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FT-IR, FT-Raman spectral and conformational studies on (*E*)-2-(2-hydroxybenzylidenamino)-3-(1H-indol-3yl) propionic acid

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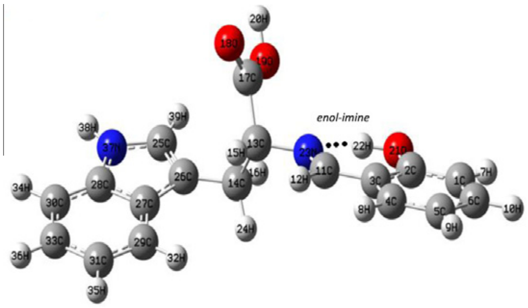
HIGHLIGHTS

- Structural properties of (*E*)-2HBA3IPA.
- Detailed vibrational assignments using TED.
- Intra-molecular charge transfer calculations.
- Hyperpolarizability calculation.
- Band gap energy.

GRAPHICAL ABSTRACT



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ABSTRACT

The (*E*)-2-(2-hydroxybenzylidenamino)-3-(1H-indol-3yl) propionic acid ((*E*)-2HBA3IPA) was synthesized. The theoretical conformational analysis was performed to identify the stable structure. Optimized molecular bond parameters were calculated by using B3LYP/6-31G(d,p) basis set. The hyperconjugative interaction energy ($E^{(2)}$) and electron densities of donor (i) and acceptor (j) bonds were calculated using NBO analysis. First order hyperpolarizability (β_0) was calculated. The band gap energy was analyzed by UV–Visible recorded spectra and compared with theoretical band gap TD-DFT/B3LYP/6-31G(d,p) values. The intra-molecular hydrogen bonding interaction was identified between nitrogen and hydroxyl hydrogen (N···H—O).

Introduction

Some Schiff bases which are derived from salicylaldehyde have attracted the interest of chemists and physicists because they show thermochromism and photochromism in the solid state by proton atom transfer from the hydroxyl oxygen atom to the nitrogen atom [1]. Indole is an aromatic heterocyclic organic compound with a bicyclic structure, it consist of a six-member benzene ring fused to five-member nitrogen containing pyrrole ring. It is of interest as it can be compare with tryptophane residue [2]. The derivative of indole is present in both-animal and plants. The most important compound of this group is tryptophan, an essential amino acid in the human diet, which is a 3-substituted indole [3]. Another important indole derivative is the indole-3acetic acid, a phytohormone, coordinating several growing processes of plants [4]. The biological activity of the indole derivatives is in connection with the nature of substitution in positions 3, on the pyrrole ring [5]. Indole derivatives have an important role through individual biological functions. It is present in the side chain of amino acid tryptophan. The chemical and spectroscopic properties of indole

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derivatives have been subject of many experimental and theoretical investigations [6]. The pineal indole, namely 5-methoxy tryptamine, one of the biogenic monoamines, would play anti-tumor effects, by either inhibiting cancer cell proliferation or stimulating the anticancer immunity [7].

Literature survey reveals that to the best of our knowledge neither the complete IR and Raman spectra nor the force field for (*E*)-2HBA3IPA have been reported so for. Therefore the present investigation was undertaken to study the vibrational spectra of the title molecule completely and to identify the various modes with greater wavenumber accuracy. The *ab initio* DFT calculation has been performed to support our wavenumber assignments, conformational analysis, bond parameters, hyperpolarizability calculation; NBO and HOMO–LUMO band gap have also been studied.

Experimental

Synthesis

The compound (*E*)-2HBA3IPA was synthesized by mixing the salicylaldehyde in ethanol and sodium salt of tryptophan in ethanol–water (50%v/v) Howard et al. [8]. The mixture was heated and refluxed on a mantel about 5 h. The reaction mixture was cooled to room temperature and neutralized by 1:1 HCl. The white Schiff base was separated, filtered off, washed thoroughly with deionised water ethanol mixture followed by ether wash. The product obtained was dried over vacuum desiccators. The melting point of the compound is 114 °C (lit 114 °C) [8].

FT-Raman and FT-IR spectra

The FT-Raman spectrum of (*E*)-2HBA3IPA was recorded using the 1064 nm line of a Nd:YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on a Bruker model IFS 66 V spectrophotometer equipped with an FRA 106 FT-Raman module accessory. The spectral measurements were carried out at Sree Chitra Tirunal Institute for Medical Sciences and Technology, Poojappura, Thiruvananthapuram, Kerala, India. The FT-IR spectrum of this compound was recorded in the region 400–4000 cm^{-1} on an IFS 66 V spectrophotometer using the KBr pellet technique. The spectrum was recorded at room temperature, with a scanning speed of 10 cm^{-1} per minute and at the spectral resolution of 2.0 cm^{-1} in CISL Laboratory, Annamalai University, Tamilnadu, India.

Computational details

The entire calculations were performed at DFT levels on a Pentium 1 V/3.02 GHz personal computer using Gaussian 03W [9] program package, invoking gradient geometry optimization [9,10]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at DFT level, adopting the standard 6-31G(d,p) basis set. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. Then, vibrationally averaged nuclear positions of (*E*)-2HBA3IPA were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. In this study, the DFT method B3LYP/6-31G(d,p) was used for the computation of molecular structure, vibrational frequencies and energies of optimized structures. The vibrational modes were assigned on the basis of TED analysis using SQM program [11].

It should be noted that Gaussian 03W package able to calculate the Raman activity. The Raman activities were transformed into Raman intensities using Raint program [12] by the expression:

$$I_i = 10^{-12} \times (\nu_0 - \nu_i)^4 \times \frac{1}{\nu_i} \times \mathrm{RA}_i \qquad (1)$$

where I_i is the Raman intensity, RA_i is the Raman scattering activities, ν_i is the wavenumber of the normal modes and ν_0 denotes the wavenumber of the excitation laser [13].

Results and discussion

Molecular geometric

The optimized structure of (*E*)-2HBA3IPA is calculated at B3LYP/6-31G(d,p) level of theory. To find stable conformer, a meticulous conformational analysis was carried out for the title compound. A selected dihedral angle was rotated by 10 degree intervals around the free rotation bonds, conformational space of the title compound was scanned by molecular mechanic simulations and then full geometry optimizations of these structures were performed by B3LYP/6-31G(d,p) method. Results of geometry optimizations were indicated that the title compound is rather flexible molecule and, in theory, may have at least twenty-eight conformers as shown in Fig. S1 (Supplementary). Ground state energies, zero point corrected energies ($E_{\mathrm{elect.}}$ + ZPE), relative energies and dipole moments of conformers were presented in Table S1 (Supplementary). Zero point corrections have not caused any significant changes in the stability order.

The bond parameters were calculated for enol–imine closed (real molecule) form and open (isolated molecule gas phase) form. The enol–imine closed form is more stable. Salicylideneanile is an aromatic Schiff base, which has long-ranged π-electron delocalization capacity during the proton transfer reaction, $\mathrm{O{-}H\cdots N} \leftrightarrow \mathrm{O\cdots H{-}N}$ [14,15]. The similar trend has been observed in our present work. Due to the π-electron donation from nitrogen to salicylidene ring, bond lengths, bond angles and dihedral angles are distorted from the stable structure. In this regard, C—O and C—N bonds are the most sensitive indicators [16]. From our investigation, the bond length of C2—O21 is about 1.340 Å is in closed form (enol-hydrogen bonding), whereas the same bond is calculated about 1.356 Å when the hydrogen is outwards to the nitrogen. Similarly the calculated C11—N23 bond lengths are 1.288 and 1.277 Å for enol imine closed and enol imine open form, respectively. The intra-molecular hydrogen bonding between nitrogen and hydrogen ($\mathrm{O_{21}{-}H_{22}\cdots N_{23}}$) atom is calculated about 1.725 Å, which is in consistent with literature values [17–19]. The bond lengths $\mathrm{C_1{-}C_2}$ (1.404), $\mathrm{C_5{-}C_6}$ (1.404) are positively deviated from the C—C values calculated by enol open form. These values are supported by Wang et al. [19]. Literature survey reveals that the C—O bond lengths in the carboxylic acid group of 5-flouro-salicylic acid are 1.225 Å (C=O) and 1.308 Å (C—O) [20]. In this study the calculated bond length $\mathrm{C_{17}{=}O_{18}}$ (1.209 Å) and $\mathrm{C_{17}{-}O_{19}}$ (1.355 Å) are in line with the literature values. The enol open form is shown in Fig. S2 (Supplementary).

To the best of our knowledge no X-ray crystallographic data of this molecule has been established. However, the theoretical results obtained are almost comparable with the molecule. For the title compound, the bond angles $\mathrm{C_{17}{-}O_{19}{-}H_{20}}$ = 105.92° and $\mathrm{C_2{-}O_{21}{-}H_{22}}$ = 107.39° of the C—O—H group, which are differ by 1.47°. This may be due to the formation of intra-molecular hydrogen bond ($\mathrm{O_{21}{-}H_{22}\cdots N_{23}}$). The shortening of bond distance of $\mathrm{C_{11}{-}N_{23}}$/1.288 Å is due to the delocalization of π-electron during the formation of intra-molecular hydrogen bond, while the bond distance for $\mathrm{C_{13}{-}N_{23}}$ is 1.457 Å. The dihedral angles $\mathrm{O_{18}{-}C_{17}{-}O_{19}{-}H_{20}}$ = 1.34° (carboxylic group) and $\mathrm{C_3{-}C_{11}{-}N_{23}{-}C_{13}}$ = 179.85°, which confirms *cis* and *trans* form respectively. The bond parameters of indole (tryptophan) in the present molecule are in