Electronic structure, electric moments and vibrational analysis of 3-(2-methoxyphenoxy) propane-1,2-diol by *ab initio* and density functional theory

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Abstract. The molecular properties and harmonic wavenumbers of 3-(2-methoxyphenoxy) propane-1,2-diol have been calculated using *ab initio* and density functional theory. The polarizability and first static hyperpolarizability of the title molecule have been calculated at different basis sets. In general a good agreement between experimental and calculated normal modes has been observed. The frontier orbital and molecular electrostatic potential surface study has also been employed to understand the active sites of 3-(2-methoxyphenoxy) propane-1,2-diol.

1   Introduction

With the standard quantum chemical models (i.e., without the inclusion of parity violation), there is no difference whatsoever in energetics, vibrational frequencies, polarizabilities, NMR spectra, or any other non-chiral property for a given pair, i.e., (R) and (S) forms of enantiomers [1–4]. Differences in the properties of enantiomers arise either only within chiral environments or interactions with other chiral compounds. The present investigation therefore deals with the quantum chemical study of molecular structural, energetic and vibrational data of one of the pair i.e., (R) enantiomer of 3-(2-methoxyphenoxy) propane-1,2-diol [MPPD], in gas phase, due to its biological and pharmaceutical importance. The drug MPPD, also known as guaifenesin, is an expectorant, used extensively in anti-tussive and is capable of increasing the excretion of phlegm from the respiratory tract. Bredikhin and others have carried out

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extensive studies on the structure, solid state properties and issues related to the effective resolution procedure for MPPD [5–7].

The vibrational spectroscopic analysis is known to provide immensely invaluable molecular structure elucidation in synergy with quantum chemical calculations. In order to obtain a complete description of molecular dynamics, vibrational wavenumber calculations along with the normal mode analysis have been carried out at the DFT level employing the basis set 6-311+G(2*d*,2*p*). The optimized geometry of molecule under investigation and its molecular properties such as equilibrium energy, frontier orbital energy gap, molecular electrostatic potential energy map, dipole moment, polarizability, first static hyperpolarizability have also been used to understand the properties and active sites of the drug.

2   Experimental

2.1   Structure and Spectra

The model molecular structure of MPPD has been given in Fig. 1. The calculated IR spectra has been shown in Fig. 2 and is found to match well with IR spectral data reported by NIST Standard Reference Database 69: NIST Chemistry Web Book [8].

3   Computational Details

Quantum chemical study of the MPPD, has been performed within the framework of Hartree Fock and the density functional theory [9] with Becke's three-parameter hybrid exchange functional [10] with Lee-Yang-Parr correlation functionals (B3LYP) [11, 12] and employing 6-311 + G(2*d*,2*p*) basis set using the Gaussian 09 program package [13]. As the DFT hybrid B3LYP functional tends to overestimate the fundamental normal modes of vibration, a scaling factor of 0.9679 has been applied and a good agreement of calculated modes with experimental ones has been obtained [14,15]. The vibrational wavenumber assignments have been carried out by combining the results of the Gaussview 5 program [16], symmetry considerations and the VEDA 4 program [17]. The calculated IR spectra have been plotted using the pure Lorentzian band shape with a band width of FWHM of 10 cm^{-1} and are shown in Fig. 2.

Density functional theory has also been used to calculate the dipole moment μ, mean polarizability α and first static hyperpolarizability β based on Finite field approach. Following Buckingham's definitions [18], the total dipole moment and the mean polarizability in a Cartesian frame is defined by

$$\mu = (\mu_x + \mu_y + \mu_z)^{1/2}, \tag{1}$$

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \tag{2}$$

The total intrinsic hyperpolarizability β_{total} and a component of the first hyperpolarizability