STRUCTURES AND VIBRATIONAL SPECTRA OF NITRO-BENZO[A]PYRENE AND NITRO-BENZO[E]PYRENE ISOMERS: A DENSITY FUNCTIONAL STUDY

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AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration between both authors. All authors read and approved the final manuscript.

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ABSTRACT

Toxicity and reactivity of nitro polycyclics have been correlated with their molecular structure and electronic properties, in particular with the nitro substituent orientation. Experimental data are scarce for mononitro derivatives of benzo[a]pyrene (BaP) and benzo[e]pyrene (BeP), so density functional B3LYP/6-311++G(d,p) calculations have been performed on all of the isomers of nitro-BaP and nitro-BeP in their singlet and triplet states. The most stable configurations are planar ones in which NO_2 interacts with the aromatic π-electron system, although the majority of structures are non-planar. Nitro substitution in the bay region of both BaP and BeP results in two stable singlet structures with very different geometries; the higher energy states show a strong O–C interaction that induces sp^3 hybridization in the aromatic carbon atom. The calculated IR spectra display differences between planar and non-planar structures that can be used to predict the nitro group orientation and thereby the potential toxicity of each isomer.

Keywords: Benzo[a]pyrene; Benzo[e]pyrene; DFT; nitro-aromatic; toxicity prediction.

1. INTRODUCTION

Benzo[a]pyrene (BaP) and benzo[e]pyrene (BeP) are polycyclic aromatic hydrocarbons (PAHs) frequently found in urban particulate matter. Each is composed of five fused aromatic rings, but the two display markedly different chemical reactivity and toxicological properties. BaP is a potent mutagen and a carcinogen, whereas there are insufficient data to classify BeP as either [1]. Nitro derivatives of PAHs have been also detected in polluted atmospheres [2]. PAHs and nitrogen oxides are frequently emitted simultaneously from combustion sources, and they may react directly at the point of emission or farther away through thermal or photochemical reactions. Nitro derivatives are often more potent carcinogens than the parent PAH [3]. 6-nitrobenzo[a]pyrene(6-nitro-BaP), 3-nitrofluoranthene, and 1-nitropyrene have all been detected in urban airborne particulate matter [4]. Many nitro-PAHs are direct mutagens [5,6], i.e. they do not require metabolic activation to initiate the mutagenic process. In bacteria studies the two principal pathways that initiate the toxicological process entail nitro reduction and ring oxidation followed by nitro reduction [7]. The molecular structure and electronic properties of nitro-PAHs are

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therefore significant in evaluating potential toxicity [8,9]. Several studies of structure-toxicity relationships in nitro-PAHs of four rings or fewer have been made [10-12]. These have successfully connected mutagenic activity to the spatial orientation of the nitro moiety with respect to the aromatic rings [13]. Isomers in which the nitro group lies out of the aromatic plane tend to present weaker mutagenic activity than those in which it is in-plane. Recently mutagenic activity/structure relationship studies of a series of nitrophenanthrene [11], nitroanthracene [14] and nitrofluoranthene [15] isomers were reported using simulated IR and Raman spectral analyses. Linear relationships between spectral parameters and mutagenic activity were found, and the potential toxicity of some unexplored isomers was predicted. For larger nitro-PAHs structural and spectral data are scarcer. The geometrical parameters of 1-, 3- and 6-nitro-BaP have been reported by Onchoke et al. [16] and correlated with their respective mutagenic activities. Theoretical vibrational spectra were also calculated and compared with experimental data. However, no data exist on the geometry, electronic properties and vibrational frequencies of other nitro derivatives of BaP and BeP, nor has there as yet been a comprehensive comparison of structure and stability across the isomers of nitro-BeP and nitro-BaP. This is in part because few nitro derivatives of BeP and BaP have been synthesized. Theoretical calculations are currently the only tool available for the comprehensive study of these molecules. Electronic, structural and spectral properties of compounds are certainly useful in identifying nitro polyciclics and evaluating their toxicity. In the present work a detailed study of the potential energy surfaces of nitro-BaP and nitro-BeP is analyzed. The singlet and triplet states and HOMO-LUMO energy differences of all isomers have been investigated using density functional theory (DFT) methods, specifically the B3LYP hybrid functional with 6-311++G(d,p) basis sets. This level of theory has been shown to yield reliable results for large polycyclic compounds [17] with reasonable computing effort. Accurate IR spectra have been computed in the harmonic approximation to investigate the correlation between spectroscopic properties and geometrical parameters.

2. METHODS

Selected isomers of nitro-BaP and nitro-BeP were preliminarily optimized using the 6-311+G(d) basis sets and BLYP, BPW91 and B3-LYP functionals. BLYP and BPW91 are based on Becke's exchange functional [18] and B3LYP [19] uses the three-parameter functional. The correlation functionals are those of Lee, Yang and Parr [20] and Perdew and Wang [21], respectively. The optimized geometries and energies of the different approximations showed no relevant differences. However, the B3-LYP results did agree slightly better with the few experimental data available. B3LYP has the additional advantage of being the most used methodology for large polycyclic compounds [17], so its use facilitates comparison with other theoretical studies on similar systems. To refine the results, geometries were fully optimized in B3LYP/6-311++G(d,p) calculations and each was confirmed to be a minimum on the potential energy surface by harmonic vibrational frequency analysis. Calculations were done with Gaussian09 [22]. The basis sets were chosen because they have been proven to give accurate results for polyaromatic compounds [14]. Vibrational spectra were calculated within the harmonic treatment at the same level of theory applied to the structure optimizations. The vibrational mode assignments were confirmed by eigenvector analysis of each mode. A uniform scale factor of 0.9679 was applied to all reported spectra to better represent vibrational fundamentals [23]. Additionally, MP2 and spin-projected PMP2[24] single-point energy calculations with the 6-311++G(d,p) basis sets were performed at the B3LYP optimized geometries for the singlet and triplet states respectively, to confirm the relative stability of the isomers. These MP2 energies results show good agreement with the B3-LYP calculations and they are presented in the supplemental online material.

3. RESULTS AND DISCUSION

The potential energy surfaces of mononitro-BaP and -BeP are complex. However, substitution at most positions results in only one isomer. In the singlet states of both nitro-BaP and nitro-BeP the majority of isomers are non-planar, but the most stable structures are planar. The HOMO-LUMO energy gaps of the nitro-BaP isomers are on the order of 70 kcal/mol (Table 1), about 10% smaller than those of the nitro-BePs. In general the HOMO-LUMO energy differences are small in comparison with those of the parent PAHs (91.3 kcal/mole for BeP and 77.19 kcal/mole for BaP), consistent with the higher photochemical reactivity observed for nitro derivatives [25].

Tables 1-4 list the calculated singlet and triplet B3LYP/6-311++G(d,p) energies of the molecules and some significant geometrical characteristics, while Figs. 1 and 2 depict the most relevant structures of low-energy isomers for each compound and state. In each Figure, oxygen atoms are depicted as larger and darker in color; carbon atoms are smaller and lighter. The size difference is to facilitate identification of the

atoms; their covalent radii are not very different.

3.1 Nitro Substituted benzo[a]pyrenes

In the three most stable singlet BaP derivatives, 9- , 8-, and 2-nitro-BaP, the three atoms of the nitro group lie in the molecular plane. The isomers are almost equally stable (Table 1). Charge distribution analysis shows greater interaction between NO_2 and the aromatic π-electron system than in the other isomers, and extended conjugation may enhance their stability. In 9-nitro-BaP (Fig. 1A), the N–C distance is 1.474 Å indicative of a single bond. Hydrogen bonds are seen between the nitro oxygens and the closest aromatic hydrogens. This interaction may be associated with the observed mild bending of the aromatic rings. No 9- and 8- nitro-BaP structures with non-planar NO_2 were found. Both 8-nitro-BaP (Fig. 1 B) and 2-nitro-BaP also display hydrogen bonding, the O–H bond lengths slightly shorter in the 2- than they are in the 9-and 8-nitro isomers. The stronger hydrogen bond appears to cause mild stretching of the C–N bond in 2-nitro-BaP. Although 8- and 9-nitro-BaP are the most stable isomers, they seem not yet to have been experimentally observed.

Less than four kcal/mol above the three low-lying isomers are the 1- and 3-nitro structures in which NO_2 tilts at about 30° to the aromatic plane (Fig. 1 C)). Both structures permit the formation of stronger H-bonds between O atoms and ring hydrogens. Rotation of the nitro brings an O closer to an aromatic H, resulting in a rather strong (2.17 Å) hydrogen bond. Experimental results disagree in their conclusions about the structures of these compounds. Infrared and Raman spectra indicate an out-of-plane NO_2 [16], whereas NMR results support planarity [13]. The theoretical results support those derived from vibrational spectroscopy, and it does seem that the flexibility of the aromatic system in 1- and 3-nitro-BaP and the relatively small dihedral angle would make NMR geometrical interpretation difficult for these isomers. Similarly in the 12-, 4-, 7- and 5-nitro isomers NO_2 lies out of plane by 30–33°, and no planar isomers were found. The structure of 6-nitro-BaP (Fig. 1 D) presents the biggest dihedral angle (62.6°) between the nitro group and the aromatic rings, a result in agreement with previous experimental and theoretical results [16,26]. The out-of-plane geometry is likely a factor in the weak mutagenic activity of this compound because it may obstruct binding of 6-nitro-BaP to the nitroreductase enzyme implicated in the first stages of the toxicological process.

Interesting, though relatively high-energy, structures are found when the NO_2 is in the bay region of BaP. In isomers 10b and 11b (Table 1) one oxygen forms a strong bond (O–C distance1.45 Å) that effectively creates an additional (non-aromatic) ring. The participant carbon shows near-tetrahedral bond angles of 1090, hence sp^3 hybridization. Fig. 1 E shows a bending of the aromatic system for 11-nitro-BaP supporting the idea that the non-pyrene ring is not part of the aromatic system since is not in the same plane as the rest of the molecule. The N–C length of 1.367Å indicates a bond stronger than a typical single bond. Within NO_2 the unattached N–O bond remains

Table 1. Optimized energies and geometrical parameters of singlet nitro-BaP isomers. ΔE is the difference between the isomer energy and the energy of the most stable isomer, ΔH-L is the difference between the energies of the HOMO and LUMO orbitals, both in kcal/mol. Distances are in Å. The dihedral angle corresponds to C-C-N-O and is in degrees

Isomer	Energy (au)	ΔE	ΔH-L	Dihedral	C_a-N	H_a-O_a	H_b-O_b	N-O_a	N-O_b	C_b-O_b	C_b-H_b
1	-974.1489505	4.27	67.85	28.72	1.472	2.366	2.173	1.228	1.228	2.327	1.078
2	-974.1543907	0.86	70.39	0.00	1.479	2.391	2.395	1.225	1.225	2.319	1.082
3	-974.1486070	4.49	68.54	31.28	1.473	2.175	2.378	1.228	1.227	2.308	1.081
4	-974.1474206	5.23	68.73	32.24	1.479	2.202	2.386	1.226	1.226	2.317	1.079
5	-974.1473024	5.31	68.31	31.77	1.480	2.385	2.189	1.226	1.226	2.317	1.082
6	-974.1428827	8.08	72.23	62.57	1.479	2.409	2.407	1.225	1.225	2.315	1.081
7	-974.1473313	5.29	67.84	32.32	1.478	2.181	2.399	1.226	1.227	2.313	1.081
8	-974.1546974	0.67	69.26	0.00	1.476	2.397	2.409	1.226	1.226	2.319	1.082
9	-974.1557608	0.00	67.53	0.00	1.474	2.404	2.353	1.227	1.227	2.321	1.080
10a	-974.1381442	11.05	71.67	57.05	1.482	2.604	2.488	1.223	1.226	2.311	1.082
10b	-974.0618768	58.91	27.40	7.10	1.367	2.537	2.051	1.228	1.438	1.454	1.112
11a	-974.1378741	11.22	73.29	56.44	1.482	2.510	2.591	1.222	1.226	2.310	1.079
11b	-974.0634561	57.92	27.53	6.97	1.367	2.053	2.529	1.434	1.228	1.454	1.111
12	-974.1481073	4.80	68.23	29.98	1.478	2.341	2.194	1.227	1.227	2.317	1.079
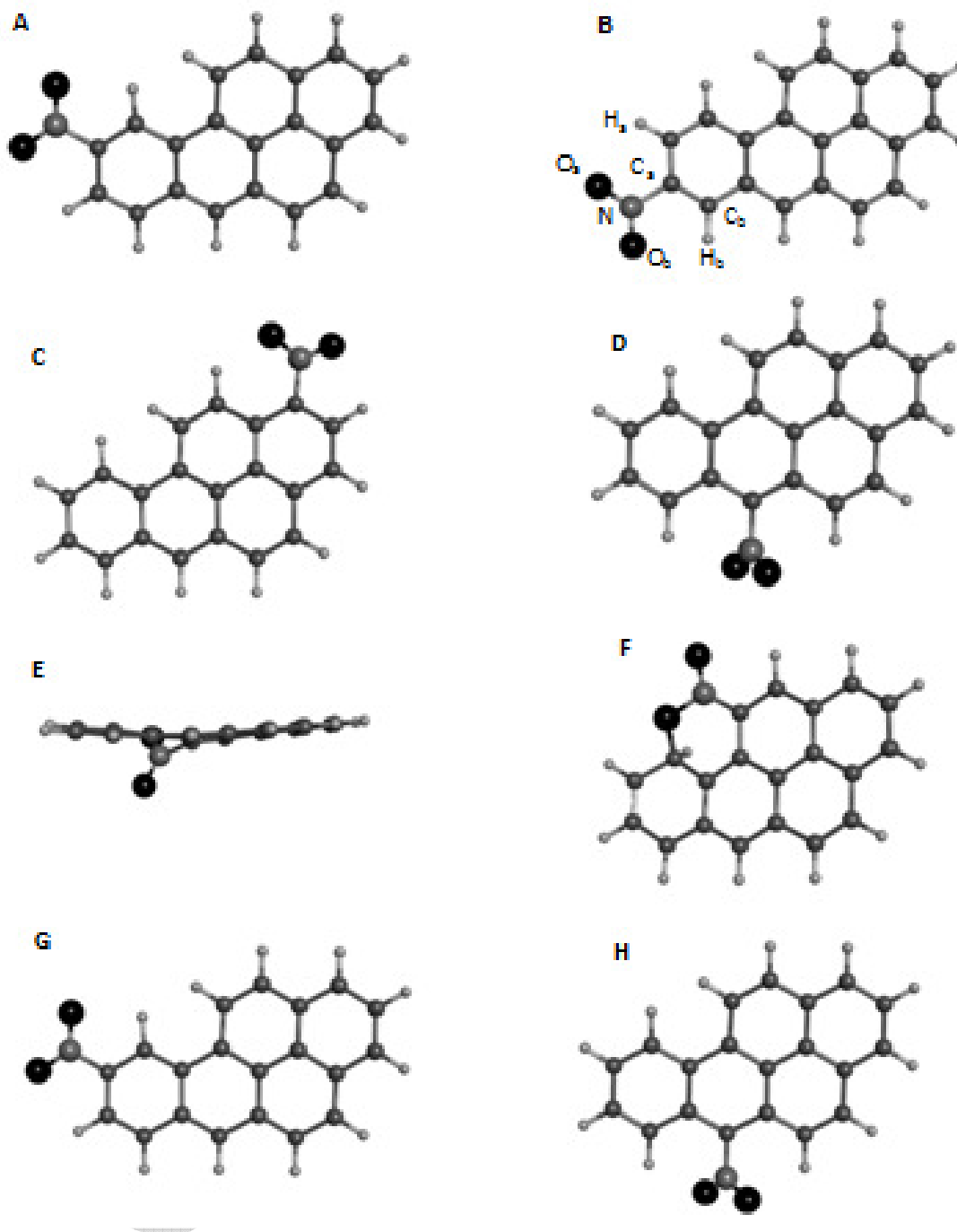
Fig. 1. Structure of selected nitro-BaP isomers. A. Singlet 9-nitro-BaP. B. Singlet 8-nitro-BaP. C. Singlet non-planar 1-nitro-BaP. D. Singlet non-planar 6-nitro-BaP. E. Singlet isomer 11a (see Table 1). F. Singlet isomer 11b. G. Triplet planar 9-nitro-BaP. H. Triplet non-planar 6-nitro-BaP

almost as it is in the free molecule, while the N-to-attached-O bond length is1.438Å. Although these configurations are relatively unstable, they may be of interest as models for structures on the path to forming a C–O bond while weakening an N–O during nitro reduction, a crucial step in initiating the toxicological process in bacteria. Moreover, the energies of these structures are only 7 kcal/mol above the corresponding triplet states (Table 2) suggesting that an easy singlet-triplet conversion may exist in these isomers, opening the possibility to different channels of reaction.

Table 2. Optimized energies and geometrical parameters of nitro-BaP isomers in the triplet state. The ΔE is informed in kcal/mol and the distances in Å. The dihedral angle corresponds to C-C-N-O and it is in degrees

Isomer	Energy (au)	ΔE	Dihedral	C_a-N	H_a-O_a	H_b-O_b	N-O_a	N-O_b	C_b-O_b	C_b-H_b
1	-974.0897757	2.68	0.00	1.446	2.239	2.049	1.240	1.240	2.301	1.080
2	-974.0888398	3.27	0.00	1.476	2.398	2.387	1.227	1.227	2.312	1.080
3	-974.0890847	3.12	4.30	1.447	2.240	2.055	1.240	1.240	2.305	1.077
4	-974.0883338	3.59	0.00	1.448	2.037	2.231	1.240	1.240	2.298	1.076
5	-974.0881702	3.69	0.00	1.449	2.231	2.007	1.240	1.241	2.298	1.079
6	-974.0818028	7.69	46.65	1.442	2.203	2.188	1.238	1.238	2.301	1.080
7	-974.0863148	4.85	0.00	1.484	2.061	2.232	1.227	1.227	2.308	1.077
8	-974.0898296	2.65	0.00	1.469	2.402	2.408	1.228	1.229	2.311	1.081
9	-974.0940500	0.00	0.01	1.451	2.400	2.350	1.235	1.235	2.304	1.081
10a	-974.0771514	10.60	16.98	1.400	2.544	2.053	1.238	1.431	1.459	1.106
10b	-974.0742960	12.40	53.70	1.479	2.586	2.580	1.223	1.227	2.315	1.081
11a	-974.0786963	9.63	19.56	1.404	2.054	2.534	1.433	1.238	1.456	1.105
11b	-974.0738117	12.70	52.04	1.479	2.589	2.562	1.223	1.228	2.315	1.081
12	-974.0884457	3.52	0.00	1.451	2.046	2.197	1.240	1.239	2.305	1.078

The 10-nitro and 11-nitro-BaP triplet display two structures each. The higher-energy species show the C–O bond formation already noted in the singlet structures. In general, for the other nitro-BaP isomers singlet-triplet energy differences are predicted to be about 39 kcal/mol. As in the singlet the lower energy isomer in the triplet state (Table 2) occurs with NO_2 at position 9 (Fig. 1 G).

It is interesting to note that there is no significant difference in the molecular geometries of these two states though their energies are significantly different. There are eight isomers lying between 2.65 and 5 kcal/mole above the triplet minimum, and in each of these the substituent lies in the molecular plane or nearly so. The isomers in which the substituent occupies positions 2 and 8 are planar in both singlet and triplet states and are relatively stable in both configurations. NO_2 at positions 1, 3, 4, 5, 7 and 12 in triplet isomers lies in or near the molecular plane, whereas in the singlet states it tilts out of the plane. Isomers with NO_2 at positions 6, 10 and 11 are non-planar, 6-nitro (Fig. 1 H) being the most stable of the triplet structures.

3.2 Nitro Substituted benzo[e]pyrenes

In the two most stable structures (Table 3), 10- and 2-nitro-BeP, NO_2 lies in the molecular plane. In 10-nitro-BeP (Fig. 2 A), the N–C distance is 1.476 Å, and there are weak hydrogen bonds between the O atoms and neighboring hydrogens. The primary factor in stabilizing the global minimum energy structure appears to be that it possesses the lowest internuclear repulsion energy. As in the case of nitro-BaP, the low energy isomers of nitro-BeP have not actually detected in the environment, indicating that thermodynamic stability of the products is not the main factor that drives BeP nitration. When NO_2 occupies other positions, the most stable isomers are non-planar. In 3- and 4-nitro-BeP NO_2 tilts, respectively, at 33° and 35° with respect to the plane (Fig. 2 B). As with singlet nitro-BaP substitution in the bay region gives rise to interesting. NO_2 at positions 1 and 9 in each case results in two isomers, one more stable in which the substituent is twisted out of the plane by more than 50° and another more than 30 kcal/mole higher in energy than the global minimum. The higher energies are just below those of the corresponding triplets, suggesting a possible minimum energy crossing point between the two potential energy surfaces. This particular feature has been previously described for carbonyl aromatic compounds [27] as well as in excited states of nitroaromatics [28] which accounts for their observed efficient intersystem crossing. In the 1a structure (Figure 2 C) the substituent is also twisted out of the plane by 53° and weak H bonds are observed, indicating reduced interaction of the nitro group with the aromatic ring. In isomer 1b (Figure 2 D) an oxygen atom bonds to a ring carbon disrupting the aromatic structure and making the isomer much less stable than its counterpart. As in the BaPs substituted in the bay region the ring containing the sp[3] carbon is slightly out of the molecular plane because it is no longer part of the aromatic system.

The energetics of the triplet nitro-BeP isomers differ somewhat from those of singlet BaP and BeP and of triplet BaP. The most stable position of substitution is 9 (Table 4), in the bay region, whereas in the singlet isomers it was 10. The stable 9-nitro-BeP isomer (Fig. 2 E) has a C–O bond, an sp[3] carbon and a short C–N distance, all features of high-energy isomers on the
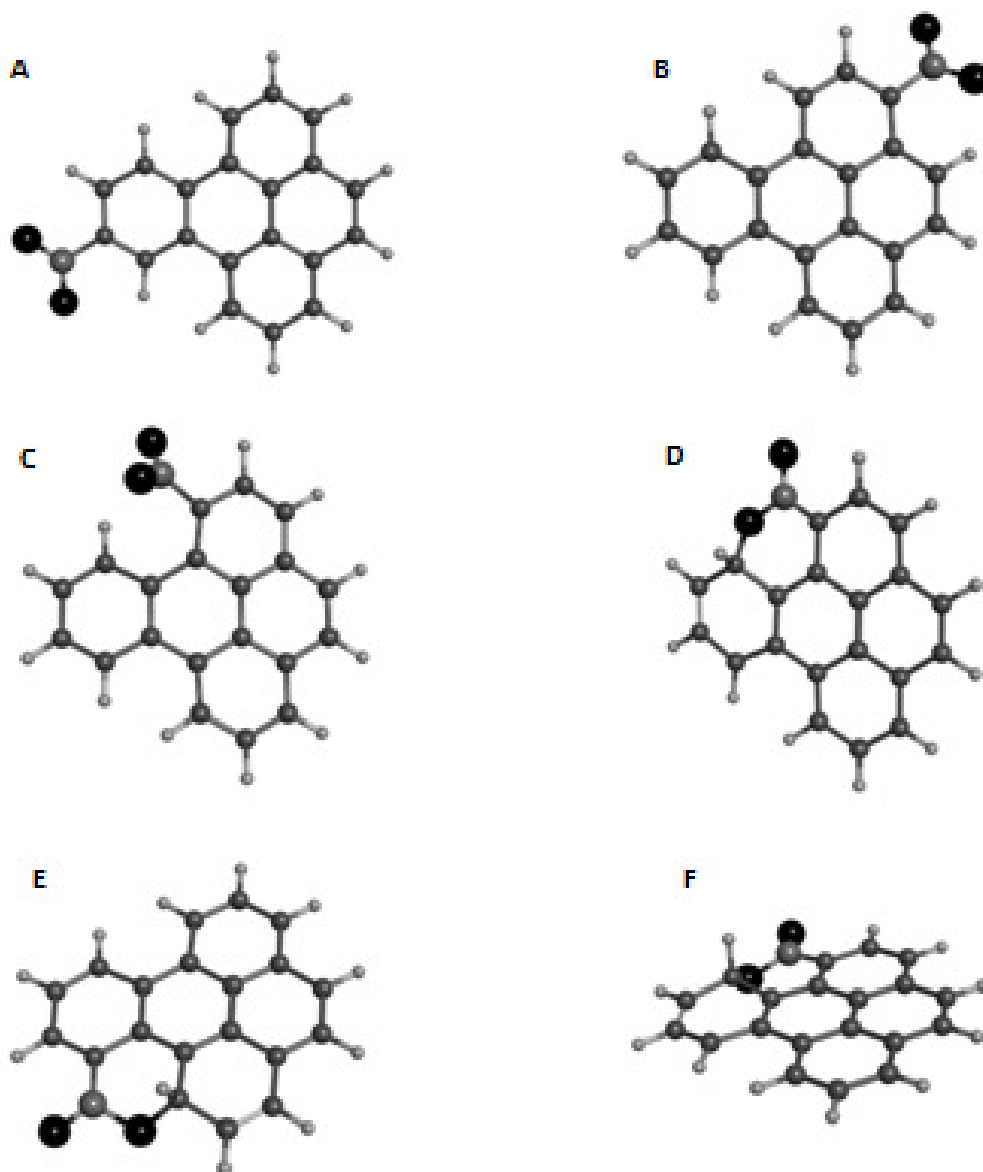
Fig. 2. Structures of nitro-BeP isomers. A. Singlet 10-nitro-BeP. B. Singlet non-planar 3-nitro-BeP. C. Singlet non-planar isomer 1a (see Table 2). D. Singlet state isomer 1b. E. Triplet 9-nitro-BeP. F. Triplet 1-nitro-BeP

other three energy surfaces. In the ring moiety carbons at positions 1 and 2 show deviations from planarity of 6°, and the oxygen atom bonded to carbon is out of plane by 20°. Furthermore, whereas additional, more nearly planar, isomers were found in each of the closely analogous structures for singlet nitro-BaP and nitro-BeP and the triplet nitro-BaP, there is only one bay-region isomer of triplet nitro-BeP. The calculated energy difference between the most stable singlet and triplet isomers is 47 kcal/mol, significantly higher than the singlet-triplet gap in

nitro-BaP. Of the remaining six isomers identified, only one, one of two substituted at position 1, lies within 4 kcal/mole of the global minimum. This structure too features an out-of-plane NO_2 (Fig. 1 F). Isomers in which the substituent occupies positions 10 and 2 are planar and structurally similar to their counterparts on the singlet surface. The structures arising from NO_2 at positions 3 and 4 show the substituent lying in the molecular plane, whereas in the singlet state geometries were non-planar.

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Table 3. Optimized energies and geometrical parameters of nitro-BeP isomers in the singlet state. ΔE and ΔH-L are in kcal/mol, and the distances in Å. The dihedral angle corresponds to C-C-N-O and is in degrees

Isomer	Energy (au)	ΔE	ΔH-L	Dihedral	C_a-N	H_a-O_a	H_b-O_b	N-O_a	N-O_b	C_b-O_b	C_b-H_b
1a	-974.1415355	10.46	79.35	52.94	1.479	2.565	2.562	1.222	1.227	2.313	1.079
1b	-974.0857935	45.44	44.17	3.88	1.347	2.537	2.054	1.229	1.431	1.455	1.108
2	-974.1581071	0.06	78.41	0.00	1.479	2.401	2.354	1.225	1.226	2.318	1.081
3	-974.1511291	4.44	77.87	32.99	1.474	2.180	2.397	1.227	1.227	2.308	1.081
4	-974.1501593	5.05	78.68	35.34	1.479	2.211	2.414	1.226	1.226	2.315	1.084
9a	-974.1404986	11.11	78.94	57.72	1.484	2.620	2.586	1.226	1.221	2.313	1.082
9b	-974.0882932	43.87	40.24	4.64	1.352	2.539	2.054	1.230	1.434	1.451	1.108
10	-974.1582041	0.00	75.32	0.04	1.476	2.419	2.359	1.226	1.226	2.313	1.079

Table 4. Optimized energies and geometrical parameters of nitro-BeP isomers in the triplet state. ΔE are in kcal/mol and the distances in Å. The dihedral is the C-C-N-O angle and is in degrees

Isomer	Energy (au)	ΔE	Dihedral	C_a-N	H_a-O_a	H_b-O_b	N-O_a	N-O_b	C_b-O_b	C_b-H_b
1a	-974.0780101	3.71	16.80	1.400	2.535	2.053	1.240	1.424	1.463	1.106
1b	-974.0663370	11.03	32.89	1.428	2.452	2.398	1.243	1.247	2.292	1.081
2	-974.0713213	7.90	0.00	1.483	2.402	2.354	1.224	1.225	2.319	1.078
3	-974.0751399	5.51	0.03	1.434	2.240	2.020	1.246	1.246	2.295	1.080
4	-974.0750333	5.57	0.00	1.433	2.001	2.220	1.247	1.248	2.286	1.076
9	-974.0839146	0.00	20.12	1.412	2.516	2.052	1.240	1.426	1.459	1.104
10	-974.0753844	5.35	0.01	1.453	2.343	2.409	1.235	1.236	2.301	1.079
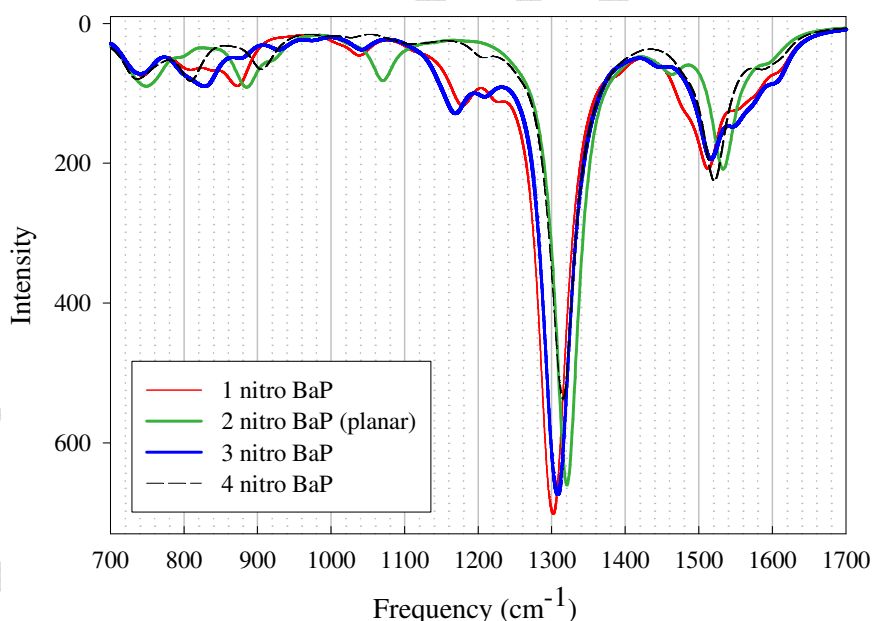
Fig. 3. Calculated infrared spectra of 1- to 4-nitro-BaP isomers in the 700–1700 cm^{-1} range. Wavenumbers are corrected by a uniform 0.9679 scaling factor (Ref. 23)

3.3 Vibrational Spectra

The corrected B3LYP/6-311++G(d,p) vibrational spectra of the molecules under study between 700 and 1700 cm^{-1} are shown in Figs. 3 to 6. This spectral region is specially interesting because contains the frequencies attributable to nitro group stretches and aromatic ring bending [29]. Symmetric NO_2 stretching bands occur in the 1300–1370 cm^{-1} range and asymmetric stretching vibration bands are observed at 1500–1550 cm^{-1}. The experimental and theoretical IR spectra of 1-, 3- and 6-nitro-BaP have been reported [16], and are in good agreement with those calculated in the present study. For 6-nitro-BaP

the theoretical nitro asymmetric stretching maximum is at 1529 cm^{-1} with the experimental fundamental appearing at 1528 cm^{-1} [16]. Overall the nitro-BaP asymmetric stretch bands appear within a narrow range of 1510-1535 cm^{-1}, showing little in the way of frequency-structure correlation. The same observation may be made for nitro-BeP isomers, with asymmetric stretching maxima at 1515-1540 cm^{-1}. In contrast, symmetric NO$_2$ stretching frequencies for both the BaP and BeP derivatives are correlated to the C-C-N-O dihedral angle. The absorption maximum increases with angle of rotation of the nitro group. For 6-, 10- and 11-nitro-BaP the symmetric NO$_2$ stretch bands

appears at frequencies higher than 1340 cm^{-1} while in the isomers with dihedral angles around 30° it appears at frequencies lower than 1320 cm^{-1}. This tendency is also observed in the BePs, and a linear relationship between dihedral angle and symmetric NO$_2$ stretching frequency (Fig. 7) can be established for all the non-planar molecules.

The intensity of the bands is consistently smaller for nitro groups rotated by about 60° than for those with rotation angles near 30°. The intensity ratio for symmetric to asymmetric stretching bands (Is/Ia) is 1.5 – 4 for dihedral angles near 30° degrees and
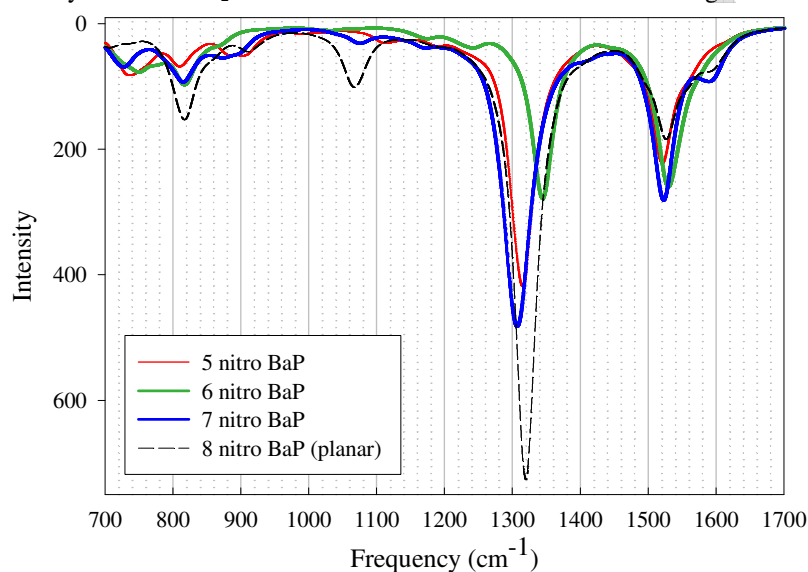
Fig. 4. Calculated infrared spectra of 5- to 8-nitro-BaP isomers in the 700–1700 cm^{-1} range. Wavenumbers are corrected by a uniform 0.9679 scaling factor (Ref. 23)
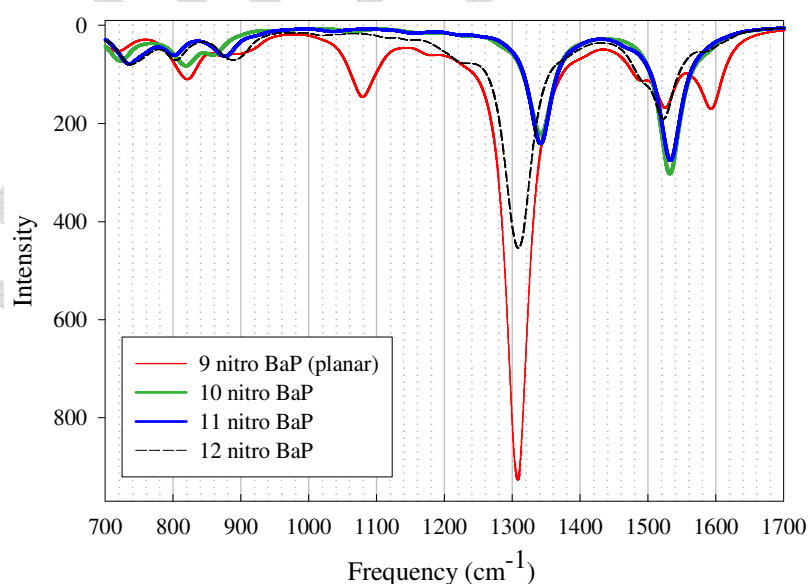
Fig. 5. Calculated infrared spectra of 9- to 12-nitro-BaP isomers in the 700–1700 cm^{-1} range. Wavenumbers are corrected by a uniform 0.9679 scaling factor (Ref. 23)

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values of 1 or less when nitro group rotation is near 60°. This profile in terms of frequency and intensity ratio has also been observed in nitropyrene [26], nitroanthracene [14] and nitrotriphenylene [10] suggesting that it can be useful in analyzing the geometries of nitro-PAHs and ultimately in assessing their potential toxicities.

Planar isomers present a different spectroscopic profile than non-planar. Their IR spectra show an intense symmetric NO_2 stretching peak around 1315 cm^{-1} and a weak asymmetric signal near 1530 cm^{-1}.

A weak but noticeable peak is observed at the 1060-1100 cm^{-1} region, characteristic of in-plane CH vibrations in aromatics. These bands are not observed in non-planar structures, the feature is common to both nitro-BaP and nitro-BeP, and it is also observed in other nitro-PAHs. The IR spectra of planar 2-nitrotriphenylene presents an absorption band near 1100 cm^{-1}, but it is not seen in non-planar 1-nitrotriphenylene [10]. Similar spectral patterns applied for nitronaphthalene [30], and nitroanthracene isomers [14] suggesting that it could be a common feature of planar nitro-PAHs.
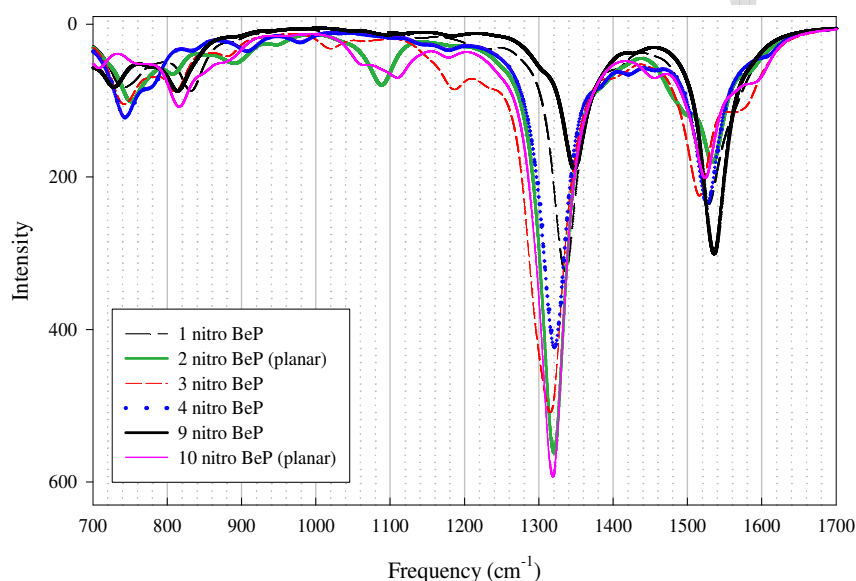

Fig. 6. Calculated infrared spectra of nitro-BeP isomers in the 700–1700 cm^{-1} range. Wavenumbers are corrected by a uniform 0.9679 scaling factor (Ref. 23)
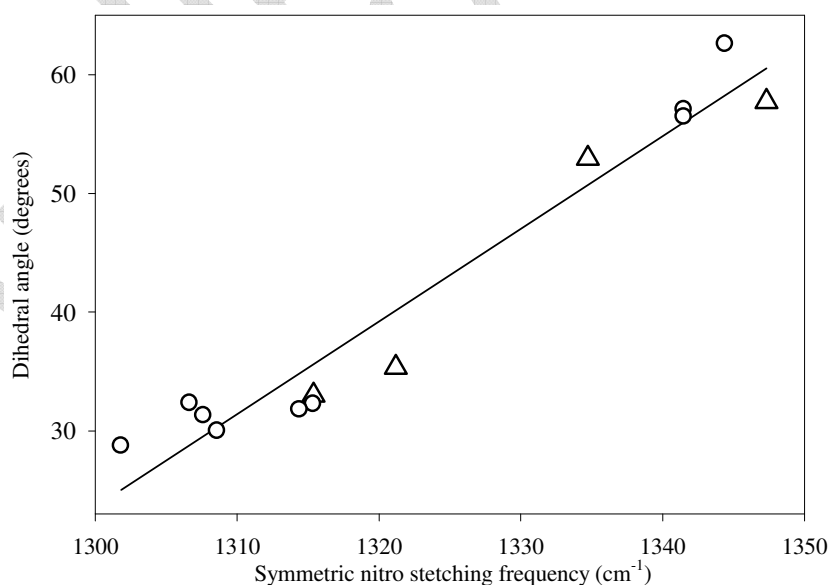

Fig. 7. Dihedral angle *vs*. symmetric NO_2 stretching frequency relationship for non- planar nitro-BaP and nitro-BeP isomers (r^2= 0.95). Circles correspond to nitro-BaPs and triangles to nitro-BePs.

4. CONCLUSION

The calculations reveal complex potential energy surfaces–competition between planarity and non-planarity of NO_2, double bond conjugation, and hydrogen bond formation. Despite the complexity, substitution at most positions yields only one minimum energy species. In the singlet states of both nitro-BaP and nitro-BeP non-planar structures are preferred at most positions, but the few planar structures are most stable. For the triplet states NO_2 at most positions lies in the molecular plane, but in triplet nitro-BeP the global minimum energy geometry is non-planar. An interesting set of structures are those resulting from substitution in the bay regions of the two molecules in which the substituent creates an additional ring structure by forming a C–O bond. In singlet nitro-BaP and nitro-BeP and in triplet nitro-BaP these are high-energy structures, forcing the bonding carbon to disrupt the aromatic system. In triplet nitro-BeP on the other hand such a structure is the global energy minimum. These structures may provide models for transition states or reactive intermediates. The relatively small HOMO-LUMO energy gaps seen in many isomers indicate that in general the nitro-BePs and -BaPs may be more photoreactive than the parent PAH.

Calculated IR spectra show distinctive band and intensity patterns for planar and non-planar structures of both nitro-BeP and nitro-BaP that are consistent with spectroscopic observations made in other nitro-PAHs. The presence or absence of band peaks around 1100 cm^{-1} could be useful in distinguishing planar from non-planar nitro-PAHs and therefore in assessing potential toxicity. Nitro-reduction is critical in the mutagenic mechanism of nitro-PAHs, and planar substrates intercalate more effectively into the active site of the nitroreductase enzyme to form the nitroreductase–nitroaromatic substrate complex. Based on the geometrical parameters and vibrational spectra here calculated, planar 2-, 8-, and 9-nitro-BaP and 2- and 10-nitro-BeP should be examined for mutagenic activity.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 92, International Agency for Research on Cancer. Lyon, France, 2010.
2. Yang D, Lan SH, Wu XW. Nitro-polycyclic aromatic hydrocarbons in particulate matter in Dongguan. Adv. Mater. Res. 2011;356:968–973.
3. Fu PP, Herreno-Saenz D. Nitro-polycyclic aromatic hydrocarbons: a class of genotoxic environmental pollutants. J. Environ. Sci. Health, Part C. 1999;17:1–43.
4. Jager J. Detection and characterization of nitro derivatives of some polycyclic aromatic hydrocarbons by fluorescence quenching after thin-layer chromatography: application to air pollution analysis. J. Chromatog. A. 1978;152:575–578.
5. Tokiwa H, Nakagawa K, Morita K, Ohnishi Y. Mutagenicity of nitro derivatives induced by exposure of aromatic compounds to nitrogen dioxide. Mutat. Res. 1981; 91:195–205.
6. Tokiwa H, Nakagawa K, Ohnishi Y. Mutagenic assay of aromatic nitro compounds with Salmonella Typhimurium. Mutat. Res. 1981;91:321–325.
7. Purohit V, Basu AK. Mutagenicity of nitroaromatic compounds. Chem. Res. Toxicol. 2000;13:673–692.
8. Fu PP, Tungeln LSV, Chiu LH, Zhan DJ, Deck J, Bucci T, Wang CJ. Structure, tumorigenicity, microsomal metabolism, and DNA binding of 7-nitrodibenz[a,h]anthracene. Chem. Res. Toxicol. 1998;11:937–945.
9. Yamagami S, Ohshima S. Structure-mutagenicity correlation of nitrated pyrenes calculated by molecular orbital method. Polycyclic Aromatic Compounds. 2012;32:133–140.
10. Onchoke KK. Structure–mutagenicity relationships and energies of 1-, and 2-nitrotriphenylenes. J. Mol. Struct.:THEOCHEM. 2009;899:79–85.
11. Alparone A, Librando V. Prediction of mutagenic activity of nitrophenanthrene and nitroanthracene isomers by simulated IR and Raman spectra. Chemosphere. 2013;90:158–163.
12. Vogt RA, Rahman S, Crespo-Hernández CE. Structure–activity relationships in nitro-aromatic compounds. Practical Aspects of Computational Chemistry. 2010:217–240.
13. Jung H, Shaikh AU, Heflich RH, Fu PP. Nitro group orientation, reduction potential, and direct-acting mutagenicity of nitro-polycyclic

aromatic hydrocarbons. Environ. Mol. Mutagen. 1991;17:169–180.

14. Alparone A, Librando, V. IR and Raman spectra of nitroanthracene isomers: substitional effects based on density functional theory study. Spectrochim. Acta A. 2012;89:129–136.

15. Onchoke KK, Ojeda JJ. A DFT study of vibrational spectra and mutagenicity predictions of mononitratedfluoranthenes. Polycyclic Aromatic Compounds. 2013;33:473–500.

16. Onchoke KK, Hadad CM, Dutta PK. Structure and vibrational spectra of mononitrated benzo [a]pyrenes. J. Phys. Chem. A. 2006;110:76–84.

17. Malloci G, Cappellini G, Mulas G, Mattoni A. Electronic and optical properties of families of polycyclic aromatic hydrocarbons: a systematic (time-dependent) density functional theory study. Chem. Phys. 2011;384:19–27.

18. Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A. 1988;38:3098–3100.

19. Becke AD. Correlation energy of an inhomogeneous electron gas: a coordinate-space model. *J*. Chem. Phys. 1988;88:1053–1062.

20. Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B. 1988;37:785–789.

21. Perdew JP, Burke K, Wang Y. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. Phys. Rev. B. 1996;54:16533.

22. Gaussian 09, Revision A.1, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr. JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian, Inc., Wallingford CT, 2009.

23. Andersson MP, Uvdal P. New scale factors for harmonic vibrational frequencies using the B3LYP density functional method with the triple- Basis Set 6-311+G(d,p). J. Phys. Chem. A. 2005;109:2937–2941.

24. Schlegel HB. Møller-Plesset perturbation theory with spin projection. J. Phys. Chem. 1988;92:3075–3078.

25. Baek SO, Field RA, Goldstone ME, Kirk PW, Lester JN, Perry R. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. Water, Air, and Soil Pollution 1991;60:279–300.

26. Li YS, Fu PP, Church JS. The conformation of some nitro-polycyclic aromatic hydrocarbons. J. Mol. Struct. 2000;550:217–223.

27. Fang WH. Ab initio determination of dark structures in radiationless transitions for aromatic carbonyl compounds. Acc. Chem. Res. 2008;41:452–457.

28. Morales-Cueto R, Esquivelzeta-Rabell M, Saucedo-Zugazagoitia J, Peon JL. Singlet excited-state dynamics of nitropolycyclic aromatic hydrocarbons: direct measurements by femtosecond fluorescence up-conversion. J. Phys. Chem. A. 2007;111:552–557.

29. Stout PJ, Mamantov G. Matrix isolation FT-IR studies of nitro polycyclic aromatic hydrocarbons. Appl. Spectrosc. 1987;41:1048–1052.

30. Govindarajan M, Karabacak M. FT-IR, FT-Raman and UV spectral investigation, computed frequency estimation analysis and electronic structure calculations on 1-nitronaphthalene. Spectrochimica Acta Part A. 2012;85:251–260.

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