



Molecular docking, TG/DTA, molecular structure, harmonic vibrational frequencies, natural bond orbital and TD-DFT analysis of diphenyl carbonate by DFT approach



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ABSTRACT

Vibrational spectral analysis of Diphenyl Carbonate (DPC) is carried out by using FT-IR and FT-Raman spectroscopic techniques. It is found that all vibrational modes are in the expected region. Gaussian computational calculations were performed using B3LYP method with 6–311++G (d, p) basis set. The computed geometric parameters are in good agreement with XRD data. The observation shows that the structure of the carbonate group is unsymmetrical by $\sim 5^\circ$ due to the attachment of the two phenyl rings. The stability of the molecule arising from hyperconjugative interaction and charge delocalization are analyzed by Natural Bond Orbital (NBO) study and the results show the lone pair transition has higher stabilization energy compared to all other. The ^1H and ^{13}C NMR chemical shifts are calculated using the Gauge-Including Atomic Orbital (GIAO) method with B3LYP/6–311++G (d, p) method. The chemical shifts computed theoretically go very closer to the experimental results. A study on the electronic and optical properties; absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies and Molecular electrostatic potential (MEP) exhibit the high reactivity nature of the molecule. The non-linear optical property of the DPC molecule predicted theoretically found to be good candidate for NLO material. TG/DTA analysis was made and decomposition of the molecule with respect to the temperature was studied. DPC having the anthelmintic activity is docked in the Hemoglobin of Fasciola hepatica protein. The DPC has been screened to antimicrobial activity and found to exhibit antibacterial effects.

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1. Introduction

Diphenyl carbonate (DPC) is the main building block of poly carbonate family. DPC is used as the chemical intermediate for the synthesis of aromatic and aliphatic polycarbonates and some various polymeric mono-isocyanates [1]. It is also used as food contact material, monomeric species for plasticizers for improving mechanical properties. The DPC has got anthelmintic activity which as antiparasite drug expels or destroys a group of worms (helminths) and other internal parasites from the body by either stunning or killing them and without causing significant damage to

the host [2]. Coleyshaw et al. [3] reported the Raman and Infrared spectral studies of four rare carbonate hydrate minerals. Mariappan et al. [4] reported the experimental and theoretical studies on molecular structure and vibrational spectra of Benzyl Phenyl Carbonate. The optimized molecular structure, natural atomic charges, vibrational frequencies and UV–Vis spectral interpretation of Benzyl phenyl carbonate were analyzed by B3LYP/6–31G (d, p) method.

Robyr et al. [5] studied the ^1H and ^{13}C NMR studies of DPC and verified the obtained results by DFT method. Meyer et al. [6] has studied the liquid phase diphenyl carbonate (DPC) with molecular simulations in the temperature range from 350 to 600 K. Despite the widespread use of the compound, small amount of information are available about their chemical behavior of the DPC molecule. The literature survey reveals that only the XRD structure of DPC

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were reported by Joseph et al. [7] so detailed studies of vibrational spectra, UV, NMR and NBO analysis were not carried out so far on DPC. Hence, in the present work, a detailed and systematic spectral analysis of DPC was carried out with the support of quantum computational theories.

2. Experimental details

The compound Diphenyl carbonate (DPC) in spectroscopic grade is purchased from Sigma–Aldrich Chemicals, USA. The FT-IR spectrum of the compound is recorded using a Bruker IFS 66 V spectrometer in the range of 4000–400 cm^{-1} . The spectral resolution is $\pm 2 \text{ cm}^{-1}$ as shown in Fig. 1. The FT-Raman spectrum of the same compound is also recorded using the same instrument with an FRA 106 Raman module equipped with an Nd:YAG laser source operating at 1.064 μm line widths with 200 mW power with spectral resolution of 2 cm^{-1} as shown in Fig. 1. The high resolution NMR spectra, are recorded in CIF (Central Instrumentation facility), Pondicherry University using sophisticated multinuclear FTNMR model Avance II (Bruker). And the instrument is equipped with a cryomagnet of field strength 9.4 T with its frequency 400 MHz for ^1H and 100 MHz for ^{13}C . The UV spectra is recorded in ethanol solvent, between the wavelength range 200 nm–400 nm, with the scanning interval of 0.2 nm and slit width 1.0 nm using the Shimadzu UV-1700 series instrument in Pharma analytical lab, Pondicherry as shown in Fig. 2. TG/DTA study was analyzed using thermo gravimetric instrument Netzsch SDT Q600 V20.9 Build 20.

3. Computational methods

Density Functional Theory (DFT) is an effective tool for treating electronic structure calculations in the molecules. The basis set 6-311++G (d, p) augmented by 'd' polarization function for heavy atom and 'p' polarization for hydrogen atoms to denote the better representation of polar bonds in the molecule [8,9]. The entire calculations in the present work are performed using the Gaussian 09W [10] program package on personal computer. Geometrical parameters and vibrational wavenumbers are computed by optimizing the geometry of the molecule using B3LYP method with 6-311++G (d, p) as basis sets. The vibrational frequency assignments are calculated by Total Energy Distribution (TED) using Vibrational Energy Distribution Analysis (VEDA) program package [11]. The optimized geometry of the DPC compound is further used to calculate NBO 5.0 program [12] implemented in Gaussian 09W package with the same method. The NMR chemical shifts of the compound are also carried out by GIAO method [13,14] under B3LYP/6-311++G (d, p) functional method. ^1H and ^{13}C isotropic Magnetic shielding (IMS) of any X atom (carbon or hydrogen) were made according to the value of TMS. $\text{CS}_X = \text{IMS}_{\text{TMS}} - \text{IMS}_X$. And the UV energy distribution from HOMO to LUMO has been calculated.

4. Results and discussion

4.1. Structural analysis

The DPC molecule is orthorhombic with space group P_{212121} with four molecule per unit cell ($Z = 4$) with following cell dimensions $a = 6.062 \text{ \AA}$, $b = 7.242 \text{ \AA}$ and $c = 23.375 \text{ \AA}$ [15]. The molecule consists of a carbonate group attached between two phenyl rings as shown in Fig. 3. The geometrical parameters of the compound are computed by B3LYP/6-311++G (d, p) method are presented in Table 1, along with the XRD values. Joseph et al. [16] reported that the two carbonyl bond lengths (O12–C13 and C13–O15) are 1.337 (2) Å and 1.354 (2) Å . The computed parameters are in good agreement with XRD values at 1.355 Å and 1.349 Å

by B3LYP/6-311++G (d, p) method. In case of carbonate group, the bond length of carbonyl group C=O is 1.193 Å which is very close to the experimental value 1.191 (3) Å . The angle of O12–C13–O14 = 127°.8' (2) and O14–C13–O15 = 127°.5' (2) when compare with XRD data with computed parameters shows that O14–C13–O15 value dominate by $\sim 5^\circ$ which shows that both rings are slightly tilted or structure of the carbonate group is highly unsymmetrical, this may be due to the twisting of the phenyl rings over 180°.

Atom O12 is connected to the C1 atom of a phenyl ring whose bond length is 1.402 Å , which is closer to the experimental value 1.415 (2) Å . Similarly the bond length O15–C16 is 1.404 Å by B3LYP/6-311++G (d, p) method. This shows that the bond length O–C connecting both phenyl rings with carbonate is equal and almost close to experimental value, but these values largely differ from the O–C bond length within carbonate group where the computational value is 1.355 Å and the experimental value is approximately 1.337 (2) Å . This shows that O–C bond length is shortened inside the carbonate group. The bond lengths of all C–C bond in the phenyl rings are found to be 1.388 to 1.394 Å computationally and 1.383 Å to 1.396 Å experimentally, which signifies that there is no demarcation of single or double bond in the phenyl rings. Thus by the addition of the carbonate group with the phenyl rings it does not alter the C–C bonds within the phenyl rings. The C–H bond lengths in both phenyl rings are found almost equal around 1.08 Å , very closer to experimental value 1.09 Å [17], which obviously indicates that C–H bond lengths remain unaffected by the substitution in both phenyl rings. This observation falls in line with observation made in a previous work by Ballone and Jones [17].

Similarly the angles of the phenyl rings C13–O15–C16, O15–C16–C17 and O15–C16–C18 are 122.12°, 119.468° and 118.626° respectively, whose experimental values are 118.4°(2), 121.2°(2) and 115.7°(2) respectively. These angles are found different from the calculated values. The observation of the bond angles within the phenyl rings shows that all the bond angles are very closer to the expected value 120°, except at the angle where *ipso* carbon atoms attached to both the phenyl ring, this shows that the hexagonal structure of benzene ring is slightly distorted due to the attachment of the carbonate group as shown in Table 1.

4.2. Natural atomic charge

The Natural Atomic Charge (NAC) of DPC is computed by B3LYP/6-311++G (d, p) method as shown in Fig. 4. As we noted from Fig. 4, in DPC molecule the C1 (0.296e) and C16 (0.293e) is more positive charge than the other carbon atoms in both rings this may be due to high electronegative C=O group attached with those carbon atom or it is caused by -I effect on carbon atoms by carbonate group. When comparing the natural charges of H11 (0.227e) and H22 (0.220e) atoms of the same environment within molecule shows some deviation this may be due to C13 = O14 which is tilted over the H22 atoms and this is also evident from unequal charge distribution observed between O12 (–0.557e) and O14 (–0.542e). The NAC analysis shows that the position of carbonate group plays an important role in determining the stability of the molecular system.

The NMR study calculated by B3LYP functional with 6-311G++(d,p) basis set supported by GIAO and chemical shifts are presented in Table 2. It was confirmed that the atoms C1 & C16 are *ipso* carbon atoms of the molecules having higher chemical shifts 152 & 151 ppm experimentally and 154 & 155 ppm theoretically. These two carbon atoms are found to be positive in the natural atomic charges. Similarly the carbon atom C13 in the carbonate group has 152 & 150 ppm both in theoretical and experimental observations. This atom too was found positive in the NAC. In the chemical shifts of the hydrogen atoms H11 and H22 which are

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