
Aniline	0.955	0.9600	0.2600	0.4100	0.8162	0.8600	1.192
Caffeine	1.500	1.6000	0.0000	1.3300	1.3632	-1.1900	-1.275
Octane	0.000	0.0000	0.0000	0.0000	1.2358	5.9520	5.620
1,4-Dioxane	0.329	0.7500	0.0000	0.6400	0.6810	-0.4960	-0.651
Butanone	0.166	0.7000	0.0000	0.5100	0.6879	0.1230	-0.033
Nitromethane	0.313	0.9500	0.0600	0.3100	0.4237	-0.1440	-0.425
Ethanol	0.246	0.4200	0.3700	0.4800	0.4491	-0.9980	-0.624
Toluene	0.601	0.5200	0.0000	0.1400	0.8573	2.9170	3.053

The following equation was produced. An output for the values of log P obs. and log Pcalc. is in Table 13.8, above.

$$\text{Log } P = 0.197 + 0.695\, R_2 - 1.220\, \pi_2^H - 0.238\, \Sigma\, \alpha_2^H - 4.921 \Sigma\, \beta_2^H + 4.388\, V_x$$

n = 33 r = 0.9901 sd = 0.241 F = 267.6 (13.7)

For this regression, seven compounds were deleted to get a good value for correlation coefficient, as shown in Table (13.9). The statistics are given in Table 13.9, and a plot of log Pobs vs log Pcalc is shown in Figure (13.4)

Table (13.9) Regression output for the Water –Diisopropylether system

VAR:	R_2	π_2^H	α_2^H	β_2^H	V_x
π_2^H	0.791				
α_2^H	0.182	0.2840			
β_2^H	0.451	0.5480	-0.0100		
V_x	0.708	0.7490	0.1040	0.6680	
Log Pobs	0.369	0.1600	-0.0020	-0.2330	0.5220

VAR:	R_2	π_2^H	α_2^H	β_2^H	V_x
COEFFS	0.695	-1.2200	-0.2380	-4.9210	4.3880
ST.DEV	0.128	0.1170	0.1340	0.1830	0.1500
T	5.417	10.3950	1.7770	26.8550	29.3010
TTEST	0.99999	1.00000	0.91320	1.00000	1.00000

OVERALL.COR. COEFF	0.99010
ST.DEV.LOG POBS-LOGP CALC	0.241
DEGREES-FREEDOM	27.00
F-STATISTIC	267.600
N0. OF POINTS	33

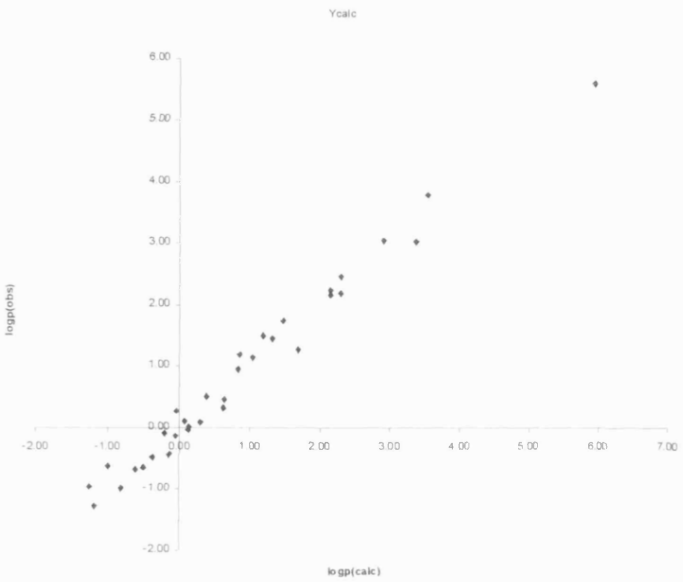

Figure 13. 4 A plot of log P(obs) versus log P(calc) for the Water - Diisopropylether system

13.4 The calculation of parameters (π,β), for N-Nitrosodialkylamines

A spreadsheet was set up which contained the coefficients (c, r, s, a, b) for a large number of systems see Table (13.1) . As noted before, the parameters R_2 and V_x can always be obtained and so only π_2^H, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ are unknown. For the N-nitrosodialkylamines, (R1 R2 N-NO) $\Sigma\alpha_2^H$ is zero because they have no hydrogen - bond acidity ,and so only π_2^H and $\Sigma\beta_2^H$ need to be determined. In Table (13.10) is an example of the calculation for N-nitrosodimethylamine. Values of log P are known for eight systems, and the π_2^H and $\Sigma\beta_2^H$ values that best reproduced these eight log P values were

obtained by trial -and-error. As best-fit criterion the smallest standard deviation between log P(calc) and log P(obs) was used.

Table (13.10) Calculation of descriptors for N-nitrosodimethylamine

R = 0.393		count :	8
π=1.080			
α= 0.000		sd (n-1) :	0.133
β = 0.564			
Vx = 0.6057		N-Nitrosodimethylamine	

	Log Pcalc	Log Pobs
avg:	-0.096	-0.119

Solvent	Log Pcalc	Log Pcalc	Log Pobs	(Po -Pc)^2
Octanol	-0.471	-0.471	-0.570	0.010
Gas-octanol	4.190	4.190	4.130	0.004
Diisopropylether	-0.975	-0.975	-0.870	0.011
Diethyl ether	-0.875	-0.875	-0.670	0.420
Toluene	-0.427	-0.427	-0.390	0.001
Dichloromethane	0.583	0.583	0.540	0.002
Alkane	-1.371	-1.371	-1.520	0.022
Isooctane	-1.421	-1.421	-1.600	0.032

The same procedure was carried out with forty two N-nitrosodialkylamines .The result was that for all the compounds the value of π_2^H was between (1.50-0.07) and for $\Sigma\ \beta_2^H$ was between (0.57-0.60) as shown in Table (13.11). There is therefore not much different between the values of π_2^H and $\Sigma\beta_2^H$ for all the N-nitrosodialkylamines .

Table (13.11) calculated values of π_2^H and $\Sigma\beta_2^H$ for N-nitroso dialkyla mines

Name	R_2	π_2^H	β_2^H	Vx	n	sd
N-Nitrosodimethylamine	0.393	1.190	0.564	0.6057	16	0.056
N-Nitrosomethylethylamine	0.374	1.100	0.585	0.7466	14	0.059
N-Nitrosodiethylamine	0.345	1.084	0.582	0.8875	17	0.052
N-Nitrosoethylpropylamine	0.340	1.050	0.610	1.0284	6	0.010
N-Nitrosomethylpropylamine	0.360	1.050	0.583	0.8875	14	0.050
N-Nitrosomethylbutylamine	0.340	1.070	0.600	1.0284	14	0.043
N-Nitrosomtehylpentylamine	0.320	1.050	0.590	1.1693	6	0.016
N-Nitrosomethylhexylamine	0.300	1.094	0.600	1.3102	4	0.067
N-Nitrosomethylheptylamine	0.310	1.080	0.600	1.4511	4	0.067
N-Nitrosoethylhexylamine	0.300	1.092	0.600	1.4511	6	0.041
N-Nitrosoethylpentylamine	0.310	1.094	0.600	1.3102	1	0.055
N-Nitrosoethylbutylamine	0.320	1.000	0.620	1.1693	14	0.055
N-Nitrosodipropylamine	0.318	1.010	0.630	1.1693	14	0.066
N-Nitrosopropylbutylamine	0.310	0.990	0.640	1.3102	16	0.097
N-Nitrosodibutylamine	0.300	0.980	0.650	1.4511	17	0.097
N-Nitrosobutylpentylamine	0.290	0.980	0.650	1.5920	4	0.041
N-Nitrosodipentylamine	0.280	0.980	0.660	1.7329	5	0.036
N-Nitrosodiisobutylamine	0.300	0.780	0.750	1.4511	13	0.011
N-Nitrosodiisopropylamine	0.300	0.950	0.670	1.1693	17	0.078
N-Nitrosomethylisopropylamin	0.360	1.200	0.633	0.8875	4	0.009

N-Nitrosoethyldiisobutylamine	0.300	1.129	0.670	1.4511	12	0.55
N-Nitrosomethyltert-butylamine	0.340	1.050	0.650	1.0284	12	0.055
NNitrosor ethyliso-propylamine	0.340	1.020	0.650	1.0284	2	0.056
N-Nitroso Ethylterabutylamine	0.320	1.040	0.670	1.1693	2	0.072
NNitrosot Methylphenalamine	1.140	1.460	0.470	1.0726	3	0.361
NNitrosot Phenalphenalamine	1.780	1.890	0.450	1.5393	6	0.023
N-Ntrosot Methylbenzyl	0.990	1.440	0.610	1.2135	5	0.045
NNitrosot methyl,2phenylethyl	1.000	1.400	0.680	1.3544	3	0.361
NNitrosot Benzylbenzylamine	1.510	1.780	0.710	1.8213	5	0.020
NNtroson Pyrrolidine	0.572	1.460	0.64 0	0.7789	8	0.139
NNitrosot Piperidine	0.592	1.330	0.540	0.9198	8	0.220
NNitrosot Morpholine	0.600	1.510	0.660	0.8376	8	0.099
NNitroso- 2,6-dimethylmorpholine	0.600	1.540	0.680	1.1194	4	0.004
NNitrosot Methylvinyl	0.500	0.990	0.350	0.7036	4	0.012
NNitroso- Ethylvinyl	0.480	0.970	0.34 0	0.8445	4	0.014
N-Nitroso Methylallyl	0.470	0.950	0.500	0.8445	5	0.017
N-Nitroso Allylallyl	0.550	1.080	0.540	1.0833	5	0.011
N-Niroso Dihexylamine	0.500	1.280	0.740	1.7975	7	0.063
N-Nitroso Methylpiperazine	0.600	1.070	1.050	1.0196	6	0.011
N-Nitroso methyl allyin	0.470	1.070	0.420	0.84 45	5	0.017
N-Nitroso Methyldicyclohexan	0.050	1.280	0.740	1.7975	7	0.063

In a second step, the value for π_2^H was taken as an average of 1.09 for the straight chain aliphatic compounds, and then the value of $\Sigma\beta_2^H$ was calculated by getting the smallest standard deviation as before. The values of $\Sigma\beta_2^H$ were hardly changed as shown in Table (13.12) except for branched-nitroso compound like N-nitrosodiisopropylamine.

Table 13.12 calc. $\Sigma\beta$ by fixing π as 1.09

Name	R_2	π_2^H	β_2^H	Vx	n	sd
N-Nitrosodimethylamine	0.393	1.090	0.562	0.6057	16	0.078
N-Nitrosomethylethylamine	0.374	1.090	0.581	0.7466	14	0.055
N-Nitrosodiethylamine	0.345	1.090	0.582	0.8875	17	0.096
N-Nitrosoethylpropylamine	0.340	1.090	0.602	1.0284	6	0.041
N-Nitrosomethylpropylamine	0.360	1.090	0.583	0.8875	14	0.099
N-Nitrosomethylbutylamine	0.340	1.090	0.580	1.0284	14	0.129
N-Nitrosomethylpentylamine	0.320	1.090	0.579	1.1693	6	0.070
N-Nitrosomethylhexylamine	0.300	1.090	0.600	1.3102	4	0.069
N-Nitrosomethylheptylamine	0.310	1.090	0.579	1.4511	4	0.056
N-Nitrosoethylhexylamine	0.300	1.090	0.614	1.4511	6	0.053
N-Nitrosoethylpentylamine	0.310	1.090	0.601	1.3102	1	0.069
N-Nitrosoethylbutylamine	0.320	1.090	0.588	1.1693	14	0.067
N-Nitrosodipropylamine	0.318	1.090	0.593	1.1693	14	0.079
N-Nitrosopropylbutylamine	0.310	1.090	0.614	1.3102	16	0.067
N-Nitrosodibutylamine	0.300	1.090	0.610	1.4511	17	0.097
N-Nitrosobutylpentylamine	0.290	1.090	0.593	1.5920	4	0.043
N-Nitrosodipentylamine	0.280	1.090	0.629	1.7329	5	0.046
N-Nitrosodiisobutylamine	0.300	1.090	0.700	1.4511	13	0.100
N-Nitrosodiisopropylamine	0.300	1.090	0.636	1.1693	17	0.071

N-Nitrosomethylisopropylamine	0.360	1.090	0.670	0.8875	4	0.067
N-Nitrosoethyldiisobutylamine	0.300	1.090	0.670	1.4511	12	0.55
N-Nitrosomethyltert-butylamine	0.340	1.090	0.658	1.0284	12	0.055
N-Nitroso ethylisopropylamine	0.340	1.090	0.630	1.0284	2	0.041
N-Nitroso ethyl-t-butylamine	0.320	1.090	0.630	1.1693	2	0.048
N-Nitroso dihexylamine	0.500	1.090	0.700	1.7975	7	0.120

There are five branched-chain nitroso compounds, and the π_2^H values for the branched-chain compounds were adjusted as recommended before, that is 1.09 with 0.03 units subtracted for each branch. Results are in Table (13.13).

Table (13.13) calculation of $\Sigma\beta_2^H$ for branched-chain N-nitrosodialkylamines

Compound Name	R_2	π_2^H	$\Sigma\beta_2^H$	V_x	n	sd
N-Nitrosodiisobutylamine	0.300	1.03	0.760	1.4511	13	0.118
N-Nitrosodiisopropylamine	0.320	1.03	0.636	1.1693	17	0.227
N-Nitrosomethylisopropylamine	0.360	1.06	0.583	0.8875	4	0.067
N-Nitrosomethyl-t-butylamine	0.340	1.03	0.660	1.0284	12	0.055
N-Nitrosoethylisopropylamine	0.340	1.06	0.600	1.1692	2	0.048

These results are then consistent with the two rules of Abraham el al. for aliphatic solutes, [36] as was mentioned in chapter 2.

13.5 Conclusion

The solvation equations for four water-solute system were obtained from the values of partition coefficients for a series of compounds. These partition coefficients were all obtained from the MedChem data base. For all four system the values of the overall regression standard deviation were less than 0.24, although a few compounds had to be eliminated in the regressions. The values for the correlation coefficient were all very good, and plots of log Pcalc. vs log Pobs showed good straight lines for all the systems. According to these results one could say that the equations extend the data set of equations, and could provide a useful tool for the prediction of further data for compounds in these systems.

The equations obtained can then be used to describe the systems in terms of its coefficients, although none of the four systems are in any way unusual. The water-diisopropylether system was useful in the calculation of descriptors for N-nitrosodialkylamines.

The values of π_2^H and $\Sigma\beta_2^H$ for the N-nitrosodialkylamines are also very useful, because they allow the calculation of numerous other partition coefficients without the necessity of direct working with these carcinogenic substances.

More importantly, we can now use the descriptors collected in Table 13.11, together with the coefficients of the two solvation equations to calculate a number of properties of environmental interest. As part of our method of determining descriptors, we have had to estimate the gas-water partition coefficient, K^W, which is equivalent to the Henry's

Law constant. We collect in Table 13.15 all the log K^W values we have calculated. In many cases there is only poor comparison to the observed values. However, the latter are quite scattered and do not conform to the general observed pattern for log K^W. It is known that for homologues, values of log K^W decrease slightly along the series, but this is not the case for the observed values for the nitroso compounds. We feel that our calculated values, Table 13.15, are a more reasonable set of values.

Various gas-solvent and water-solvent partition coefficients can trivially be calculated from the known descriptors and the coefficients given in Table 13.14 to obtain estimates of log P and of log K for all the combinations of processes and compounds. The water-octanol partition coefficient, P(oct), is a very important measure of lipophilicity, and so we give also in Table 13.15 our calculated values of log P(oct). There is good agreement with observed values, but this is rather artificial.

Table 13.14. Coefficients in eqn.(13.1) for partition between water and solvents.

Solvent	c	r	s	a	b	v
Hexane	0.361	0.579	-1.723	-3.599	-4.764	4.344
Isooctane	0.288	0.382	-1.668	-3.639	-5.000	4.561
Ether	0.251	0.588	-1.019	-0.238	-4.523	4.043
Di-isopropyl ether	0.510	0.520	-0.827	-0.742	-5.288	4.097
Dichloromethane	0.314	0.001	0.022	-3.238	-4.137	4.259
Toluene	0.143	0.527	-0.720	-3.010	-4.824	4.545
Octan-1-ol	0.088	0.562	-1.054	0.034	-3.460	3.814

Gas phase	-0.994	0.577	2.549	3.813	4.841	-0.869

Table 13.15. Some calculated properties of N-nitrosodialkylamines (R_1R_2N-NO)

Name	Log K^W Calc	Log K^W Obs [a]	Log P(oct) Calc	Log P(oct) Obs [b]
N-nitrosodimethylamine	4.40	2.11, 4.41	-0.57	-0.57
N-nitrosodiethylamine	4.00	3.69, 3.78	0.49	0.48
N-nitrosodipropylamine	3.89	3.38, 3.90	1.48	1.50
N-nitrosodibutylamine	3.60	4.32	2.54	2.63
N-nitrosodipentylamine	3.40		3.54	
N-nitrosodiisopropylamine	3.78	3.78	1.40	1.38
N-nitrosodiisobutylamine	3.75		2.30	2.29
N-nitrosomethylethylamine	4.20	3.28	-0.05	-0.02
N-nitrosomethylpropylamine	4.00		0.49	0.51
N-nitrosomethylbutylamine	3.94	3.80	1.00	1.02
N-nitrosomethylpentylamine	3.72	4.00	1.58	
N-nitrosomethylheptylamine	3.60		2.56	
Nnitrosomethylisopropylamine	4.10		0.42	0.41
N-nitrosomethyltertbutylamine	4.10		0.85	0.76
N-nitrosoethylpropylamine	3.95		0.98	0.99
N-nitrosethylbutylamine	3.80	3.70	1.53	1.57
N-nitrosoethylisopropylamine	4.06		0.88	
N-nitrosoethyltertbutylamine	4.08		1.31	
N-nitrosopropylbutylamine	3.75		2.00	2.03

[a] (Hiat,1995)[41]. [b] (Leo, 2000)[33]

13.6 References

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Conclusions

The solvation descriptors for the 209 PCBs have been determined, using data on the 209 compounds from GLC experiments, together with more limited data from HIPLC experiments, and on log Poct values. The calculated descriptors for a number off PCBs were linearly related to the number of chlorine atoms, N, with due regard to the position of the chlorine atom. The effect for ortho-substitution was noted, so that the sets of the descriptors for the PCBs were divided into four groups. These groups were as follows: (1), 2,2'6-substituted PCBs, (2), 2,2',6,6'-substituted PCBs, (3), 2,2'-ortho-substituted PCBs, (4), 2-ortho-subsituted and non-substituted. From the obtained linear equations, descriptors for any of the 209 PCBs could be calculated by fitting a given PCB to a specific group. Using the calculated descriptors, values of log Poct were predicted for all the PCBs. Good agreement with experimentally obtained log Poct values was found. In chapter 8 it was possible to calculated L_{OA} for partition from air to dry octanol. In this work such a calculation for all 209 PCBs has been an achieved for the first time. The calculation of log P oct for all 209 PCBs in this work, is not the first calculation, but seems to be more reliable than other calculations of log P oct.

Using the general solvation equation the aqueous solubility (log Sw) for the 136 PCBs was calculated bearing in mind the term $\Sigma\, \alpha_2^H$ is zero, since PCBs have no hydrogen bound acidity. The log Sw values for the 136 PCBs, were first calculated using the descriptors calculated in this work, and are compared with the experimental datta obtained from the literature by Patil, and with the predicted values also obtained by Patil. A comparison of our calculated values and experimental values showed good agreement.

It has been shown that, in addition to GLC, HPLC has great potential for the analysis of halogenated aromatics. All the results on HPLC capacity factors and log Poct values, suggested that the rotation energy in the PCBs could be important, and so a study was made to obtain the energy barriers to the rotation about the C-C bond for a number of ortho-substituted PCBs. The results of this wok was that the rotational energy maximum for all the PCBs studied were more or less the same, except for 2, 2', 6, 6'-PCB where the energy maximum was much larger. This helps to explain the effect of substituents on descriptors.

Similar to PCBs, PCN are persistent and lipophilic compounds. Therefore in chapter 11, the solvation descriptors for the 75 polychloronaphthalenes have been derived from literature data on various properties. These descriptors were the usual ones, (R_2, π_2^H, β_2^H, log L^{16}, Vx). The initial work indicated that the π_2^H descriptor is almost additive (like the R_2 descriptor) except for compounds that have adjacent chlorine atoms. Also the β_2^H descriptor was quite small, never more than 0.14, and for the very lipophilic PCNs β_2^H is actually zero. Once the descriptors were obtained, it was possible to predict values for water-octanol partition coefficients, as log P oct, the aqueous solubility as log Sw, the gas-water partition coefficient as log K^W, and the gas-dry octanol partition coefficient as log K^{oct}.

Finally, the carcinogenic compounds, the N-nitrosodialkylamines were studied. Firstly, the solvation equations for four water-solute systems were obtained from the values of partition coefficients for a series of compounds. These partition coefficients were all obtained from the Med Chem database. Using some of these water-solvent systems the values of π_2^H and β_2^H for forty two N-nitrosodialklyamines could be calculated. From the results obtained the values for π_2^H and β_2^H hardly changed for straight chain compounds, but values for branched-chain nitroso compounds were a

little different. The solvation descriptors were then used to calculated the gas-water partition coefficient, K^W which is equivalent to Henry's law constant. Various gas-solvent and water-solvent partitions can trivially be calculated from the known descriptors and the coefficients could be used to obtain estimates of log P for all the combinations of processes and compounds. There was good agreement between the calculated values and observed values, where the latter was available.

Finally, it can be concluded that the two general solvation equations provided a very good way to obtain descriptors. These descriptors together with the already published equations could be used to predict a number of environmentally important physicochemical properties of PCBs, PCNs, and the N-notrosocompounds, in the hope that they may be useful in cases where the experimental determination is difficult. Since some of them are carcinogenic and thus not easily handled, the ability to predict a large number of properties should be of considerable use.

As future wok other properties of the PCNs can be predicted from the descriptors and the various regression equations that have been published. Examples are the rate of permeation of human skin from aqueous solution, and the partition of PCNs between air and plant cuticular matrix and between water and plant cuticular matrix. Also there are a number of other important biological and environmental properties of the N-nitrosodialkylamines that can also be predicted using the descriptors. These include human intestinal adsorption, blood-brain distribution, skin permeation, as well as adsorption from air or water by plant cell matrix. In the present study, there were eight of the most common N-nitrosodialkylamines found in foods, these are N-nitroso-dimethyl, methylethyl, diethyl, dipropyl, dibutyl-amines as well as N-nitrosomorphloine, N-nitrosopiperdine and N-nitrosopyrollidine, and so estimation of

biological and environmental properties for these particular compounds would be of considerable value.