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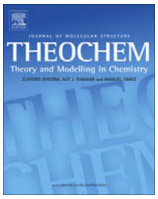

Theoretical analysis of anthracene and its carbonyl and carboxyl derivatives using DFT and TD-DFT

Diana Barraza-Jimenez, Alberto Flores-Hidalgo, Daniel Glossman-Mitnik *

Red MONEAR and PRINATEC—Centro de Investigación en Materiales Avanzados, S.C., Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chih. 31109, Mexico

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ABSTRACT

The geometric parameters characterization and ground state energies for anthracene and four of its derivatives which contained as substituents the carboxyl and carbonyl groups in the 9-position were calculated using Density Functional Theory (DFT). The excited state energies, as well as absorption wavelength, were computed using Time Dependent-Density Functional Theory (TD-DFT). For the emission wavelength the excited state geometry optimization was carried through the use of Hartree–Fock Configuration Interaction Singles (HF/CIS). After applying the HF/CIS we calculated the vertical energy calculations using TD-DFT. The theoretical data so obtained is compared with experimental data to achieve a better perspective. From our study, one of the more important conclusions is that these materials show characteristics which make them interesting for optical applications.

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1. Introduction

Organic electronics is a field with great potential for future markets. Organic materials with conjugated systems have been extensively employed in the electronics and optoelectronics industries for more than 40 years [1]. Several applications of organic materials with conjugated systems can be observed in the organic semiconductor area, among such applications one can find light-emitting diodes, transistors, biosensors, among others [2–6].

Anthracene stands out within the group of organic materials due to its natural characteristics of luminescence [7]. Another feature is that its central ring oxidizes and reduces easily, because of the action of the central atoms that keep two phenylic rings and its aromatic system intact; this action enables the incorporation of substituent groups which might increase its capabilities for applications in energy production [8]. Carbonyl and carboxyl are substituent groups commonly aggregated to anthracene in position 9.

Diverse studies both experimental and theoretical have been carried out for anthracene and its derivatives [9–14]. In regards to theoretical studies, the molecular structure plays an important role because it is directly related to energy parameters such as the ionization potential, electron affinity, and excited states energies.

Even though many theoretical studies have been related to anthracene and its derivatives to the best of our knowledge, a comparative study of anthracene and its carboxyl and carbonyl derivatives in the position 9 has not been reported to date. Furthermore, we could not find any related studies that analyze these compounds geometry in their excited states and how the geometries change with respect to that of the ground state. In addition, our work has a theoretical perspective about the influence and effects caused by the substituent groups that were used on carbon 9. We also analyzed how the energy depends on the bond type within the substituent group. Finally, we compared our data with relevant experimental data available.

2. Theory and computational details

The ground state geometries of anthracene and its derivatives were optimized by using the Gaussian-03 series of programs [15]. For this purpose the B3LYP DFT approach, which includes the interchange hybrid functional from Becke [16] in combination with the three-parameter correlation functional by Lee–Yang–Parr [17], was employed in combination with the basis set 6-31G* [18]. Final energies were obtained using the same functional and a 6-31+G* basis set expansion, which includes diffuse functions which are required to get more reliable vertical energies [19].

Vibrational frequencies were obtained at the same level used for the geometry optimizations and allowed us to verify that the stationary points found are local minima of the potential energy surface [20].

To obtain the ultraviolet absorption spectrum energy we calculated the inferior excited states excitation energies by resolution of

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* Corresponding author. Fax: +52 614 4394852.
E-mail address: daniel.glossman@cimav.edu.mx (D. Glossman-Mitnik).

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the Time-Dependent Density Functional Theory Kohn-Sham equations (TD-DFT).

The first excited state was optimized using HF/configuration interaction singles (CIS) methodology, the frequency calculations allowed to verify that those structures did not present imaginary frequencies and that we had global minima. With this optimized geometry we proceeded to calculate the emission spectrum in TD-DFT. Also, the same way as ground state computations, excited state were calculated in the Gaussian 03 program series using the set of tools released in this software version [21,22].

3. Results and discussion

3.1. Ground state molecular geometries

The studied molecules are presented at Fig. 1: 9-anthracene, 9-anthracene methanol, 9-acetylanthracene, anthracene-9-carboxylic acid, 9-anthraldehyde. For simplification we will call them molecule A, molecule B, molecule C, molecule D and molecule E respectively.

For these molecules, Tables 1 and 2 contain geometric parameters obtained in the geometry optimization; the data is organized in a way that allows the reader to compare our theoretical results with experimental data acquired by X-ray crystallography [23–26].

One of our observations, shown at Table 1, is that for the five molecules the bond length variation is not significant when we focus in the measurements made over the anthracene unit bond lengths.

At Table 2, we can observe from the theoretical calculations made on the anthracene unit a fluctuating trend among the differences of the bond angles that goes from 0.4 degrees for the C(10)–C(12)–C(11) bond to 2.2 degrees for C(1)–C(11)–C(12) bond. The bond angle C(9)–C(15)–O(17) on molecule E is the maximum value at 127.4 degrees. On the other hand, C(9)–C(15)–O(16) bond angle for molecule B showed the minimum value at 109.4 degrees. Our theoretical results are providing new data for molecule B since, so far as we know, there is no experimental data available.

3.2. Excited states molecular geometries

At Tables 3 and 4 are included bond lengths and bond angles for the five excited states structure optimizations. At those tables, it is noticeable that a slight variation between the bond lengths was obtained when compared to those obtained in the ground state. The biggest variation observed is 0.041 Å for molecule A at C(2)–C(3) and C(6)–C(7).

On anthracene bond angles (molecule A), those forming the central ring presented the biggest change, extending them from 121.8 degrees to 122.9 degrees. Molecule C at its C(16)–C(15)–O(17) bond showed a larger difference between the excited state and the ground state (2.2 degrees of variation); such effect could be due to the extra carbon contained in its substitution group.

At Table 5 is shown a summary for dihedral angles. An analysis for the five molecules will be discussed to define the changes we

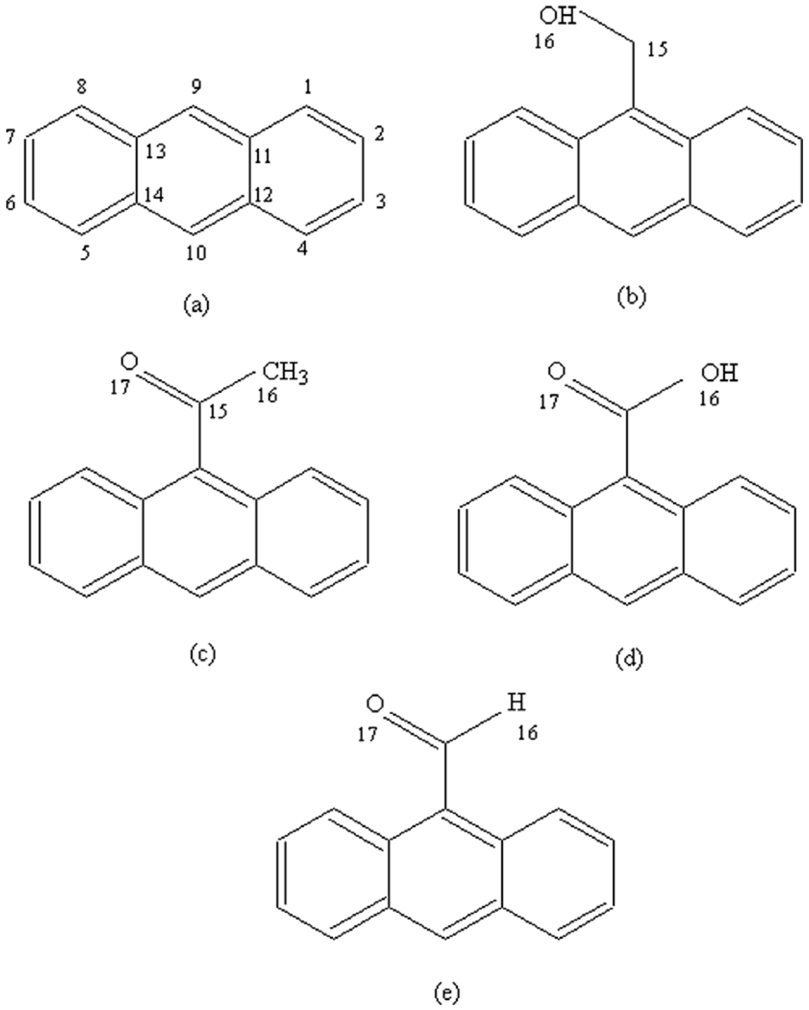

Fig. 1. Molecular structure of (a) Anthracene, (b) 9-Anthracene methanol, (c) 9-Acetylanthracene, (d) Anthracene 9- carboxylic Acid, (e) 9-Anthraldehyde. Numeration for anthracene unity of the five molecules is given in (a) (b), (c), (d) and (e) show numeration for atoms in substituent group.

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