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Normal co-ordinate analysis, molecular structural, non-linear optical, second order perturbation studies of Tizanidine by density functional theory

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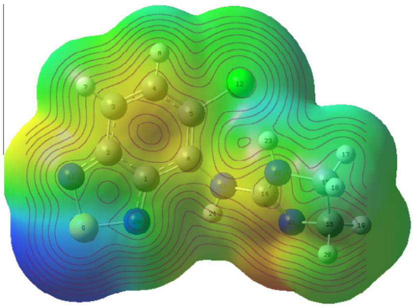
HIGHLIGHTS

- In this work, the experimental and theoretical spectra of 5CDIBTA are studied.
- The complete assignments are performed on the basis of the potential energy distribution (PED).
- Hyperpolarizabilities and HOMO–LUMO energies were performed by DFT approach.
- Thermodynamic properties at different temperatures have been calculated in gas phase.

GRAPHICAL ABSTRACT

The Fourier Transform Infrared and Raman spectra of 5-chloro-N-(4,5-dihydro-1H-imidazol-2-yl)-2,1,3-benzothiadiazol-4-amine are recorded in solid phase, the harmonic vibrational frequencies, infrared intensities, Raman activities, bond length, bond angle are calculated by DFT methods using 6-311++G(d,p) basis set. To predict reactive sites for electrophilic and nucleophilic attack for the title molecule, molecular electrostatic potential (MEP) at the B3LYP/6-311++G(d,p) optimized geometry is calculated.



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ABSTRACT

The spectroscopic techniques and semi-empirical molecular calculations have been utilized to analyze the drug Tizanidine (5CDIBTA). The solid phase Fourier Transform Infrared (FTIR) and Fourier Transform Raman (FTR) spectral analysis of 5CDIBTA is carried out along with density functional theory (DFT) calculations (B3LYP) with the 6-311++G(d,p) basis set. Detailed interpretation of the vibrational spectra of the compound has been made on the basis of the calculated potential energy distribution (PED). The individual atomic charges by NPA using B3LYP method is studied. A study on the Mulliken atomic charges, frontier molecular orbitals (HOMO–LUMO), molecular electrostatic potential (MEP) and thermodynamic properties were performed. The electric dipole moment (μ) and the first hyperpolarizability (α) values of the investigated molecule were also computed.

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Introduction

The 5-chloro-N-(4,5-dihydro-1H-imidazol-2-yl)-2,1,3-benzothiadiazol-4-amine (5CDIBTA) is α_2-adrenergic agonist and centrally active myotonolytic skeletal muscle relaxant with a chemical structure unrelated to other muscle relaxants [1]. It is in a class of

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medications called skeletal muscle relaxants, works by slowing action in the brain and nervous system to allow the muscle to relax owing to the presence of nitrate group in the structure. Various studies like spectrometric estimation and validation of 5CDIBTA [2,3] determination of 5CDIBTA in human plasma [4] and vibrational spectroscopic studies [5] was reported earlier.

As per the literature study, no detailed quantum chemical computational calculations and normal coordinate analysis *t* have been performed on the chosen compound. A detailed quantum chemical investigation will aid in understanding the vibrational modes of 5CDIBTA and clarifying the experimental data available for this molecule. DFT calculations are known to provide excellent vibrational wavenumbers scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and anharmonicity effects [6–10]. DFT is the best method rather than the ab initio method for the computation of molecular structure, vibrational wavenumber and energies of molecule [11]. In this work by using the B3LYP method, vibrational wavenumbers and molecular geometric parameters of 5CDIBTA have been calculated. These calculations are available for providing insight into the vibrational spectra and molecular parameters.

Experimental details

The spectrometric pure sample of 5CDIBTA is procured from reputed pharmaceutical forms in Chennai, India and used as such without any further purification. The FTIR spectrum of the 5CDIBTA is recorded over the region 4000–400 cm^{-1} by using globar source adopting the KBr pellet technique at Sophisticated Analytical Instrumentation Facility (SAIF), IIT, Chennai. The FTR spectrum is recorded on a Nexus 670 spectrometer at central Electro Chemical Research Institute Laboratory, Karaikudi, India. The laser frequency of 15,798 cm^{-1} is used as the excitation source. The spectrometer is fitted with an XT-KBr beam splitter and a DTGS detector. A base line correction is made for the spectrum recorded.

Computational details

The quantum chemical calculations have been performed at DFT (B3LYP) methods with 6-311++G(d,p) basis sets using the Gaussian 03 program [12]. The optimized structural parameters have been evaluated for the calculations of vibrational frequencies at B3LYP method with variety of basis sets by assuming C_1 point group symmetry. The transformation of force field from Cartesian to symmetry coordinate, the scaling, the subsequent normal coordinate analysis, calculation of potential energy distribution (PED) and IR and Raman intensities were done using MOLVIB program written by Sundius [13]. In order to improve the calculated values in agreement with the experimental values, a spectral uniform scaling factor was used to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity. Hence, the vibrational frequencies calculated at B3LYP/6-311++G(d,p) level are scaled by 0.958 for the wave numbers above 1700 cm^{-1} and for below 1700 cm^{-1} scaled as 0.983 [14,15]. After scaled with the scaling factor, the deviation from the experiments is less than 10 cm^{-1} with a few exceptions. The assignments of the calculated normal modes have been made on the basis of the corresponding PEDs. The NBO calculations [16] were performed using NBO 3.1 [17] program as implemented in the Gaussian 03 W package at the DFT/B3LYP level in order to understand the intra-molecular delocalization or hyper conjugation.

Prediction of Raman intensities

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 [18].

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 S_i}{\upsilon_i[1 - \exp(hc\upsilon_i/k_bT)]}$$

where υ_0 is the exciting frequency (in cm^{-1}), υ_i is the vibrational wave number of the 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}.

Quantum chemical calculations

Molecular geometry

The optimized molecular structure for 5CDIBTA in the ground state is computed by the B3LYP calculations computed by the 6-311++G(d,p) basis set. The values of the total energy for 5CDIBTA from the B3LYP calculation by employing the 6-311++G(d,p) basis set is found to be −1479.9041 a.u. The calculated geometrical parameters (bond lengths and bond angles) are compared with experimentally obtained X-ray Diffraction (XRD) data [19]. As the experimental values for 5CDIBTA are known, the theoretically calculated values may give an idea about the geometry of the molecule changes from the DFT method of calculation. The optimized structural parameters of 5CDIBTA from the B3lYP/6-311++G(d,p) calculations and the XRD values are listed in Table 1, in accordance with the atom numbering scheme given in Fig. 1. The slight deviation in XRD data from the computed geometry is probably due to the fact that the inter-molecular interactions in the crystalline state are dominant. The B3LYP method leads to geometry parameters, which are close to experimental data.

Vibrational assignments

The title molecule 5CDIBTA with 24 atoms and 66 normal modes of fundamental vibrations has C_1 point group symmetry. Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose the full set of 112 standard internal valence coordinates were defined and were presented in Table 2. From these a non-redundant set of local symmetry coordinates were constructed much like the internal coordinates recommended by Fogarasi and Pulay and were presented in Table 3. The calculation and visualization of contribution of internal co-ordinates in each normal mode is carried out by Gaussian 03 W package [12] and Chemcraft program [20]. The harmonic vibrational frequencies calculated for the title compound at B3LYP level using 6-311++G(d,p) along with the observed FTIR and FTR frequencies for various modes of vibrations are presented in Table 4. The experimental and theoretically predicted FTIR and FTR spectra of 5CDIBTA with their scaled frequencies using scaled factors for each mode are shown in Figs. 2 and 3 respectively, for comparison. A linearity between the experimental and scaled calculated wavenumbers for DFT method of 5CDIBTA can be estimated by plotting the calculated versus experimental wavenumbers as shown in Fig. 4. The correlation coefficient (*r*) for experimental and observed wavenumbers computed from DFT method is found to be 0.9991. It can be noted from the ‘*r*’ values that the theoretical prediction are in good agreement with the experimental wavenumbers. Also, Fig. 4 reveals the overestimation of the calculated vibrational mode due to neglect of anharmonicity in real system.

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