



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Vibrational and electronic spectra of 2-nitrobenzanthrone: An experimental and computational study

Kefa K. Onchoke*, Saad N. Chaudhry, Jorge J. Ojeda

Department of Chemistry & Biochemistry, Stephen F. Austin State University, Box 13006 – SFA Station, Nacogdoches, TX, 75962-3006, United States



ARTICLE INFO

Article history:

Received 28 April 2015

Received in revised form 18 August 2015

Accepted 30 August 2015

Available online 3 September 2015

Keywords:

Benzanthrone

2-Nitrobenzanthrone

FT-IR spectra

FT-Raman spectra

UV-Vis spectral properties

Fluorescence quantum yields

DFT calculation

PEDs

ABSTRACT

The environmental pollutant 2-nitrobenzanthrone (2-NBA) poses human health hazards, and is formed by atmospheric reactions of NO_x gases with atmospheric particulates. Though its mutagenic effects have been studied in biological systems, its comprehensive spectroscopic experimental data are scarce. Thus, vibrational and optical spectroscopic analysis (UV-Vis, and fluorescence) of 2-NBA was studied using both experimental and density functional theory employing B3LYP method with 6-311 + G(d,p) basis set. The scaled theoretical vibrational frequencies show good agreement to experiment to within ~5 cm⁻¹ and <20 cm⁻¹ for frequencies <1800 cm⁻¹ and 2700–3200 cm⁻¹, respectively. In addition, predictions of the DFT frequencies below 1800 cm⁻¹ yield an overall root mean square (RMS) of ±20.1 and ±20.6 cm⁻¹ for benzanthrone and 2-NBA, respectively. On the basis of normal coordinate analysis complete assignments of harmonic experimental infrared and Raman bands are made. The influence of the nitro group substitution upon the benzanthrone structure and symmetric CH vibrations, and electronic spectra is noted. This study is useful for the development of spectroscopy-mutagenicity relationships in nitrated polycyclic aromatic hydrocarbons.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Nitropolycyclic aromatic hydrocarbons (nitro-PAHs) are environmental pollutants and toxicants whose properties merit continuous investigation. They are formed from atmospheric reactions on particulate matter surfaces when nitrogen oxide gases (NO_x) react with PAHs at high temperature conditions, such as power plant emissions, automobiles and combustion machines [1–4]. Nitro-PAHs play a significant role in atmospheric reactions, allergenic, carcinogenic, and mutagenic effects in biological systems. Studies have shown that nitroreductases transform nitro-PAHs to more hazardous metabolites which exhibit carcinogenic and mutagenic properties in human and bacterial systems [4–6]. Therefore, the spectroscopic understanding of these nitro-PAHs is pertinent to deciphering the adverse chemical reactions they evoke in cells.

Nitrobenzanthrones, including 2-nitrobenzanthrone (2-NBA), exhibit more carcinogenic and mutagenic effects than the parent PAH, benzanthrone [7–9]. Although Arlt et al. [9,10] has studied the mutagenic and carcinogenic effects of 3-NBA upon bacterial and human cells, much less studies are available for 2-NBA. These studies have entailed developing better methods of detection and the mutagenic effects of 3-NBA DNA adducts. In contrast to 3-nitrobenzanthrone (a powerful bacterial mutagen and a human carcinogen found in diesel and urban

particulate matter [7,8]), 2-nitrobenzanthrone is formed by reactions of NO_x gases with benzanthrone on particulate matter surfaces [11, 12]. Through the use of HPLC, NMR, and fluorescence techniques, Phousongphouang and Arey, and Tang et al. [13,14] found 2-NBA and 3-NBA concentration ratios of 495 and 6.8 pg/m³, respectively, in ambient air samples in USA and Japan. Although other nitrobenzanthrone isomers exist, tedious chromatographic separations often make experimental characterization challenging. In a previous study Onchoke [15] noted that some NBA isomers have very close dipole moments. The calculated dipole moments were found in the order: 2-NBA (2.03 D) < 11-NBA (2.25 D) < 1-NBA (3.27 D) < BA (3.85 D) < 3-NBA (4.00 D) < 10-NBA (6.02 D) < 9-NBA (8.83 D) [15]. Thus, 2-NBA can be purified by tedious column chromatographic separation. However, as demonstrated by Kalasinsky et al. [16], compounds with small differences in dipole moments, such as closely related isomers, may be distinguished using FTIR techniques. The availability of 2-NBA in this study enabled us to perform its spectroscopic and electronic (UV-Vis, fluorescence) optical studies.

In this paper, a thorough experimental and computational study of the vibrational, UV-vis, and fluorescence properties of 2-nitrobenzanthrone is reported. This data provides detailed benchmark reference information necessary for deciphering physico-chemical properties essential for understanding the a priori observed mutagenic properties in cells. In addition, electronic-mutagenicity correlations between observed mutagenic potentials for BA and 2-NBA are discussed. The physico-spectroscopic-electronic properties are

* Corresponding author.

E-mail address: onchokekk@sfasu.edu (K.K. Onchoke).

essential to deciphering spectroscopy–structure–mutagenic potencies, especially observed biological activities in cells.

2. Experimental and computational details

Caution: Benzanthrone (BA) and 2-nitrobenzanthrone (2-NBA) are known mutagens and carcinogens. Therefore necessary safety precautions must be taken in handling them.

2.1. Materials and instrumentation

Benzanthrone (99.8% purity) and 2-nitrobenzanthrone ($\geq 95\%$) were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used as purchased. Purity of BA and 2-NBA were confirmed with HPLC. Additionally, the elution profile and retention times of 2-NBA and BA from a C-18 HPLC column (50:50 v/v, methanol/acetonitrile solvent mixture, flow rate of 0.75 mL/min, pressure of 34–40 bar) were determined as 5.77 and 6.42 min, respectively. The FT-IR spectra in the 230–4000 cm^{-1} region (diffuse reflectance spectroscopy (DRIFTS) on an abrasive pad, ATR and in KBr pellet (4 cm^{-1} resolution)) were measured on a PerkinElmer Spectrum 100 spectrometer equipped with a Ge/CsI beam splitter and a DTGS detector. Four to eight scans or greater were collected in the transmission or Kubelka–Munk modes. Solid-phase FT-Raman spectra (4 cm^{-1} resolution, scan acquisition time and accumulation = 3 s and 3, CCD detector operating at $-50 \text{ }^\circ\text{C}$), were recorded on a Perkin Elmer 400 Raman Station multichannel spectrometer. Benzanthrone and 2-nitrobenzanthrone samples were positioned using a motorized X–Y stage, and excited with 785 nm wavelength (corresponding to Raman shifts of 75–3200 cm^{-1}) and laser power of $< 50 \text{ mW}$. The CCD Raman detector was equipped with a built-in thermoelectric cooler working at $-50 \text{ }^\circ\text{C}$.

2.2. UV–Vis absorption, fluorescence measurements and quantum yields

Spectral properties of BA and 2-NBA were measured in high grade analytical solvents chloroform, acetonitrile, ethyl acetate, hexane, ethanol, methanol at ambient temperature in 10 mm quartz cuvettes. UV–Vis spectra was recorded with a Shimadzu 2550 PC spectrophotometer from 200 to 600 nm and confirmed to reported literature [17,18]. The fluorescence emission spectra were recorded using a Perkin Elmer LS 55 fluorescence spectrometer. The fluorescence emission spectra and quantum yields were recorded using pyrene ($\Phi = 0.72$) and chrysene ($\Phi = 0.23$) in EtOH [19] as reference standards. Fluorescence quantum yields were calculated with a comparative method using equations given in references [19–21]. For fluorescence measurements, only dilute degassed solutions with an absorbance of ~ 0.10 were used at two wavelengths of 276 and 334 nm in 1-cm quartz cuvettes. An amount of the UV/Vis solution was transferred to a 10 mm optical path length quartz fluorescence cell (Hellma 110-QS, 110-10-40) and subjected to a fluorescence measurement. Subsequently, the absorption of the sample was measured again to exclude photobleaching effects.

2.3. Computational details

DFT quantum chemical calculations for geometry optimizations, vibrational frequencies, were performed at the B3LYP/6-311 + G(d,p) level of theory using the default optimization algorithm coded in Gaussian 09, Revision B.01 [22]. We previously reported optimized geometries at the Cs symmetry, energies, and dipole moments for BA and 2-NBA at the same level of theory [15]. Harmonic and anharmonic vibrational frequencies $< 2000 \text{ cm}^{-1}$ were uniformly scaled by 0.98 [23]. A scaling factor was derived from linear regression fitting approaches [24,25]. Normal mode assignments in this study are based upon the description of the motions and inspections of eigenvectors using Chemcraft [26], Gaussview 5.0 programs [27], and comparisons between calculated/observed bands. For unequivocal IR and Raman normal mode assignments, potential energy

distribution (PEDs) were calculated using the VEDA 4 program [28] and Gaussview 5.0 visualization interface. The optimized structures and atomic labels used in text for benzanthrone and 2-nitrobenzanthrone (2-NBA) are shown in Fig. 1. The normal modes, % PEDs and assignments are available in Supporting Information Tables S1–S2. The calculation using the time dependent DFT method and interpretation of the UV–Vis assignments was reported in Ref # [15].

3. Results

3.1. Ground state geometrical structures

Benzanthrone and nitrobenzene were previously used to assess the computational methodology at the B3LYP/6-311 + G(d,p) level of theory [15]. The optimized equilibrium geometrical parameters were taken from Ref # [15]. The reported optimized geometries in ref # [15] predict benzanthrone and 2-nitrobenzanthrone planar with dipole moments 3.85 D and 2.03 D, respectively [15]. This is in agreement with the determined retention times of 5.77 and 6.42 min for 2-NBA and BA, respectively, using a C-18 HPLC column (50:50 v/v, methanol/acetonitrile solvent mixture, flow rate of 0.75 mL/min, pressure of 34–39 bar). The calculated $r(\text{CC})$, $r(\text{C}=\text{O})$ and $r(\text{C}-\text{H})$ bond lengths in benzanthrone

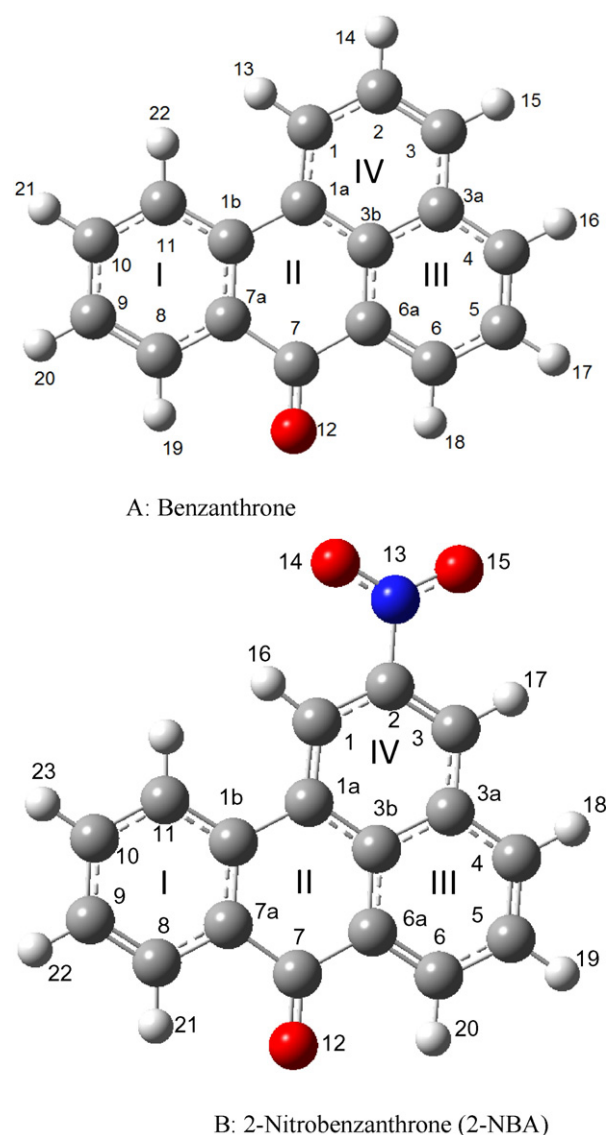


Fig. 1. Optimized B3LYP/6-311 + G(d,p) structures and IUPAC atom labeling of: (A) benzanthrone and 2-nitrobenzanthrone (B, 2-NBA).

Download English Version:

<https://daneshyari.com/en/article/1228742>

Download Persian Version:

<https://daneshyari.com/article/1228742>

[Daneshyari.com](https://daneshyari.com)