

Similar chemical structures, dissimilar triplet quantum yields; CASPT2 model rationalizing the trend of triplet quantum yield in nitroaromatic systems

Angelo Giussani^{*,†,‡} and Graham A. Worth[†]

[†] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

^{*}To whom correspondence should be addressed. Email: Angelo.Giussani@uv.es

[‡] Current address: Instituto de Ciencia Molecular, Universitat de València, Apartado22085, ES-46071 Valencia, Spain

Abstract

The photophysics of nitroaromatics compounds stand out for being characterized by an ultrafast decay into the triplet manifold and by a significant value of the triplet quantum yield. The latter quantity change dramatically depending on the system, as shown for 2-nitronaphthalene, 1-nitronaphthalene, and 2-methyl-1-nitronaphthalene, whose triplet quantum yield have been previously measured to be 0.93 ± 0.15 , 0.64 ± 0.12 , and 0.33 ± 0.05 , respectively (J. Phys. Chem. A 2013, 117, 14100). In this study we rationalize the reported trend for the triplet quantum yield on the basis of the different ability that the excited S_1 state has to reach a non-previously reported conical intersection with the ground state. Such a path is in competition with the one leading to triplet states, which appears equally favorable in the three systems. The energy barriers from the S_1 CASPT2//CASSCF minima to a CASPT2 minimum-energy-crossing-point of the S_1/S_0 conical intersection have been computed to follow the same trend as the values of triplet quantum yields in the nitroaromatics system under analysis here. The path has been characterized also for nitrobenzene, obtaining an energy barrier that nicely fits in the derived model, and in agreement with its triplet quantum yield value (>0.8). The ability of the present model to not only rationalize the experimental data of a single molecule but to reproduce a trend for four slightly different systems speaks in favor of its reliability.

Introduction

Nitroaromatic compounds (NCs) are an important class of molecules playing a prominent role in various fields such as atmospheric pollution, energetic materials, and in the drug delivery sector. Being formed as a result of incomplete combustion,¹ and having mutagenic and carcinogenic properties, NCs such as 1-nitronaphthalene (1NN), 2-nitronaphthalene (2NN), and nitrofluorene constitute a considerable concern for urban air quality.²⁻⁵ NCs and in particular nitrobenzene (NB) are common ingredients in energetic explosives, and NB-derived molecules are currently studied in order to obtain energetic compounds with better thermal stability.⁶ Due to their photochemical properties, NB-derived molecules can be used as drugs able to photorelease with precise spatiotemporal resolution nitric oxide (NO),⁷ which in turn is a key molecule having a variety of biological effects in the human body.

Beside their importance in the above mentioned fields, NCs usually display a rich photophysics and photochemistry, making them fascinating systems in the study of molecule-light interactions. Regarding their photochemistry, most NCs photodegrade under UV excitation forming NO and the corresponding aryloxy radical,⁸⁻¹¹ although other photoproducts, as NO_2 and O, can also be obtained.¹² More intriguingly is the fact that more than one single mechanism can be involved in the formation of the same photoproduct, as is the case of NO photoproduction in NB where so-called roaming mechanisms can operate.¹³ Regarding their photophysics, it is mainly characterized by a rapid decay into the triplet manifold after light absorption. In particular 1NN is the organic compound with the fastest multiplicity change ever measured, decaying into the triplet state in

around 100 fs.^{14–17} The same time for triplet state population has also been claimed to characterize 2NN, although recent semiclassical non-adiabatic dynamics concluded that such a time scale is instead due to an S_2 - S_1 internal conversion, while the intersystem crossing process leading to the triplet manifold should happen in around 0.7 ps.¹⁸

In order to understand the photophysics of NCs, a great deal of insight can be obtained by the study of a common property in a series of slightly different systems belonging to the same class of compounds. Such an approach was used by Vogt and Crespo-Hernández who experimentally determined, among others properties, the triplet quantum yield for the three molecules 2NN, 1NN and 2-methyl-1-nitronaphthalene (2M1NN).^{19,20} The results from this series of molecules is particularly interesting as, despite their relative chemical similarity, the corresponding triplet quantum yield varies significantly: 0.93 ± 0.15 , 0.64 ± 0.12 , and 0.33 ± 0.05 for 2NN, 1NN, and 2M1NN, respectively. Performing DFT optimizations and vertical TD-DFT computations, Vogt and Crespo-Hernández obtained the following two results. First, in the ground state at larger torsion angles of the nitro group with respect to the plane of the naphthalene ring, a larger energy gap between the S_1 and triplet states is observed. Second, the value of the torsion angle in the ground state minima increases along the series, being for example in acetonitrile equal to 0.3, 39.3, and 55.4 degrees for, 2NN, 1NN, and 2M1NN, respectively. These results made the authors conclude that the difference in the triplet quantum yield is related to the different torsion angles of the corresponding ground state minima, which in turn strongly influences the energy gap between singlet and triplet states, and then the probability of intersystem crossing.

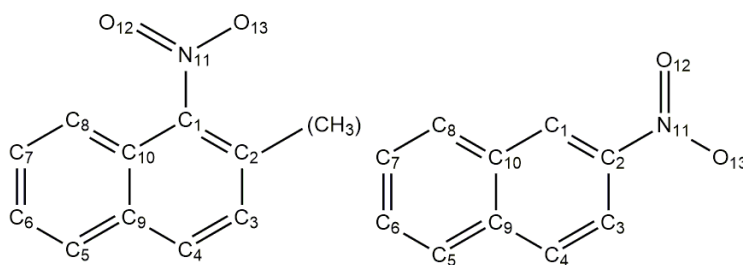


Figure 1. On the left, atom labeling for 1NN and 2M1NN; on the right, atom labeling for 2NN.

In the present contribution the reason behind the experimentally recorded trend for the triplet quantum yield in the series 2NN, 1NN, and 2M1NN (see Figure 1) is reconsidered performing ab-initio CASPT2//CASSCF and CASPT2//CASPT2 computations. The work has been conducted in the light of the very low fluorescence emission recorded in the systems,¹⁴ which consequently points to the presence of an accessible non-radiative relaxation process, and of a recently characterized S_1/S_0 conical intersection (CI) in the related molecule NB.²¹ The obtained results shown that CIs displaying similar structural deformations are indeed present also for the three nitronaphthalene systems here under consideration, and that the different ability that the three molecules have to reach such a crossing point constitutes a model able to rationalize the experimental trend of the triplet quantum yield along the 2NN, 1NN, and 2M1NN series, rather than a different ability to reach a singlet-triplet crossing region leading to the triplet states .

Methods

The present study has been performed employing the well-tested CASPT2 and CASSCF methods^{22–24} as implemented in the OpenMolcas software.²⁵ Geometries optimizations have been performed either at the CASSCF level or at the CASPT2 level, in the latter case computing the required gradients numerically. In both cases, the final energies have been computed at the CASPT2 level to take into account the dynamic correlation effects. No restrictions to the symmetry of the molecule have been imposed (C_1 symmetry). The basis set of atomic natural orbital (ANO) of L-type contracted to C,N [4s,3p,1d]/H[2s1p] has been employed.^{26,27}

An active space composed of 18 active electrons distributed in 14 active orbitals has been used in all the final vertical calculations, and in both CASSCF and CASPT2 optimizations. As shown in Figure S1 of the Supporting Information (SI), the selected active space takes into account both the π nature of the system and the lone pairs of the oxygen atoms. Such an active space will be the employed one throughout the work, unless otherwise specified.

Within the CASPT2 calculations, an imaginary level-shift correction of 0.2 au has been used to minimize the effects of possible intruder states. The CASPT2 standard zeroth-order Hamiltonian has been used as originally implemented.²³ The core orbitals have been frozen in the CASPT2 calculations. Such a CASPT2 approach has been validated in many different studies on organic molecules, providing a correct prediction, description, and interpretation of photophysical experimental data.^{24,28,29}

In order to connect some important regions of the potential energy hypersurface (PEH), linear interpolation of internal coordinate (LIIC) calculations have been performed.³⁰ Minimum energy crossing points have been optimized using the projected constrained optimization method as recently implemented in Molcas.³¹ The CI optimizations has been performed at the CASPT2 level, and not as CASPT2 vertical calculations performed along a CASSCF CI optimization.³² In the regions of the potential energy hypersurfaces where two or more states of different spin multiplicity are degenerate, the spin orbit coupling (SOC) has been calculated as described elsewhere.³³ The Cholesky decomposition has been used to speed up the calculation of two-electron integrals.³⁴

In the present work minimum geometries have been characterized for the S_0 and S_1 states. For S_0 the minimizations have been performed at the CASPT2 level, while for S_1 at the CASSCF level. In both case, the nature of the obtained minima have been verified computing CASSCF frequencies. As described in the result section, for all minima the computed CASSCF frequencies are all positive, so, even the S_0 minima obtained performing CASPT2 optimizations, are indeed CASSCF minima. Consequently, the here adopted approach can be framed in the CASPT2//CASSCF protocol: CASSCF minima, CASPT2 conical intersections, all energies corrected at the CASPT2 level.

Results and discussions

The significant diversity in the value of the triplet quantum yield in the three molecules 2NN, 1NN, and 2M1NN (significantly decreasing along the series), reflects the different ability that the three systems have to decay into the triplet manifold. This in turn can be originated from either the fact that the decay path leading into the triplet manifold is less favorable along the series of molecules, and/or by the presence of a competing decay path not involving the population of the triplet states which becomes more and more favorable along the series of molecules. In order to evaluate the ability of the three systems to decay into the triplet manifold, the main decay path open to the excited S_1 bright state has been characterized from the respective ground-state minima. The latter equilibrium geometries have been obtained at the CASPT2 level, since for the related system NB CASSCF-optimized ground state structures have been shown to display geometrical parameters that differ significantly with respect to the ones resulting from electron diffraction measurements, especially regarding the NO bond distances.²¹⁻²³ In the CASPT2 optimizations a CAS(18,14) active space has been employed, only the ground state root has been computed, and the corresponding CASPT2 gradients have been evaluated numerically using the OpenMolcas software.

Due most probably to the use of just one root, the CAS(18,14) active space differ from the one later used for the computation of excited states by the presence of two sigma orbitals instead that the full valence π space. The same effect was observed in a previous study on NB performed with a similar computational protocol.²¹ In order to characterize the S_0 minima so obtained, CASSCF(18,14)

frequencies computations were performed, which have provided for all three cases no imaginary frequencies. CASPT2 frequencies computations have not been attempted due to the high computational cost required for the systems here under analysis, and for the limited precision that it is expected out of a numerical evaluation of them, so the frequencies at the computed S_0 minima have been evaluated at the CASSCF level. We can however conclude, based on the obtained CASSCF(18,14) frequencies, that the CASPT2 ground-state minima are at least true CASSCF minima. The so obtained S_0 minima are hereafter label as $^1(\text{gs})_{\text{min}}$.

As shown in Figure 2, the three $^1(\text{gs})_{\text{min}}$ minima display similar geometrical parameters, the most remarkable difference being the angle formed between the plane of the rings and the nitro group, as reflected by the values of the $\text{C}_{10}\text{C}_1\text{N}_{11}\text{O}_{12}$ and $\text{C}_2\text{C}_1\text{N}_{11}\text{O}_{12}$ ($\text{C}_1\text{C}_2\text{N}_{11}\text{O}_{12}$ and $\text{C}_3\text{C}_2\text{N}_{11}\text{O}_{12}$ for 2NN) dihedral angles. In qualitative agreement with previous DFT computations,¹⁹ the ground state minimum is a planar geometry for the 2NN system, while for both 1NN and 2M1NN the nitro group is out of the plane defined by the rings by around 45 and 70 degrees, respectively. Comparing the CASPT2(18,14) 1NN S_0 minimum with a previously CASSCF(16,13) optimized structure³⁷ (see Figure S2), the most significant differences are seen in the values of the NO bond lengths, between 0.02-0.04 Å shorter at the CASSCF level.

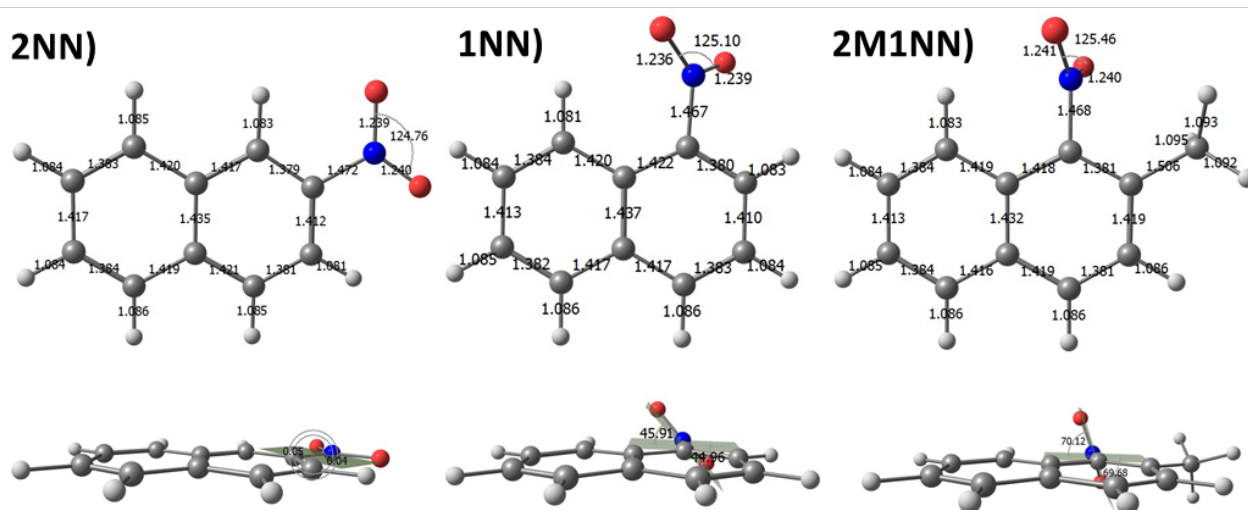


Figure 2. $^1(\text{gs})_{\text{min}}$ minima of 2NN, 1NN, and 2M1NN. Selected bond lengths (in Å), angles, and dihedral angles (in degrees) are also reported.

The electronic structure of the obtained minima have been characterized computing the low-lying singlet and triplet excited states. In particular four singlet and five triplet excited states have been calculated, and the corresponding vertical energies, natures, and oscillator strengths are reported in Table 1. In all cases a very similar ordering of the states is observed, and the S_1 ($n_A\pi^*$) state appears nearly degenerate with the T_3 ($^3(\pi_O\pi^*)$) state. The latter two states are strongly coupled, as reflected by the corresponding SOC terms, equal to 75.71, 76.15, and 78.26 cm^{-1} for 2NN, 1NN, and 2M1NN, respectively. The second lowest singlet state, S_2 , having a $^1(L_b\pi\pi^*)$ nature, is separated from the S_1 ($n_A\pi^*$) state in the three molecules by 0.20, 0.34, and 0.28 eV, respectively. The nature of the characterized states is exemplified for 2NN in Table S1.

In the recording of the triplet quantum yields, Vogt and Crespo-Hernández employed an excitation wavelength of 355 nm (3.49 eV), accordingly to which they claimed to initially populate the S_1 state.¹⁹ From TD-DFT computations, Vogt and Crespo-Hernández concluded that the lowest and initially excited singlet state has $\pi\pi^*$ nature. On the basis of our results, however, it is concluded that at such experimental excitation the S_1 ($n_A\pi^*$) state is populated, being the only state below such an excitation energy apart from the S_2 ($^1(L_b\pi\pi^*)$) state in 2NN, which is however expected to

decay in an ultrafast fashion into the $^1(n_A\pi^*)$ state.¹⁸ A rapid decay from the $^1(L_b\pi\pi^*)$ to the $^1(n_A\pi^*)$ state is also here envisaged based on the energies at the 2NN ground state minimum (see Table 2): the two states are separated by 0.20 eV, for which it is reasonable to expect that a stabilization of the $^1(L_b\pi\pi^*)$ state will lead to a further reduction of such a gap and to a consequently high probability of decay to the $^1(n_A\pi^*)$ state. It should be noted that the measurements were conducted in acetonitrile, and in their TDDFT computations such an environment was simulated using a PCM-like model. It can occur that in the solvent the ordering of the states may differ with respect to the gas-phase, and that a $\pi\pi^*$ instead of the $n\pi^*$ state becomes the S_1 root. On the basis of a simple analysis based on the value of the dipole moments (see Table S2) an inversion of the $^1(L_b\pi\pi^*)$ and $^1(n_A\pi^*)$ states when passing from the gas-phase to an acetonitrile solution is not predicted, as the two states are characterized by similar values of the dipole moment. It can also be noted that the $^1(L_b\pi\pi^*)$ state has a much smaller coupling to the triplet manifold and in particular with the $^3(\pi_O\pi^*)$ state, consequently making population of the triplet states an improbable process, in contrast to the significant triplet quantum yields recorded in the molecules. Finally, the reported S_1 oscillator strengths in the paper of Vogt and Crespo-Hernández are much closer to the ones here characterizing the $^1(L_a\pi\pi^*)$ state. Thus we assume that the TDDFT computed state is the $^1(L_a\pi\pi^*)$, an assumption supported by the partial charge-transfer character of such a root,³⁸ the excited state energy underestimation of charge-transfer states in TDDFT,³⁹ and the general issue related with excited state ordering when computed with such a level of theory.⁴⁰

Another important point worth commenting on is the zero oscillator strength characterizing the $^1(n_A\pi^*)$ state at the here obtained 2NN ground state minimum. Being completely planar and with C_s symmetry, the transition from the ground to the $^1(n_A\pi^*)$ state is forbidden. The same scenario is found in NB, whose ground state equilibrium structure is also totally planar.²¹ In the latter system population of the $^1(n_A\pi^*)$ state is however possible due to low energy barrier along the torsional angle of the nitro group, which determines the coexistence of non-planar geometries from which $^1(n_A\pi^*)$ promotions are allowed. In order to evaluate if such an explanation is also plausible for 2NN, the properties of a structure obtained from the $^1(g_s)_{\min}$ 2NN by rotating the torsion of the nitro group by 45 degrees with respect to the plane of the naphthalene ring have been computed. At such a geometry the ground state energy has increased of only 0.03 eV with respect to the $^1(g_s)_{\min}$ 2NN minimum, while the $^1(n_A\pi^*)$ oscillator strength is now equal to 0.0029, for which it is possible to conclude that similarly to NB, the excitation of $^1(n_A\pi^*)$ in 2NN can take place from accessible non-planar ground state structures.

Table 1. CASPT2(18,14) Vertical Excitation Energies of Nitronaphthalenes at the Ground-State Minima (E_{VA} , eV) for the Lowest Valence Singlet and Spin Forbidden Triplet Excited States.^a

2NN		1NN		2M1NN	
State	E_{VA} (eV)	State	E_{VA} (eV)	State	E_{VA} (eV)
T_1 $^3(\pi\pi^*)$	2.66	T_1 $^3(\pi\pi^*)$	2.53	T_1 $^3(\pi\pi^*)$	2.63
T_2 $^3(n_A\pi^*)$	3.09	T_2 $^3(n_A\pi^*)$	3.10	T_2 $^3(n_A\pi^*)$	3.12
T_3 $^3(\pi_O\pi^*)$	3.23	T_3 $^3(\pi_O\pi^*)$	3.32	S_1 $^1(n_A\pi^*)$	3.33 (0.0013)
S_1 $^1(n_A\pi^*)$	3.26 (0.0000)	S_1 $^1(n_A\pi^*)$	3.36 (0.0041)	T_3 $^3(\pi_O\pi^*)$	3.36
T_4 $^3(\pi\pi^*)$	3.43	T_4 $^3(\pi\pi^*)$	3.52	T_4 $^3(\pi\pi^*)$	3.56
S_2 $^1(L_b\pi\pi^*)$	3.46 (0.0069)	S_2 $^1(L_b\pi\pi^*)$	3.70 (0.0021)	S_2 $^1(L_b\pi\pi^*)$	3.61(0.0160)
T_5 $^3(n_B\pi^*)$	3.70	T_5 $^3(n_B\pi^*)$	3.73	T_5 $^3(n_B\pi^*)$	3.72
S_3 $^1(n_B\pi^*)$	3.79 (10^{-5})	S_3 $^1(n_B\pi^*)$	3.79 (0.0005)	S_3 $^1(n_B\pi^*)$	3.89 (10^{-5})
S_4 $^1(L_a\pi\pi^*)$	4.30 (0.1764)	S_4 $^1(L_a\pi\pi^*)$	4.05 (0.1057)	S_4 $^1(L_a\pi\pi^*)$	4.12 (0.1159)

^a The computed oscillator strengths for the singlet–singlet transitions are reported in parentheses.

One of the main focuses of the present work is the explanation of the recorded trend for the triplet quantum yield. Since the latter has been measured exciting the systems into the S_1 state, after having characterized the excited states at the Franck-Condon regions, as described above, the following exploration of the potential surfaces was made computing two singlet and two triplet states. The corresponding Franck-Condon energies are reported in Table 2. Compared to the 5-roots results, a blue shift in the $^1(n_A\pi^*)$ state is observed, leading to the lost of degeneracy with the triplet $^3(\pi_O\pi^*)$ state, whose energetic position appears to be less affected by the number of computed roots. From the three ground state minima, the relaxation experienced by the $^1(n_A\pi^*)$ state has been evaluated computing the corresponding excited-state minima, performing CASSCF(18,14) optimizations. Attempts to optimize the $^1(n_A\pi^*)$ state of the three molecules at the CASPT2 level were unsuccessful with the energy continually fluctuating during the procedure. The so-obtained equilibrium geometries, hereafter indicated as $^1(n_A\pi^*)_{\min}$, are shown in Figure 3, while the energies of the low-lying singlet and triplet states are reported in Table 2. To verify that true CASSCF minima have been obtained, the corresponding CASSCF frequencies have been calculated. No imaginary frequencies were present. In the three minima the $^1(n_A\pi^*)$ state is almost degenerate in energy with the triplet $^3(\pi_O\pi^*)$ state (energy difference equal to 0.07, 0.05, and 0.05 eV for 2NN, 1NN, and 2M1NN, respectively) and again a large SOC characterizes the two roots (67.36, 65.00, and 65.99 cm^{-1} , respectively). Regarding the $^1(n_A\pi^*)_{\min}$ geometries, all three minima are non-planar structures in which the nitro group displays a partial pyramidalization.

Table 2. CASPT2(18,14) Energies (eV) for the Most Relevant Singlet and Triplet States of Nitronaphthalenes at Different Critical Points.^a

State Geometry	2NN				1NN				2M1NN			
	gs	$^1(n_A\pi^*)$	$^3(\pi_O\pi^*)$	$^3(n_A\pi^*)$	gs	$^1(n_A\pi^*)$	$^3(\pi_O\pi^*)$	$^3(n_A\pi^*)$	gs	$^1(n_A\pi^*)$	$^3(\pi_O\pi^*)$	$^3(n_A\pi^*)$
$^1(\text{gs})_{\min}$	0.00	3.51	3.21	3.25	0.00	3.59	3.35	3.16	0.00	3.56	3.48	3.26
$^1(n_A\pi^*)_{\min}$	1.15	2.88	2.95	2.93	1.63	3.04	3.09	3.14	1.48	3.05	3.10	3.13
$(^1n_A\pi^*/\text{gs})_{\text{Cl}}$	3.13	3.13	4.49	3.09	3.16	3.17	4.55	3.12	3.04	3.05	4.64	3.01

^a All the reported values are referred to the corresponding ground state optimized geometry, $^1(\text{gs})_{\min}$.

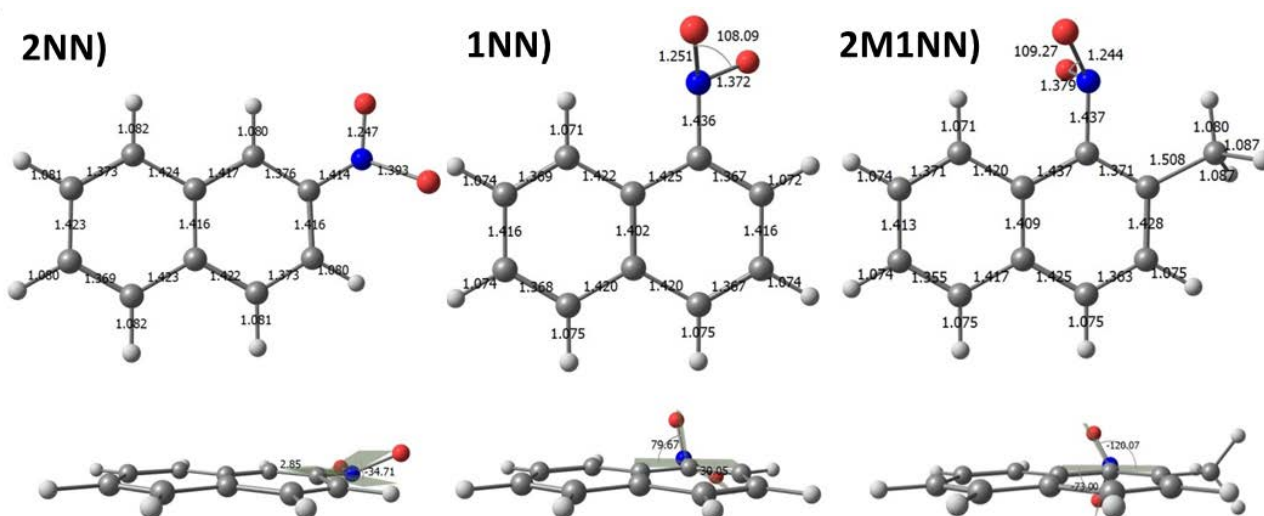


Figure 3. $^1(n_A\pi^*)_{\min}$ minima of 2NN, 1NN, and 2M1NN. Selected bond lengths (in Å), angles, and dihedral angles (in degrees) are also reported.

Based on the outcomes presented above, we can then conclude that the same static description is shared in the three molecules. The bright ${}^1(n_A\pi^*)_{\min}$ is strongly coupled with the triplet ${}^3(\pi_O\pi^*)$ state, as reflected by the reported high SOC values, and in its minimum the two roots are degenerate, making the corresponding intersystem crossing process a particularly favorable outcome. This scenario was already characterized for 1NN and used as a rationalization for the ultrafast singlet to triplet decay experimentally recorded in the molecule.^{37,41,42} On the basis of the obtained static results, it is then likely that after ${}^1(n_A\pi^*)$ absorption, the path leading to triplet state population is equally favorable in the three molecules. This consequently points out to the presence of a competing path whose presence justifies the loss in triplet quantum yield observed along the series. Such a consideration, together with the particularly low or even absent fluorescence emission in the molecules, makes plausible the presence of an accessible non-radiative decay path in competition with the singlet to triplet decay route.

In our previous article on the related system NB, a non-radiative decay from the ${}^1(n_A\pi^*)$ to the ground state was described, involving the presence of an accessible CI between the two states.²¹ The latter geometry is characterized by a shortening of the CN bond, together with an enlargement of both NO distances, and a decrease in the ONO angles. In order to evaluate if such a path is also possible in the three nitronaphthalene systems, CASPT2 CI optimizations have been carried out using the projected constrained optimization method as recently implemented in the Molcas software, obtaining minimum energies crossing points (MECPs) between the ${}^1(n_A\pi^*)$ and the ground state. MECPs are in general used as a model for the description of a CI seam and in order to evaluate the relation between other critical point and the CI region.⁴³ Care should however be taken in the use of such a model, which is based on the assumption that MECP are the most representative point of a CI and from which internal conversion phenomena are most likely to occur. In reality, population transfer can occur at all points along a CI seam and what is in general more important is the first encountered CI point rather than the MECP, as shown for example in the photophysics of guanine.⁴⁴ In the present contribution we however decided to compute MECPs as a way of characterizing the CIs, since it will provide a strategy in order to compare the CI regions in the various molecules here studied. For each system here under study a MECP has been found, hereafter denoted as $({}^1n_A\pi^*/gs)_{CI}$, which displays indeed the same main geometrical deformations present in the related CI of NB (see Figure 4, Table S3, and ref. 21).

The computed MECPs can be considered to lie along the same “deformation direction” characterizing the evolution of the systems from the ground state minima towards the ${}^1(n_A\pi^*)$ equilibrium structures: at least with respect to the nitro group, the MECPs geometries display the same major deformations seen in the ${}^1(n_A\pi^*)$ minima. These are, as in the case of NB, a decrease in the CN distance and ONO angle, together with an enlargement of the NO bonds (see Figures 2-4, and Table S3).

Comparing the energies of the low-lying singlet and triplet states at the computed crossing point to the energies of the ground-state and ${}^1(n_A\pi^*)$ minima (see Table 2), the following observations can be drawn. First, each MECP is energetically below the corresponding ${}^1(n_A\pi^*)$ vertical excitation energy at the ground state equilibrium structure, specifically 0.38, 0.42, and 0.51 eV lower in energy for 2NN, 1NN, and 2M1NN, respectively. This in turn means that after excitation each of the three molecules should have enough energy to reach the corresponding CI. Second, the energy difference between the ${}^1(n_A\pi^*)$ minimum and the MECP increases along the series: 0.25 eV for 2NN, 0.13 eV for 1NN, and 0.00 eV for 2M1NN. The trend in the energy differences shows that the accessibility of the CI region becomes more and more favorable along the series of molecules, following the same trend as the experimental value of the triplet quantum yield.

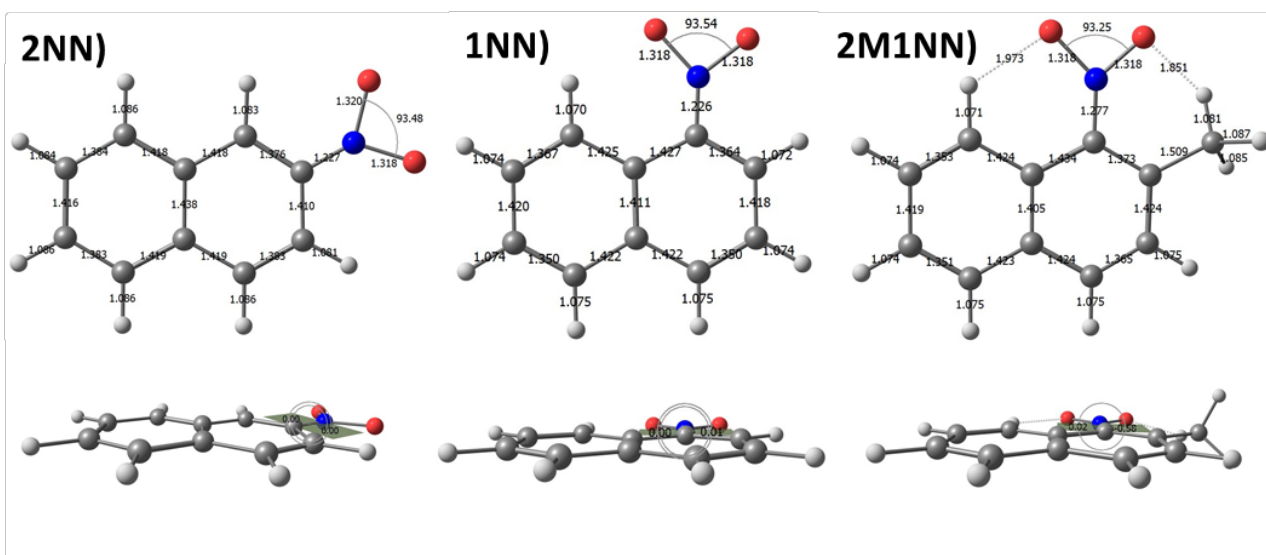


Figure 4. $^1(n_A\pi^*/gs)_{CI}$ MECP of 2NN, 1NN, and 2M1NN. Selected bond lengths (in Å), angles, and dihedral angles (in degrees) are also reported.

In order to better characterize the potential energy hypersurfaces between the $^1(n_A\pi^*)$ minima and the related MECP, LIIC computations between the two critical points have been performed. The computed CASPT2(18,14) energies along these are presented in Table 3. As shown in Table 3, the $^1(n_A\pi^*)$ energy initially decreases along the LIIC paths, despite the fact that the starting points were the $^1(n_A\pi^*)$ minima. The behavior is probable due to the fact that the minima were obtained at the CASSCF(18,14) level, while the final energies are evaluated performing CASPT2(18,14) calculations. Evaluating the energy barrier as the difference between the lowest point along the LIIC path and the MECP, values were obtained that again follow the same trend as the one shown for the triplet quantum yields: 0.47, 0.42, and 0.19 eV for 2NN, 1NN, and 2M1NN, respectively.

Based on the results, we can formulate the following model that rationalizes the trend for the values of the triplet quantum yield in the molecules 2NN, 1NN, and 2M1NN. After excitation into the S_1 $^1(n_A\pi^*)$ state, the latter evolves in the three systems toward a minimum structure characterized by a strong coupling with the triplet $^3(\pi_O\pi^*)$ state (large SOC and almost degenerate energy). This consequently constitutes a particularly favorable decay path leading into the triplet manifold. In the three molecules a non-radiative internal conversion decay path coexists along with the decay route into the triplet state, mediated by the presence of a CI between the $^1(n_A\pi^*)$ and the ground state. While the decay path leading to triplet state population is equally favorable in the systems, the non-radiative re-population of the ground state appear to be more and more favorable along the series of molecules, as reflected by the decreasing value of the energy barrier needed in order to reach the corresponding MECP from the related $^1(n_A\pi^*)$ minimum. The importance that the non-radiative decay path acquires along the series makes it competitive with the triplet route, consequently determining the loss of triplet quantum yield experimentally registered. The decay paths are summarised in Figure 5.

The computed energy barriers are not very high, and in addition it needs to be taken into account that they have been obtained from LIIC paths, meaning that the reported values constitute upper bounds of the true energy barriers. This fact, together with the favorable geometrical disposition of the excited minima and MECPs (i.e. being placed along the same deformation direction for the nitro group) means that the non-radiative internal conversion decay should be relatively efficient. Nevertheless, most of the excited-state population, except for 2M1NN, decays into the triplet manifold, indicating that despite the presence of an accessible non-radiative decay, the singlet-triplet coupling is strong enough to make the intersystem crossing process the most favorable relaxation route. It should be noticed that energy barriers of around 0.2 eV have been associated to

excited state lifetimes of the order of the picosecond in DNA related systems;⁴⁵ considering that nitroaromatics systems can have ultrafast decay into the triplet manifold (as in 1NN, whose triplet states is populated in 100 fs after S_1 absorption) it is then justifiable that the triplet route remains the main decay route in the nitroaromatics systems here studied.

In order to further validate the present static model, the latter has also been applied to the related system NB, in which the presence of a $(^1n_A\pi^*/gs)_{CI}$ CI was originally described. From an optimized minimum energy crossing point obtained starting from the NB CASPT2(14,11) CI, the corresponding LIIC path between this crossing region and the previously published CASSCF(14,11) $(^1n_A\pi^*)$ minimum has been computed.²¹ A similar scenario to the one described for the nitronaphthalene systems has resulted, obtaining an energy difference between the minimum and the MECP of 0.35 eV, and an energy difference between the lowest LIIC point and the MECP of 0.48 eV (see Table 3). Performing picosecond time-resolved transient grating measurements in ethanol after excitation into the NB S_1 state, Terazima and co-workers determined that the triplet quantum yield of NB is greater than 0.8.^{46,47} Such quantities match with the proposed model: a 0.36 (0.48) eV barrier match with a triplet quantum yield greater than the one for 1NN and 2M1NN, having respectively a 0.13 (0.42) eV and 0.00 (0.19) eV energy barrier, and of the order of the triplet quantum yield characterizing the 2NN molecule, for which a barrier of 0.25 (0.47) eV have been obtained. As NB is the system for which the highest barrier has been computed, we would expect that the molecule displays the larger triplet quantum yield, a hypothesis that is plausible with the experimental determination of a value greater than 0.8.

It is interesting to notice that the system characterized by the higher energy gaps between the $(^1n_A\pi^*)$ minimum and the corresponding MECP, i.e. NB, is also the system displaying the smallest geometrical differences between such two critical points. In NB both the minimum and the MECPs are totally planar, and the same main deformations are present. In the 2NN, 1NN, and 2M1NN molecules, the $(^1n_A\pi^*/gs)_{CI}$ MECPs are again planar structures, but instead in the corresponding $(^1n_A\pi^*)$ minima the nitro group is no longer coplanar with the naphthalene ring, and in both cases it has lost its own planar conformation displaying a certain degree of pyramidalization. Despite the larger geometrical deformations required in 2NN, 1NN, and 2M1NN than in NB for evolving from the $(^1n_A\pi^*)$ minimum to the $(^1n_A\pi^*/gs)_{CI}$ MECP, the former systems are, as reported above, characterized by a lower energy barrier than NB.

As a final consideration, and since the present model is also based on the energy of the $(^1n_A\pi^*)$ minimum, the 2NN CASSCF(18,14) equilibrium structure has been re-optimized starting from the previously described geometry obtained from the 2NN ground state minimum in which the nitro group has been placed at 45 degrees with respect to the plane of the rings. From such a geometry, characterized by a significant value of the oscillator strength for the electronic promotion into the $(^1n_A\pi^*)$ state, the $(^1n_A\pi^*)$ CASSCF(18,14) optimization has ended in the same region as described above, consequently validating the conclusion drawn from such a minimum.

Table 3. CASPT2(18,14) Computed Energies (eV) for the $(^1n_A\pi^*)$ States of Nitroaromatics Along the Computed LIIC Paths between $(^1n_A\pi^*)_{min}$ Minima and $(^1n_A\pi^*/gs)_{CI}$ MECPs.

Molecule	Geometry										ΔE^a
	$(^1n_A\pi^*)_{min}$	LIICg1	LIICg2	LIICg3	LIICg4	LIICg5	LIICg6	LIICg7	LIICg8	$(^1n_A\pi^*/gs)_{CI}$	
2NN	2.88	2.75	2.77	2.73	2.69	2.66	2.67	2.73	2.88	3.13	0.47
1NN	3.04	2.96	2.96	2.83	2.78	2.75	2.75	2.89	3.03	3.17	0.42
2M1NN	3.05	3.01	2.91	2.91	2.90	2.88	2.86	2.86	3.00	3.05	0.19
NB	2.85	2.79	2.75	2.73	2.72	2.74	2.79	2.88	3.01	3.20	0.48

^a Energy difference (eV) between the MECP and the lowest computed point along the LIIC.

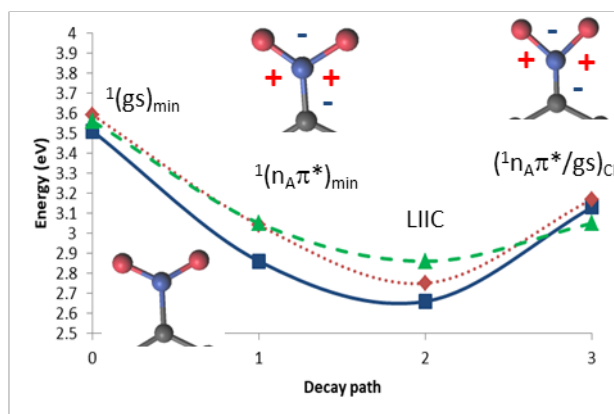


Figure 5. Schematic representation of the CASPT2(18,14) PEHs of the $^1(n_A\pi^*)$ state for the 2NN, 1NN, and 2M1NN molecules along the characterized critical points. Solid blue, dotted red, and dashed green lines correspond to the $^1(n_A\pi^*)$ state for the 2NN, 1NN, and 2M1NN systems, respectively. The main geometrical deformations of the nitro group are reported employing red plus (+) and minus blue symbols, indicating an increase and decrease, respectively, with respect to the S_0 minima (see Table S3)

Conclusions

On the basis of high-level ab initio CASPT2//CASSCF and CASPT2 computations, a model rationalizing the experimental trend of the triplet quantum yield for the molecules 2NN, 1NN, and 2M1NN (0.93 ± 0.15 , 0.64 ± 0.12 , and 0.33 ± 0.05 , respectively) after excitation into the S_1 state has been proposed. The remarkable decrease in the triplet quantum yield observed along the series of molecules is shown here not to be caused by an increasing difficulty in reaching the singlet-triplet crossing region leading to the triplet manifold, but to be attributable to an increase in the possibility of instead decaying along a competitive non-radiative internal conversion path mediated by an accessible non-previously reported conical intersection between the S_1 and the ground-state. The S_1 state in the three molecules has been here characterized to have the same $n\pi^*$ nature, in agreement with previous CASPT2//CASSCF computation^{37,41} but in dissonance with previous TDDFT computations.^{18,19}

The S_1 state evolves in the three systems towards an equilibrium structure in which it is degenerate and strongly coupled with a triplet state, which can consequently be easily populated. This decay is common to the three molecules, for which we conclude that the path leading to the intersystem crossing process is equally favorable in all the here studied molecules. From this S_1 minimum, the systems can also further evolve towards the mentioned S_1/S_0 conical intersection, and consequently decay non-radiatively. The probability to evolve along this non-radiative path appears to be system-dependent, determined by the computed energy barriers to reach the conical intersection from the S_1 minimum in the three systems. The values of these barriers follow the same trend as the experimental values of the triplet quantum yields: larger for the systems characterized by a larger triplet quantum yield.

In order to compare the three CI regions in the three systems, CASPT2 minimum-energy crossing point for each CI have been obtained. The derived model has also been applied to the related system NB, and the results obtained match with the experimental value of the triplet quantum yield for that molecule.

The present contribution thus sheds light onto the remarkably different photophysical behavior that the nitronaphthalene molecules display, despite their similar chemical structures. This in turn constitutes a nice example of how presumably small chemical modifications (such as the functional group position and methylation) can have dramatic effects in the system behavior, and should be taken into consideration when comparing presumably similar systems, as for example thymine and uracil, and cytosine and 5methyl-cytosine, two pairs of molecules differentiated by a methyl group but characterized by different photoresponses.

Author information

Corresponding Author

*E-mail: angelo.giussani@uv.es.

ORCID

Angelo Giussani: 0000-0002-9452-7641

Notes

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