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Studies of the molecular geometry, vibrational spectra, Frontier molecular orbital, nonlinear optical and thermodynamics properties of Aceclofenac by quantum chemical calculations

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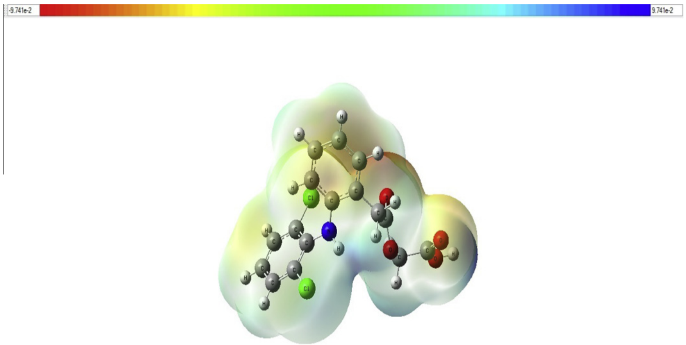
HIGHLIGHTS

- FTIR, FT-Raman and NMR investigations of Aceclofenac were carried out.
- HOMO and LUMO, absorption wavelength and excitation energies were performed.
- NLO and NBO analysis of the molecule were studied.
- The Chemical shift ^{13}C NMR and ^{1}H NMR analysis explained for the Aceclofenac.

GRAPHICAL ABSTRACT

Aceclofenac (2-[2-[2-[(2,6-dichlorophenyl)amino]phenyl]acetyl]oxyaceticacid) is a non-steroidal anti-inflammatory drug (NSAID). It is used for the relief of pain and inflammation in rheumatoid arthritis, osteoarthritis and ankylosing spondylitis. The equilibrium geometries, harmonic vibrational frequencies, infrared intensities and Raman scattering activities were calculated by DFT and HF method with 6-311++G(d,p) basis sets using Gaussian 03W program. A study on the electronic properties, such as HOMO and LUMO energies, molecular electrostatic potential (MEP) were also performed.



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ABSTRACT

The solid phase FT-IR and FT-Raman spectra of 2-[2-[2-[(2,6-dichlorophenyl)amino]phenyl]acetyl] oxyacetic acid (Aceclofenac) have been recorded in the region 4000–400 and 4000–100 cm^{-1} respectively. The optimized molecular geometry and fundamental vibrational frequencies are interpreted with the aid of structure optimizations and normal coordinate force field calculations based on density functional theory (DFT) method and a comparative study between Hartree Fork (HF) method 6-311++G(d,p) level basis set. The calculated harmonic vibrational frequencies were scaled and have been compared with experimental by obtained 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). The time dependent DFT method employed to study its absorption energy and oscillator strength. The linear polarizability (α) and the first order hyper polarizability (β) values of the investigated molecule have been computed. The electronic properties, such as HOMO and LUMO energies, molecular electrostatic

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potential (MESP) were also performed. Stability of the molecule arising from hyper conjugative interaction, charge delocalization has been analyzed using natural bond orbital (NBO) analysis.

Introduction

Aceclofenac, is chemically known as 2-[2-[2-[(2,6-dichlorophenyl)amino]phenyl]acetyl]oxyaceticacid. It is a Non-steroidal Anti-inflammatory drug (NSAID) has been indicated for various painful indications [1] and proved as effective as other NSAIDs with lower indications of gastro-intestinal adverse effects and thus, resulted in a greater compliance with treatment [2]. Its molecular formula is $C_{16}H_{13}Cl_2NO_4$. It possesses free carboxylic acid in the structure [3,4]. Aceclofenac exhibits very slight solubility in water, and as a consequence, it exhibits low bioavailability after oral administration [5,6]. In recent past, the quantum chemical computational methods have proven to be an essential tool in analyzing the vibrational spectra [7]. The entire scaled quantum mechanical method and density force fields calculations are performed by combining the experimental and theoretical aspects of Pulay and Rauhut [8]. Their training set and test set have been used to check the reliability of fitting. The overall scaling factors for theoretical harmonic frequencies have been verified with least-square fits [9].

To the best of our knowledge, no work on vibrational assignments, molecular structure, and stability have been reported so far. This study may reveal the molecule is not only finding its applications in pharmaceutical importance but also finds its importance in NLO applications. The aim of the work is to investigate the molecular structure, vibrational spectra, frontier molecular orbital, Natural bond orbital (NBO) analysis and NLO properties of the title molecule due to its biological and pharmaceutical importance been analyzed by density functional theory (DFT) and Hartree Fork (HF) methods in the basis set 6-311++G(d,p).

Experimental

The fine powder sample of Aceclofenac was obtained from M/s. Sigma Chemical Co., USA with a stated purity of 99% and was used as such without further purification. The FT-Raman spectrum of Aceclofenac has been recorded using Nd:YAG laser has excitation wavelength in the region 4000–100 cm^{-1} on a Brucker Model IFS 66V spectrophotometer equipped with FRA 106 FT-Raman module accessory. The FT-IR spectrum of these compounds were recorded in the region 4000–400 cm^{-1} on Brucker Model IFS 66V spectrophotometer using KBr pellet technique. The spectra were recorded at room temperature, with a spectral resolution of 4.0 cm^{-1} at SAIF, IIT Madras, Chennai, India. The optical properties of the Aceclofenac were examined using UV–Vis spectrum recorded at room temperature in the range of 200–400 nm with Perkin–Elmer-Lambda 950-UV–Vis spectrometer.

Quantum chemical calculations

The entire quantum chemical calculations have been performed at HF and DFT (B3LYP) methods with 6-311++G(d,p) basis set using the Gaussian 03W program [10]. The calculated vibrational frequencies calculated at HF level are scaled by 0.9067, and the range of wave numbers above 1700 cm^{-1} are scaled as 0.958 and below 1700 cm^{-1} scaled as 0.983 for B3LYP [11,12] in order to fairly agree with experimental data. After scaled with the scaling factor, the deviation from the experiments is less than 10 cm^{-1} with a few exceptions.

It should be noted that Gaussian 03 package does not calculate the Raman intensity. The Raman activities were transformed into Raman intensities using RaInt program [13] by using the expression:

$$I_i = 10^{-12}(n_0 - n_i)^4 1/n_i \cdot S$$

where I_i is the Raman intensity, S is the Raman scattering activities, n_i is the wavenumber of ith normal modes, and n_0 denotes the wavenumber of the excitation laser [14]. The assignments of the calculated normal modes have been made on the basis of the corresponding PEDs. The PEDs are computed from quantum chemically calculated vibrational frequencies using VEDA program [15]. The electronic absorption spectra for optimized molecule calculated with the time dependent density functional theory (TD-DFT) at B3LYP/6-311++G(d,p) level. The polarizability (α), and the hyperpolarizability (β) of the title molecule were calculated by DFT method based on the finite field approach.

Results and discussion

Molecular geometry

Aceclofenac was subjected to geometry optimization in the ground state. The optimized structure belongs to C_1 point group symmetry. The molecular structure is shown in Fig. 1 with atomic numbering scheme adopted in the study. The comparative optimized geometrical parameters of Aceclofenac calculated by B3LYP and HF levels with the 6-311++G(d,p) basis set are listed in Table 1. It is observed that carbon–carbon bond distances are

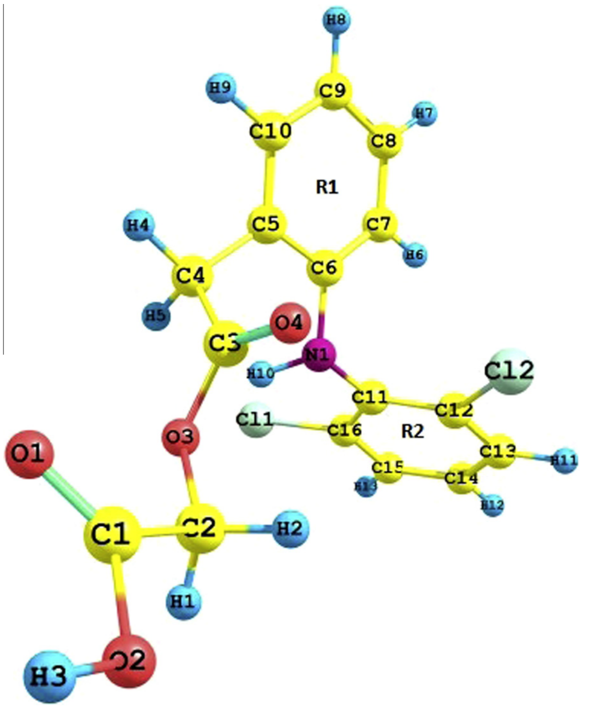

Fig. 1. Molecular structure of Aceclofenac.