



DFT/TD-DFT investigation of optical absorption spectra, electron affinities, and ionization potentials of mono-nitrated benzantrones

Kefa K. Onchoke*

Department of Chemistry, Stephen F. Austin State University, Box 3006, SFA Station, Nacogdoches, TX 75962-13006, USA

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ABSTRACT

Density functional theory (DFT) method B3LYP with basis sets 6-311+G(d,p), 6-31G(d) and 6-311G(d,p) have been used to compute molecular structures, UV–vis absorption spectra, electron affinities (EAs), and ionization potentials (IPs) of benzantrone and 1-, 2-, 3-, 9-, 10-, and 11-nitrobenzantrones. With the use of the time-dependent TD-B3LYP/6-311G(d,p) approach, the UV/vis absorption spectral bands, vertical excitation energies and oscillator strengths was studied. The calculated vertical excitation energies lie within <0.15 eV of the observed values. In comparison to benzantrone, calculated absorption spectra of nitrated nitrobenzantrones show red-shifting to >383 nm, which is correlated to their relative reactivity. Detailed clarification of the singlet-singlet excited states (and energies) are made. The calculated electron affinities are ~0.5 eV greater than in benzantrone (BA); being in the order 3-NBA > 10-NBA > 1-NBA > 2-NBA > 9-NBA > 11-NBA > BA. Similarly, ionization potentials follow a very close order in nitro-BAs. The calculated EAs and IPs implicate both reductive and oxidative pathways on transformation to mutagenic metabolites. The implications of the results are discussed in the context of their differential mutagenic potencies.

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1. Introduction

Understanding the structural properties of chemical compounds is not only of fundamental importance in chemistry, but also a prerequisite for deciphering their interaction with biological systems. Among hundreds of known polycyclic aromatic hydrocarbons (PAHs), nitro substituted PAHs (nitro-PAHs) are of particular interest because of the significant mutagenic, carcinogenic, tumorigenic, teratogenic activities they pose to humans and animals [1–3]. Nitro-PAHs are ubiquitous environmental contaminants found in airborne particulate matter, fossil fuel combustion products, coal fly ash, cigarette smoke and vehicular emissions, and are products of reactions between the parent PAHs with nitrogen oxides, and atmospheric gas-phase reactions on the surfaces of particulate matter [1,4–7]. Apart from exhibiting a high direct-acting mutagenic potency in bacterial and mammalian cells, epidemiological studies have shown an association between mortality and morbidity from cardiovascular and respiratory diseases, and ambient air pollution [8–12].

Benzantrone (7H-benz(de)anthracen-7-one) is one of the ubiquitous PAHs recently detected in the environment [13–17]. Benzantrones's mono nitrated derivatives, namely 1-, 2-, 3-, 9-, 10-, and 11-nitrobenzantrones (1-, 2-, 3-, 9-, 10-, 11-NBA), are

present in the environment in various matrices such as rain water, surface soil and sediments [18]. While 3-NBA was first found [14] to be a product of reactions of benzantrone with nitrogen oxides and diesel extracts in the presence of ozone, 2-NBA was detected as a nitration product of BA [18,19]. Subsequent investigations revealed 1-, 2-, 3-, 9-, 10-, and 11-NBAs to be present in ambient particulate samples [10].

Chromatographic and spectroscopic methods including HPLC, gas-liquid chromatography, electrochemistry, $^1\text{H}/^{13}\text{C}$ NMR and UV–vis techniques have been reported on concentrations of benzantrone (BA), 1-, 2-, 3-, 9-, 10-, and 11-NBA in the environment [14,15,18]. Though biological investigations on 3-, and 2-NBAs, notably by Volker [9–11,16] are available, there is a scarcity of experimental and theoretical structural reports of nitro-BA isomers.

Early studies [1,20,21] used the conformation of the nitro group in nitro-PAHs, as a predictor of their observed biological effects. Because 3-NBA was found more mutagenic than 1-, 2-, 9-, 10-, or 11-NBA, the nitro group in 3-NBA is thought more planar to the aromatic moiety. However, there is a lack of detailed experimental (X-ray, neutron or electron diffraction) data to corroborate such conclusion. Absorption and fluorescence quantum yields of the mono nitrated benzantrones have been done [22], without detailed characterization of the structures, ground state excited states and assignments of transitions. In this paper, quantum mechanical calculations using the popular B3LYP functional and

* Tel.: +1 936 468 2386; fax: +1 936 468 7634.

E-mail addresses: Onchokekk@sfasu.edu, kefaon@yahoo.com

6-31G(d) and 6-311+G(d,p) basis sets were utilized to provide better structural information. In addition, ground state absorption spectral properties of these NBAs were examined with the time-dependent DFT, B3LYP/6-311+G(d,p)//TD-B3LYP/6-311G(d,p), level. Detailed assignments of the electronic transitions and absorption spectra of the nitrated BAs, are correlated to the structural changes with trends in the mutagenic potencies, especially from the observed biological activities. Also an understanding of the reducibility of the nitro group via electron affinity (EA), HOMO/LUMO, and ionization potential (IP) energies was made in this study.

2. Computational methods

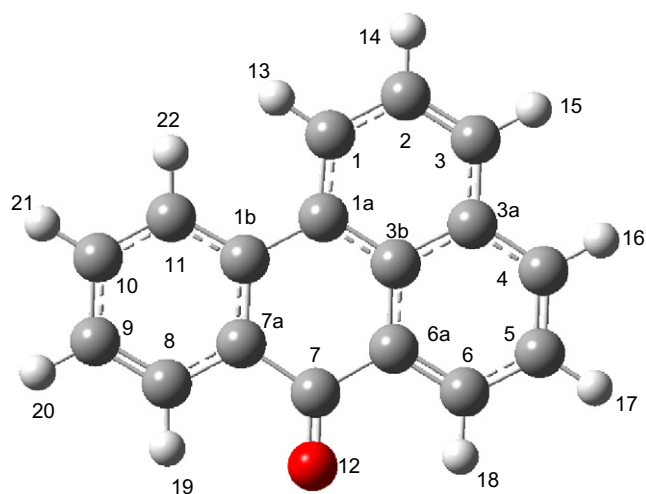
Geometry optimization of the ground states without any geometrical restriction were performed at the B3LYP/6-311+G(d,p) [23,24] level of theory using the Gaussian 03 software package [25]. The B3LYP functional [26,27] was used with same basis sets used for geometry optimization. The B3LYP/6-311+G(d,p) level of theory generally yields accurate structural parameters (bond lengths, angles) of straight and nitrated PAHs [28,29] in good agreement to neutron and X-ray diffraction data. Optimized geometries of all structures were confirmed to be minima on their potential energy surfaces as revealed by lack of imaginary frequencies. Time-dependent-DFT (TD-B3LYP method with basis set 6-311G(d,p) [30] was performed using B3LYP/6-311+G(d,p) optimized geometries. The vertical excitation energies for the first 30 dipole-allowed singlet-singlet states were calculated. The molecular orbital density plots were constructed using the GaussView program [31]. The simulated absorption spectra were fitted with a Lorentzian-type line shape with half-width at a half-maximum of 10 nm.

In order to evaluate the relative reducibility of nitrated benzantrones, vertical electron affinities (EA) and vertical ionization potentials (IPs) were calculated with the B3LYP functional with 6-311+G(d,p) and 6-31G(d) basis sets, respectively. The EAs and IPs were obtained via the Δ SCF method in which the energies of ions (the anion and cation) are separately calculated as follows:

$$IP = E_{\text{cation}} - E_{\text{neutral}}, \text{ and}$$

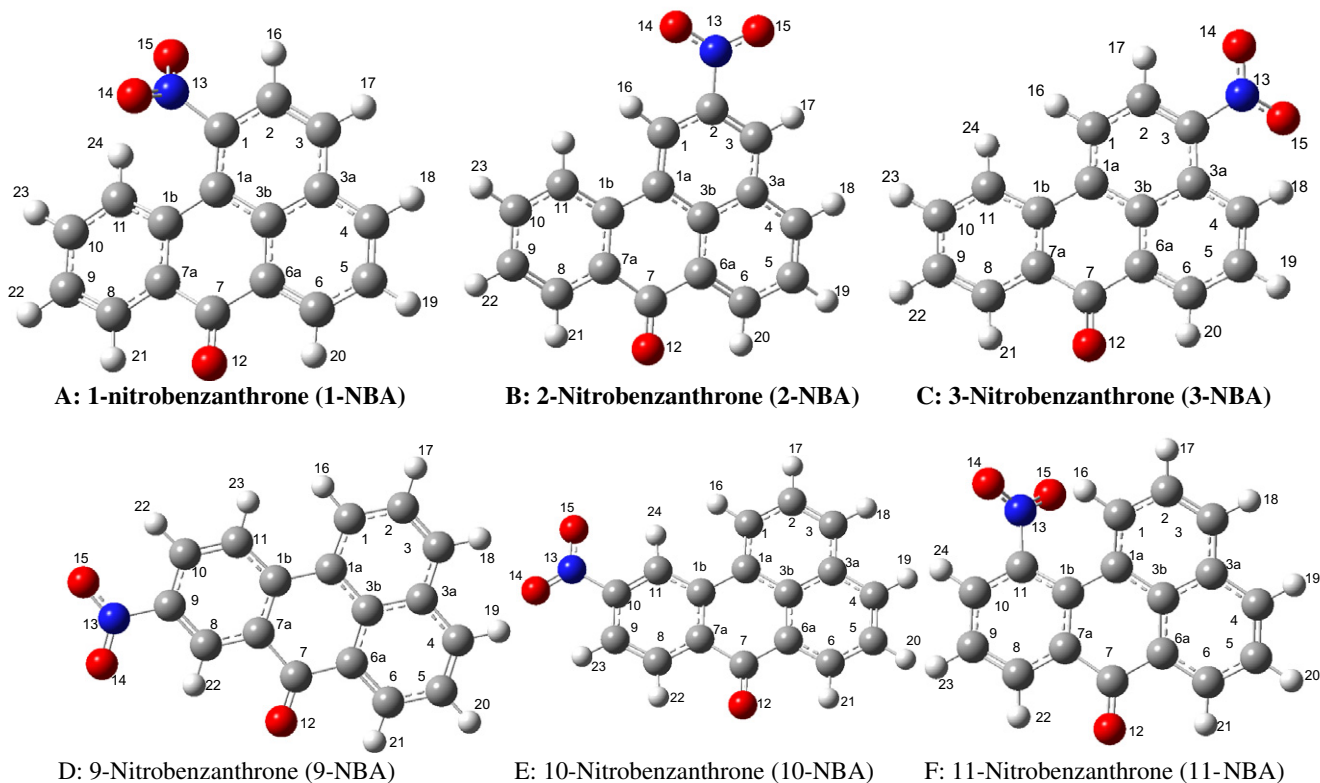
$$EA = E_{\text{neutral}} - E_{\text{anion}}.$$

For neutral ground state the restricted B3LYP functional was used in computing the total energy, while unrestricted (UB3LYP) formalism was used for radical cations and anions.



Benzanthrone (BA)

Fig. 1. Optimized B3LYP/6-311+G(d,p) structure and atom labeling of benzantrone.



A: 1-Nitrobenzantrone (1-NBA)

B: 2-Nitrobenzantrone (2-NBA)

C: 3-Nitrobenzantrone (3-NBA)

D: 9-Nitrobenzantrone (9-NBA)

E: 10-Nitrobenzantrone (10-NBA)

F: 11-Nitrobenzantrone (11-NBA)

Fig. 2. Optimized B3LYP/6-311+G(d,p) structures and atom labeling of 1-, 2-, 3-, 9-, 10-, and 11-nitrobenzantrone (A–F).

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