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Vibrational, UV spectra, NBO, first order hyperpolarizability and HOMO–LUMO analysis of carvedilol

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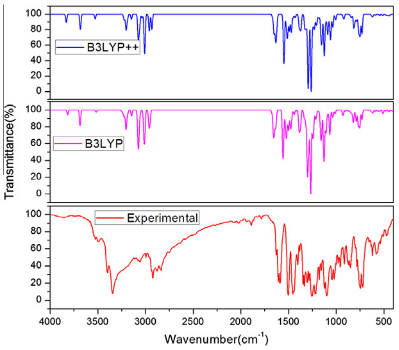
HIGHLIGHTS

- FT-IR, FT-Raman and UV–Vis spectra of carvedilol was examined.
- The optimized geometry and vibrational wavenumbers were computed using DFT methods.
- HOMO–LUMO and MEP analysis were made.
- Topological charge distribution explained the intramolecular hydrogen bonding.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we have investigated experimentally and theoretically on the molecular structure, vibrational spectra, UV spectral analysis and NBO studies of cardio-protective drug carvedilol. The FT-Raman and FT-IR spectra for carvedilol in the solid phase have been recorded in the region 4000–100 cm^{-1} and 4000–400 cm^{-1} respectively. Theoretical calculations were performed by using density functional theory (DFT) method at B3LYP/6-31G(d,p) and B3LYP/6-31++G(d,p) basis set levels. The harmonic vibrational frequencies, the optimized geometric parameters have been interpreted and compared with the reported experimental values. The complete vibrational assignments were performed on the basis of potential energy distribution (PED) of the vibrational modes. The thermodynamic properties and molecular electrostatic potential surfaces of the molecule were constructed. The electronic absorption spectrum was recorded in the region 400–200 nm and electronic properties such as HOMO and LUMO energies were calculated. The stability of the molecule arising from hyper conjugative interactions and charge delocalization have been analyzed from natural bond orbital (NBO) analysis. The first order hyperpolarizability of the title molecule was also calculated. The photo stability of carvedilol under different storage conditions were analyzed using UV–Vis spectral technique.

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Introduction

Carvedilol is a non selective beta blocker/alpha-1 blocker used for the treatment of mild to severe congestive heart failure. Norepinephrine stimulates the nerve that controls the muscles of the heart by binding to the β1 and β2 – adrenergic receptors. Carvedilol blocks the binding to those receptors, which slows the heart beat rhythm and hence reduces the force of the heart's pumping. Carvedilol inhibits clinical progression in patients with mild symptoms of heart failure [1]. The activation energy of carvedilol was determined using thermogravimetry analysis by Talvani et al. [2]. Also, they used differential scanning calorimetry, Fourier transform infrared spectroscopy, and optical microscopy were used to test binary mixtures of carvedilol and selected excipients. Almeida et al. [3,4] recorded the NMR spectrum of carvedilol and also studied their electronic structure. The Density Functional Theory (DFT) method has proved to be a powerful tool for the investigation of molecular structure and vibrational spectra [5,6]. Hence, the title molecule is of considerable interest in the field of medicinal and pharmaceutical science. Literature survey reveals that so far there is no complete experimental and theoretical study for the title molecule was carried out. In the present study, detailed vibrational analyses have been made using FT-IR and FT-Raman spectra of carvedilol. A complete vibrational band assignment were made by using DFT method. The electronic parameters such as frontier molecular orbital, natural bonding orbital (NBO) and first hyperpolarizability analysis of carvedilol were made in the present study.

Experimental section

The spectroscopic pure sample of carvedilol was obtained from Sigma–Aldrich chemical company, with stated purity of 99% and it was used as such without further purification. The solid phase FT-IR spectrum of this compound was recorded in the region 4000–400 cm^{-1} in evacuation mode on Nexus 670 DTGS using KBr pellet technique (solid phase) with 4.0 cm^{-1} resolution. The FT-Raman spectrum was recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 4000–400 cm^{-1} on Bruker IFS 66V spectrophotometer equipped with FRA 106 Raman module was used as an accessory. All sharp bands observed in the spectra are expected to have an accuracy of ±1 cm^{-1}. UV–Vis spectral measurements have been made using Cary 5E-UV–Vis spectrophotometer in the wavelength region 200–400 nm.

Computational details

All the theoretical computations were performed using density functional theory (DFT) at B3LYP level using B3LYP/6-31G(d,p) and B3LYP/6-31++G (d,p) basis sets on a Pentium IV/1.6 GHz personal computer using the Gaussian 09W software [7]. The stable molecular structure of carvedilol in the ground state is optimized and the structural parameters have been computed by using Becke's three parameter hybrid functional (B3) [8] related with gradient corrected correlation functional of Lee–Yang–Parr (LYP) [9] with using B3LYP levels with 6-31G(d,p) and 6-31++G(d,p) basis sets to characterize all stationary points as minima by using Gaussian 09W program package without any constraint on the geometry The optimized molecular geometry, harmonic vibrational spectrum of carvedilol were obtained using Gaussian 09W resulting IR frequencies together with intensities of the present compound. The potential energy distributions of the vibrational modes of the compounds are also calculated. The comparison is made between the theoretically calculated frequencies and experimentally measured frequencies [10]. The vibrational frequency assignments were made with a high degree of accuracy with the help of chemcraft software program [11]. Vibrational spectra of carvedilol have been analyzed on the basis of calculated potential energy distribution (PED). The redistribution of electron density in various bonding and antibonding orbitals along with energies have been calculated by natural bond orbital (NBO) analysis using DFT method to give clear evidence of stabilization originating from the hyper-conjugation of various intramolecular interactions. The UV spectroscopic studies along with HOMO, LUMO analysis calculated by DFT method have been used to elucidate information regarding charge transfer within the molecule. The properties of the structural geometry, molecular electrostatic potential (MEP) of the title compound were studied with the aid of DFT studies. The first order hyperpolarizability of the title compound was obtained based on theoretical calculations.

Molecular geometry

The optimized molecular structure along with numbering of atoms of carvedilol was obtained from chemcraft program was shown in Fig. 1. The optimized structural parameters (bond length and bond angle) calculated by DFT/B3LYP with 6-31G(d,p) and 6-31++G(d,p) basis sets are compared with experimental data [12] and are presented in Table 1. By allowing the relaxation of all parameters, the calculations converge to optimized geometries, which correspond to true energy minima, as revealed by the lack of imaginary frequencies in the vibrational mode calculation [13]. The vibrationally averaged nuclear positions of carvedilol were used for harmonic vibrational frequency calculations. The bond length between $C_2—C_3$ is 1.5248 Å and 1.524 Å in B3LYP/6-31G(d,p) and B3LYP/6-31++G(d,p) methods respectively. The bond length of $N_1—C_2$ is 1.4585 Å and 1.4611 Å in B3LYP/6-31G(d,p) and B3LYP/6-31++G(d,p) methods respectively and those for N—C is 1.465 Å and 1.468 Å in 6-31G(d,p) and 6-31++G(d,p) methods respectively [14]. The bond angle of the atoms $C_6—C_5—C_{10}$ is 119.4° in both methods. Similarly, bond angle of the atoms $C_7—C_8—C_9$ is 120.0° and 119.9° in B3LYP/6-31G(d,p) and B3LYP/6-31++G(d,p) methods respectively. Further the results of our calculations, the experimental and calculated geometric parameters agree well with remaining geometrical parameters. From the theoretical values, it is found that some of the calculated parameters are slightly deviated from the experimental values, due to fact that the theoretical calculations belong to molecule in the gaseous phase and the experimental results belong to molecule in solid state.

Vibrational analysis

In order to obtain the spectroscopic signature of carvedilol, we performed a frequency calculation analysis. The aim of the vibrational assignments is to conclude which of the vibrational modes give rise to each of these observed bands. The experimental and theoretical FT-IR and FT-Raman spectra of carvedilol were shown in Figs. 2 and 3 respectively. Theoretically computed frequencies using B3LYP level with 6-31G(d,p) and 6-31++G(d,p) basis sets along with their relative intensities, probable assignments and potential energy distribution (PED) are summarized in Table 2. The molecule carvedilol has 56 atoms and it belongs to C_1 symmetry as revealed from its geometry optimization. Theoretical calculations were made for a molecule in vacuum, where experiments were performed in solid phase. Therefore the vibrational analysis obtained for carvedilol with theoretically computed values are generally somewhat greater than the experimental values due to neglect of anharmonicity in real system.

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