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Molecular orbital studies (hardness, chemical potential, electronegativity and electrophilicity), vibrational spectroscopic investigation and normal coordinate analysis of 5-{1-hydroxy-2-[(propan-2-yl)amino]ethyl}benzene-1,3-diol

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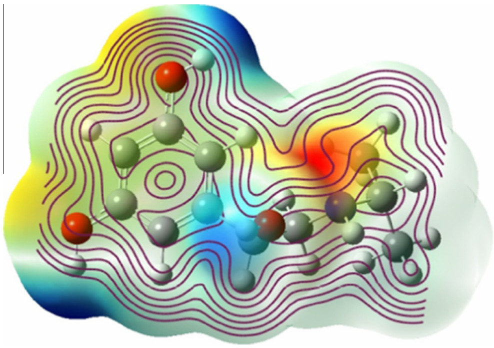
HIGHLIGHTS

- Molecular structure was studied using HF and B3LYP/6-31G(d,p) methods.
- The complete vibrational assignments are performed on the basis of the PED.
- The chemical parameters were calculated from HOMO and LUMO values.
- Thermodynamic parameters have been calculated.

GRAPHICAL ABSTRACT

The Fourier transform infrared and Raman spectra of HPAEBD are recorded in solid phase, the harmonic vibrational frequencies, infrared intensities, Raman activities, bond length, bond angle are calculated by HF and DFT methods by using 6-31G(d,p)basis set. The observed and calculated frequencies showed very good agreement with experimental values. HOMO and LUMO energies are calculated that these energies show charge transfer occurs within the molecule. Thermodynamic properties were calculated.



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ABSTRACT

FT-IR and FT-Raman spectra of 5-{1-hydroxy-2-[(propan-2-yl) amino] ethyl} benzene-1,3-diol (abbrevi- 54 ated as HPAEBD) were recorded in the region 4000–450 cm^{-1} and 4000–100 cm^{-1} respectively. The structure of the molecule was optimized and the structural characteristics were determined by density functional theory (B3LYP) and HF method with 6-31 G(d,p) as basis set. The theoretical wave numbers were scaled and compared with experimental FT-IR and FT-Raman spectra. A detailed interpretation of the vibrational spectra of this compound has been made on the basis of the calculated Potential energy distribution (PED). Stability of the molecule arising from hyperconjugation and charge delocalization is confirmed by the natural bond orbital analysis (NBO). The results show that electron density (ED) in the σ antibonding orbitals and E (2) energies confirm the occurrence of intra molecular charge transfer (ICT) within the molecule. The molecule orbital contributions were studied by using the total (TDOS), sum of α and β electron ($\alpha\beta$DOS) density of States. Mulliken population analysis of atomic charges is also calculated. The calculated HOMO and LUMO energy gap shows that charge transfer occurs within the

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molecule. The electron density-based local reactivity descriptors such as Fukui functions were calculated to explain the chemical selectivity or reactivity site in this compound. On the basis of vibrational analyses, the thermodynamic properties of title compound at different temperatures have been calculated.

Introduction

5-{1-Hydroxy-2-[(propan-2-yl)amino]ethyl}benzene-1,3-diol (HP AEBD) is used to prevent and treat wheezing, shortness of breath, coughing, and chest tightness caused by asthma, chronic bronchitis, emphysema, and other lung diseases. It is a moderately selective beta2-adrenergic receptor agonist that stimulates receptors of the smooth muscle in the lungs, uterus, and vasculature supplying skeletal muscle. The pharmacologic effects of beta adrenergic agonist drugs are at least in part attributable to stimulation through beta adrenergic receptors of intracellular adenyl cyclase, the enzyme which catalyzes the conversion of ATP to cAMP. Increased cAMP levels are associated with relaxation of bronchial smooth muscle and inhibition of release of mediators of immediate hypersensitivity from many cells, especially from mast cells. Dobutamine and soterenol stimulated cAMP accumulation to a greater extent than HPALBD. Finally, the stimulatory effects of isoproterenol and zinterol are both more sensitive to inhibition by β_1-antagonists than by β_2-antagonists [1]. HPAEBD can improve pulmonary function of both large and small airways when added to moderate theophylline doses without risking increased side effects in asthmatic children [2]. HPAEBD is a beta-adrenoceptor stimulant, was studied for adverse effects on pregnant rabbits and their foetuses [3].

FT-IR spectroscopy has been extensively used in both qualitative and quantitative pharmaceutical analyses. Raman spectroscopy is now becoming widely utilized in the pharmaceutical sciences, too. Conventional applications of vibrational spectroscopy include the identification of drugs and raw materials, quality control, as well as characterization of polymorphs, salts, and hydrates. Recently, a survey of the analysis of pharmaceutical substances and formulated products by vibrational spectroscopy has been given by Clark [4] and studies on polymorphs of drugs have been addressed by Threlfall [5]. Density functional theory (DFT) computations have become an efficient tool in the prediction of molecular structure, harmonic force fields, vibrational wave numbers as well as the IR and Raman intensities of pharmaceutically important molecule. In this work, detailed vibrational and electronic structure theory studies of HPAEBD were performed using the scaled quantum mechanical (SQM) force field technique based on DFT calculations. Natural bond orbital (NBO) analysis has been performed to understand the molecular information such as electron delocalization and intramolecular charge transfer (ICT) of HPAEBD.

Experimental details

The fine polycrystalline of HPAEBD sample was purchased from Sigma–Aldrich Chemical Company with a stated purity 97% and it was used as such without further purification. The sample was prepared using a KBr disc technique because of solid state. The FTIR spectrum of molecule was recorded in the region 450–4000 cm^{-1} on a Perkin Elmer FTIR BX spectrometer calibrated using polystyrene bands. FT-Raman spectrum of the sample was recorded using 1064 nm line of Nd:YAG laser as excitation wave length in the region 100–4000 cm^{-1} on a Bruker RFS 100/S FT-Raman spectrometer. Liquid nitrogen cooled Gediode was used as a detector. Spectra were collected for samples with 1000 scan accumulated for over 30 min duration. The spectral resolution after apodization was 4 cm^{-1}. A correction according to the fourth power scattering factor was performed, but no instrumental correction was done. The spectral measurements are carried out at Sophisticated Analytical Instruments Facility (SAIF), Indian Institute of Technology (IIT), Chennai.

Computational details

In order to obtain stable structures, the geometrical parameters of HPAEBD in the ground state was optimized at DFT-B3LYP level of theory and ab initio-HF methods using 6-31G (d,p)basis set. There is no significant difference between geometric and vibrational frequencies by the selection of the different basis sets. The calculated vibrational frequencies are scaled by 0.901 for HF/6-31G (d,p) and 0.961 for B3LYP/6-31G(d,p) [6]. The molecular geometry was not restricted and all the calculations (vibrational wave numbers, geometric parameters and other molecular properties) were performed by using Gauss View molecular visualization program [7] and Gaussian 03 program package on a computing system [8].

The optimized geometry corresponding to the minimum on the potential energy surface has been obtained by solving self-consistent field equation iteratively. The harmonic vibrational wave numbers have been analytically calculated by taking the second-order derivative of energy using the similar level of theory. Multiple scaling of the force field has been performed by the SQM procedure [9,10] to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity [11]. Normal coordinate analysis has been performed to obtain full description of the molecular motion pertaining to the normal modes using the MOLVIB program version 7.0 written by Sundius [12,13]. The Raman activities (S_i) calculated by Gaussian 03 program have been suitably adjusted by the scaling procedure with MOLVIB and subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [14,15].

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 S_i}{\upsilon_i[1 - \exp(h\,c\,\upsilon\,i/k_b T)]}$$

where υ_0 is the exciting frequency (in cm^{-1}), υ_i is the vibrational wave number of the ith normal mode, h, c and k_b are universal constants, and f is the suitably chosen common scaling factor for all the peak intensities. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes are used with full width at half maximum of 10 cm^{-1}.

Results and discussion

Optimized geometries

The first task for the computational work is to determine the optimized geometries of the studied molecule. The optimized molecular structure of HPAEBD with the numbering scheme of the atoms obtained from Gauss View program is shown in Fig. 1. The optimized structural parameters such as bond lengths, bond angles are determined by HF and B3LYP method with 6-31G(d,p) as basis set were compared with experimental values [16]. The geometry of the molecule is considered by possessing C1 point group symmetry. From the structural data given in Table 1 it is