



IR and Raman spectra of nitroanthracene isomers: Substitutional effects based on density functional theory study

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ABSTRACT

Structure, IR and Raman spectra of 1-, 2- and 9-nitroanthracene isomers (**1-NA**, **2-NA** and **9-NA**) were calculated and analyzed through density functional theory computations using the B3LYP functional with the 6-311+G** basis set. Steric and π -conjugative effects determine the characteristic O–N–C dihedral angles, which vary from 0° (**2-NA**) to 28–29° (**1-NA**) and 59° (**9-NA**), influencing the relative order of stability along the series **9-NA** < **1-NA** < **2-NA**. The spectral regions at wavenumber values >3000 cm⁻¹ and <1000 cm⁻¹ little depend on the substituent position. The Raman and IR intensity values of the characteristic symmetric nitro group stretching transition, appearing between 1310 and 1345 cm⁻¹, are rather sensitive to the position of the substituent, decreasing regularly on passing from the planar to the NO₂-rotated isomers (**9-NA** < **1-NA** < **2-NA**). In the medium-energy spectral region (1000–1700 cm⁻¹), the number and the relative position of the strongest Raman bands are of potential utility to discriminate the **NA** isomers. Structural and spectroscopic results suggest that the unknown mutagenic activity of **1-NA** is expected to be between that of **9-NA** and **2-NA**.

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1. Introduction

Nitroanthracenes (**NAs**) belong to a class of widely distributed environmental contaminants known as nitrated polycyclic aromatic hydrocarbons (NPAHs) [1–5]. NPAHs are usually released in the environment during incomplete combustion processes or by reaction between polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides present in the atmosphere [5–8]. Many NPAHs exhibit extremely high mutagenic and carcinogenic potencies, often greater than those of their parents PAHs [2–4]. It is well recognized that mutagenic and carcinogenic activities of NPAHs are dramatically affected by the structure. Planar NPAHs exhibit higher mutagenic potencies than the corresponding isomers with the nitro group oriented perpendicularly to the aromatic moiety [2–4].

Nitroanthracenes exist as three isomers (Fig. 1): **1-NA** and **9-NA** are predicted to be non planar, while **2-NA** exhibits a planar arrangement. Experimental structures of **NAs** are not available in the literature, except for the geometry of **9-NA** in the solid [9]. This isomer characterized by the NO₂ group arranged perpendicularly to the aromatic plane, is a prototypical molecule for

the study of photochemical degradation reactions [10–13]. Photodegradation mechanisms are by far the most important natural phenomena of removal of NPAH pollutants in the environment [4]. On the theoretical side, semiempirical PM3 [14] and density functional theory (DFT) structures of **NAs** [15] were previously reported, while Lee et al. [16] computed the electronic second-order hyperpolarizability by using a finite-field procedure. The different retention times for **2-NA** and **9-NA** as determined by HPLC analyses are consistent with their distinct structure and dipolar character [17].

The mutagenic activities of the **NA** isomers are somewhat different to each other. On the basis of the Ames test, which commonly uses the *Salmonella typhimurium* strains TA98 and TA100, **2-NA** is estimated to be three order of magnitudes more mutagenic than **9-NA** [18–22]. The mutagenic potency for **1-NA** is unknown so far. Therefore it is of great importance to identify analytic methodologies suitable to discriminate structurally different isomers. To this purpose, IR and Raman spectroscopies can be very helpful. Vibrational spectra can be accurately simulated through high-level quantum mechanical calculations [23,24].

In the present work, we determined and analyzed the vibrational spectra for the series of the **NA** isomers by using DFT computations. The spectroscopic properties and complete normal mode assignments are reported here for the first time. To our knowledge, some experimental wavenumber values are available only for **2-NA** [25] and **9-NA** [26]. The main goal of this work is to explore the effects of the position of the substituent on the IR and

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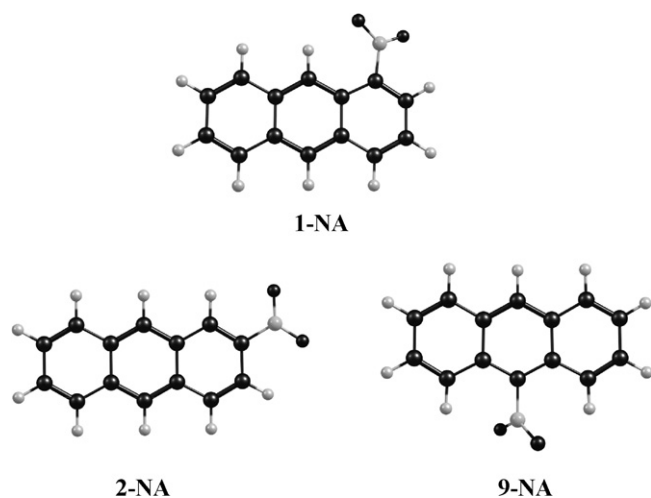


Fig. 1. Structure of nitroanthracene isomers.

Raman spectra, in order to identify vibrational markers potentially useful to distinguish the **NA** isomers.

2. Computational details

All computations were performed with the Gaussian 03 program [27]. The ground-state geometries of the **NA** isomers were optimized by using the DFT-B3LYP functional [28,29] with the 6-31G* and 6-311+G** basis sets. IR and Raman spectra were calculated under the harmonic approximation at the B3LYP/6-31G* and B3LYP/6-311+G** levels using the geometries computed at the same levels. The absence of imaginary wavenumber values confirms that all the structures correspond to equilibrium minima on the potential energy surfaces. In general DFT harmonic treatments overestimate observed vibrational wavenumbers owing to neglecting of anharmonic corrections, incompleteness of basis set and electron correlation contributions. These discrepancies are commonly corrected either by computing explicitly anharmonic terms [30,31] or by performing scaled quantum mechanical force field procedures [32], or directly by scaling the calculated wavenumbers with a given factor [33]. For this series of compounds anharmonic treatments are computationally impracticable and therefore we adopted the scaling approach employing a single factor of 0.9594 and 0.9679, specifically determined for the B3LYP/6-31G* [33] and the B3LYP/6-311+G** [34] levels of calculation, respectively. This approach was proven to give good results for the vibrational spectra of substituted PAHs [35–42]. Complete vibrational assignments were carried out on the basis of normal modes, as displacements in redundant internal coordinates (in Gaussian 03, option Freq = IntModes) and also by means of the visualization software Chemcraft [43].

3. Results and discussion

The experimental geometry is available only for **9-NA** from X-ray measurements [9]. As can be seen from the data reported in Table 1, the B3LYP/6-311+G** level furnishes the best results, in agreement with the comparison between the observed [44] and calculated data of nitrobenzene (**NB**). For **9-NA** the B3LYP/6-31G* and B3LYP/6-311+G** computations, respectively, underestimate the experimental C–N bond length by 0.010 and 0.003 Å, the O–N–C–C dihedral angles by 34° and 26°, while overestimate the O–N bond length by 0.016 and 0.009 Å. These differences can be principally attributed to crystal packing effects. In fact, in carbon tetrachloride solution the O–N–C–C dihedral angle for the most stable

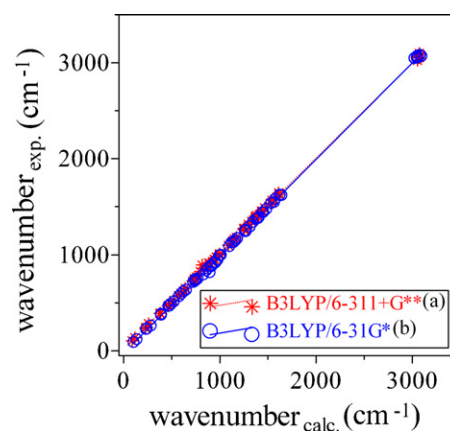
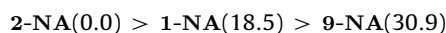


Fig. 2. Experimental [47] vs. calculated wavenumbers relationships for anthracene. (a) $\text{wavenumber}_{\text{exp.}} = 21.51 + 0.99 \times \text{wavenumber}_{\text{calc.}}$, $r^2 = 1.00$; (b) $\text{wavenumber}_{\text{exp.}} = -21.89 + 1.01 \times \text{wavenumber}_{\text{calc.}}$, $r^2 = 1.00$.

configuration of **9-NA** was estimated to be 64° [26], somewhat close to the gas phase B3LYP/6-311+G** datum. At the B3LYP/6-311+G** level on passing from **2-NA** to **1-NA** and **9-NA** the C–N bond length increases by 0.003 and 0.005 Å, respectively. In addition, the O–N–C–C dihedral angles, which crucially characterize the structure of NPAHs, are calculated to be 28° and 29°, 0° and 0°, 59° and 59° for **1-NA**, **2-NA**, **9-NA**, respectively. The relative stability for the **NA** isomers computed at the B3LYP/6-311+G** level decreases in the order (in parentheses is reported the relative energy corrected for the zero-point vibrational contribution expressed in kJ/mol):



The corresponding values computed at the B3LYP/6-31G* level are rather similar, being 0.0, 17.9 and 32.9 kJ/mol, respectively. This trend is consistent with the structural data and is consequence of the steric repulsions between the hydrogen atoms and the closest oxygen atoms for the NO₂-rotated structures, which decrease the π -conjugative interaction between the nitro group and the aromatic moiety.

To the best of our knowledge experimental and theoretical vibrational studies of **NAs** are not available, except for a SERS study of **9-NA** [45], FT-IR and FT-Raman spectra of **2-NA** [25] and the vibrational wavenumber values for the NO₂ symmetric stretching vibration of **9-NA** in carbon tetrachloride solution and solid phases [26]. However, complete normal mode assignments are lacking so far. On the other hand, several experimental and theoretical vibrational spectra of the parent compounds anthracene (**A**) [46–48] and **NB** [49] are known and were here employed to validate the theoretical approach. Present simulated spectra were obtained by convoluting the computed wavenumber values using pure Lorentzian band shapes with a full width at half maximum of 10 cm⁻¹, as commonly adopted in the literature [50–55].

3.1. IR and Raman spectra of anthracene and nitrobenzene

The B3LYP/6-311+G** wavenumber, IR intensity (I_{IR}) and Raman activity (A_{Raman}) values for **A** and **NB** are listed in Tables 2 and 3, respectively, together with the available experimental data reported in Refs. [47] and [49]. Present corrected wavenumber values are in reasonable agreement with both experimental and previous DFT data [46–49] (Figs. 2 and 3). In comparison to the observed wavenumber values, a root-mean-square deviation of 19 cm⁻¹ is found for both **A** and **NB** (20 cm⁻¹ using the less expensive B3LYP/6-31G* level), which raises to 45 and 49 cm⁻¹ in the case of the uncorrected data, respectively.

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