



Spectral investigations, DFT based global reactivity descriptors, Inhibition efficiency and analysis of 5-chloro-2-nitroanisole as π -spacer with donor-acceptor variations effect for DSSCs performance



R. Meenakshi

PG Department of Physics, Cauvery College For Women, Tiruchirappalli, 620 018, India

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ABSTRACT

FTIR, FT-Raman, UV, NMR and quantum chemical calculation studies are performed on 5-chloro-2-nitroanisole, in order to gain the insights of its structural, spectroscopic and electronic properties (Fukui indices, HOMO and LUMO energy gap, MESP and Global reactivity descriptors). A complete vibrational analysis of 5-chloro-2-nitroanisole is performed by HF/B3LYP methods using 6-31G(d,p) basis set. To estimate the electronic transitions, the UV spectra of title compound are predicted in gas phase and ethanol. The obtained absorption maxima at 389.94 nm (in ethanol) is predicted possibly due to HOMO \rightarrow LUMO transition with 85% contribution and assigned as π - π^* . The MESP map shows that the negative potential sites are localized on oxygen atom (O10) as well as the positive potential sites are identified around the hydrogen and ring carbon atoms. The analysis of Fukui indices is also carried out to distinguish the nucleophilic and electrophilic centers. The prediction of reactive sites by MESP is well supported by this Fukui indices analysis. The correlations between the statistical thermodynamics and temperature are also obtained. It is seen that the heat capacities, entropies and enthalpies increase with increasing the intensities of the molecular vibrations. Furthermore, the first hyperpolarizability of 5-chloro-2-nitroanisole is calculated and the results are discussed. This result indicates that 5-chloro-2-nitroanisole is a good candidate of nonlinear optical materials.

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1. Introduction

Anisole is a recognized monosubstituted benzene derivative, which has an asymmetric substituent attached to the phenyl ring. It is of considerable interest owing to the environmental concern [1] and also as a model compound for a lot of chemically and biologically interesting systems. Several experimental [2–4] and theoretical [5–8] studies had been carried out on anisole. Its interaction with macrocyclic polyethers has also been studied [9,10]. The number of methoxy substituents and their orientations are vital for the pharmacological properties of drugs [11,12].

Scientifically, one of the most critical problems is correlated to a serious defect in bottled wine perceived as a musty, mouldy and earthy off-flavor. The occurrence of so-called cork taint is usually interrelated to the presence in wine of certain chlorophenols and chloroanisoles at the ng L⁻¹ level [13–16]. Chloroanisoles present very low olfactory threshold levels in wine samples [17]. Members

of the halogenated anisoles consisting of 19 chloroanisoles, 19 bromoanisoles, and 96 bromo-chloroanisoles have been found in the marine atmosphere, in marine algae, in effluents of municipal wastewater treatment plants, in sediments and in food [17]. The environmental effects of chloroanisoles depend on their physical and chemical properties, and it is therefore important to make out the structure–property relationships that permit a complete understanding of their environmental consequences. The application of nitroanisole as a detector for middle infrared interferometry [18] has been confirmed. Nitroanisole is used to measure the mono phenolase activity of polyphenol oxidize from fruits and vegetables [19]. The nitroanisole exhibits a thermal lens effect [20–22], in which the refractive index is dependent upon temperature. Owing to these applications and the reliable properties of anisole, a complete vibrational study on 5-chloro-2-nitroanisole (CNA) is undertaken.

The Fourier transform infrared and laser Raman spectra of *p*-nitroanisole are studied by Krishnakumar et al. [23] in the region of 100–4000 cm⁻¹, respectively. Shishkov et al. [24] have studied the geometric structure and conformational properties of thioanisole

E-mail address: lr.santhameena@gmail.com.

by gas-phase electron diffraction (GED) and quantum chemical calculations. Literature survey confirms that, to the best of our knowledge no *ab initio* (HF) and DFT (B3LYP) with 6-31G (d,p) basis set calculations of 5-chloro-2-nitroanisole (CNA) are reported so far.

Therefore, in the present study, the molecular structure of CNA is studied with the *ab initio* (HF) and density functional theory (B3LYP) methods. Additionally, this study focuses on a complete description of isotropic chemical shifts, excitation energy and HOMO–LUMO energies of CNA. The global reactivity descriptors, namely, hardness (η), chemical potential (μ) and electrophilicity index (ω) are also calculated to understand the reactive nature of the compound. Besides, the dipole moment, and first hyperpolarizability are also studied using the DFT/B3LYP employing the 6-31G(d,p) basis set. Furthermore, the natural bond analysis (NBO) was carried out to clarify the intra molecular bonding and interaction among bonds. Moreover, the thermodynamic properties (heat capacity, entropy and enthalpy changes) of the title compound at different temperatures are also calculated.

2. Experimental details

The compound under investigation namely CNA was purchased from Sigma–Aldrich chemicals. The FT-IR spectrum of the compound is recorded in Bruker IFS 66V spectrometer in the range of 4000–400 cm^{-1} . The spectral resolution is $\pm 2 \text{ cm}^{-1}$. The FT-Raman spectrum is also recorded in Bruker IFS 66V with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1064 nm excitation wavelengths, line widths with 200 mW power in the range of 3500–50 cm^{-1} .

3. Computational details

The geometry of CNA is optimized using Hartree–Fock (HF/6-31G(d,p)) and Becke's three parameter hybrid density functional, B3LYP/6-31G[d,p], which includes both Hartree–Fock exchange and DFT exchange correlation functionals, respectively. The above calculations are performed using Gaussian 09W suite of program [25]. The optimized geometry is characterized by the harmonic vibrational frequencies, which confirmed that the obtained structure is minima on the potential energy surface.

4. Results and discussions

4.1. Molecular geometry

The optimized molecular structure of CNA is shown in Fig. 1. The comparative structural parameters such as bond lengths, bond angles and dihedral angles are presented in Table 1. From the calculated values, it is observed that most of the optimized bond lengths are slightly larger than the experimental values due to that the theoretical calculations belong to isolated molecule in gaseous phase and the experimental results belong to molecule in solid state [26]. Comparing the bond angles and lengths of B3LYP with those of HF, as a whole the formers are bigger than later and the B3LYP values correlate well with the experimental data. The optimized geometry shows that O–CH₃ and NO₂ groups substituted in first and second positions of ring. From the theoretical values, it is found out that most of the optimized bond lengths are higher than the experimental values to some extent. According to the calculated values of B3LYP/6-31G (d, p), the order of the bond length is as C5–C6 < C3–C4 < C4–C5 < C2–C3 < C1–C6 < C1–C2. From the order, it is clear that the ring symmetry is distorted and particularly the bond lengths are more elongated in the substitution place. The bond length of N–O is differed from 0.006 Å to 0.079 Å with

experimental value (1.227 Å) [27,28]. The bond length between C and N is 0.0358 Å times smaller than the experimental value (1.491 Å) [29] when compared with B3LYP/6-31G (d, p) basis set. All the calculated bond length of the ring C–H are smaller than the experimental value (1.090 Å) [30] except the methyl C11–H12. According to the experimental value, the bond angle of C2–N15–O16 and C2–N15–O17 are same as 117.80° which are 0.6117° and 0.3353° differed from the calculated values by B3LYP/6-31G(d, p).

4.2. Vibrational analysis

The compound CNA consists of 18 atoms, so it has 48 normal vibrational modes. The experimental FT-IR and FT-Raman spectra are shown in Figs. 2 and 3 respectively. Calculations are made for a free molecule in vacuum, while experiments are performed for solid samples; therefore, there are disagreements between calculated and observed vibrational wavenumbers. Hence, the scaling of the frequencies is carried out to remove these discrepancies by MOLVIB [31] program. The observed, calculated and scaled frequencies are presented in Table 2. A complete assignment of the fundamentals is proposed based on the calculated TED values.

4.2.1. C–H vibrations

Generally the aromatic structure shows the presence of C–H stretching vibration in the region 3100–3000 cm^{-1} , which is the characteristic region for the C–H stretching vibration [32,33]. In this region, the bands are not affected considerably by the nature of the substituent. There are four expected C–H stretching vibrations correspond to stretching modes of C3–H, C4–H, C6–H units. Therefore in this present work, the FT-IR bands observed at 3113, 3092 and 3071 cm^{-1} are assigned to C–H stretching vibrations. The bands at 3100 and 3050 cm^{-1} in the Raman spectrum are assigned to C–H stretching vibrations. The scaled vibration by B3LYP/6-31G (d, p) method shows very good agreement with recorded spectral data. The aromatic C–H in-plane bending vibrations are normally occur in the region 1300–1000 cm^{-1} and these bands are observed sharp but have weak to medium intensity. In this present case, the C–H in-plane bending vibrations are found at 1307, 1259 cm^{-1} in FT-IR spectrum and the Raman bands at 1305, 1259, 1235 cm^{-1} , respectively. The C–H out-of-plane bending vibrations are observed with strong to medium intensity at 749, 686 and 615 cm^{-1} . These C–H in-plane and out-of-plane bending vibrations show good agreement with literature data [34,35].

4.2.2. C–C vibrations

The ring carbon–carbon stretching vibrations usually arise in the region 1625–1430 cm^{-1} [36]. In general, the bands with variable intensity are observed at 1610–1590, 1590–1575, 1540–1470, 1465–1430 and 1380–1280 cm^{-1} from the frequency ranges given by Varsanyi [37] for five bands in the region. In the present work, the C=C stretching vibrations are observed at 1610, 1571 and 1545 cm^{-1} in the FT-IR spectrum and the corresponding Raman bands identified at 1610, 1585 cm^{-1} . The FT-IR bands at 1482, 1459 and 1400 cm^{-1} are assigned to C–C stretching vibrations. The computed values by B3LYP/6-31G (d, p) are in agreement with experimentally observed values. The ring CCC in-plane bending vibrations are observed at 1081, 945 and 889 cm^{-1} and CCC out-of-plane bending vibrations are observed at 350, 269 and 232 cm^{-1} . These vibrations are coincided agreeably with computed values of B3LYP/6-31G (d, p).

4.2.3. Methyl group vibrations

The assignments of methyl group vibration make a noteworthy contribution to the spectra of title compound. The presence of C–H

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