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Vibrational spectroscopic studies of Isoleucine by quantum chemical calculations

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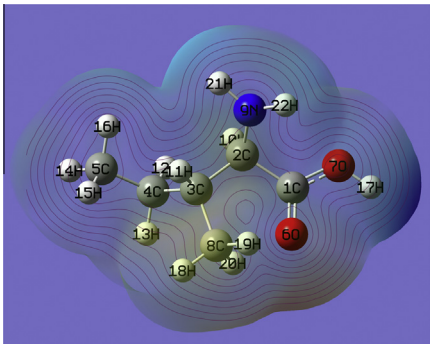
HIGHLIGHTS

- FT-IR, FT-Raman and UV–visible spectra of Isoleucine in the solid phase were recorded and analyzed.
- The optimized geometry and vibrational wavenumbers were computed using MP2 and DFT (B3LYP) methods.
- Vibrational assignment made by PED calculation by VEDA program.
- Natural atomic analysis explained the intramolecular hydrogen bonding.
- Chemical shift of the title compound were found.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we reported a combined experimental and theoretical study on molecular structure, vibrational spectra and NBO analysis of Isoleucine (2-Amino-3-methylpentanoic acid). The optimized molecular structure, vibrational frequencies, corresponding vibrational assignments, thermodynamics properties, NBO analyses, NMR chemical shifts and ultraviolet–visible spectral interpretation of Isoleucine have been studied by performing MP2 and DFT/cc-pVDZ level of theory. The FTIR, FT-Raman spectra were recorded in the region 4000–400 cm^{-1} and 3500–50 cm^{-1} respectively. The UV–visible absorption spectra of the compound were recorded in the range of 200–800 nm. Computational calculations at MP2 and B3LYP level with basis set of cc-pVDZ is employed in complete assignments of Isoleucine molecule on the basis of the potential energy distribution (PED) of the vibrational modes, calculated using VEDA-4 program. The calculated wavenumbers are compared with the experimental values. The difference between the observed and calculated wavenumber values of most of the fundamentals is very small. ^{13}C and ^{1}H nuclear magnetic resonance chemical shifts of the molecule were calculated using the gauge independent atomic orbital (GIAO) method and compared with experimental results. The formation of hydrogen bond was investigated in terms of the charge density by the NBO calculations. Based on the UV spectra and TD-DFT calculations, the electronic structure and the assignments of the absorption bands were carried out. Besides, molecular electrostatic potential (MEP) were investigated using theoretical calculations.

Introduction

Isoleucine (2-Amino-3-methylpentanoic acid) is one of the branched-chain aliphatic amino acids (BCAAs) that are essential substrates for protein synthesis in all organisms. Isoleucine is especially important to serious athletes and body builders because of its role in boosting energy production and assisting the body recover from strenuous physical activity. Branched-chain-amino-acids promote muscle recovery after physical exercise and it is needed for the formation of hemoglobin as well as assisting with regulation of blood sugar levels. It is also involved in blood-clot

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formation. Therapeutic doses of Isoleucine may be very helpful in preventing muscle wasting and promoting tissue repair after surgery. Isoleucine is also converted in the liver to blood sugar; therefore, it can be helpful in maintaining proper blood glucose levels. Due to the hydrophobic character of Isoleucine, it is mostly found in the interior of proteins [1].

Isoleucine plays an important role in the therapy of burn vitamins [2] and directs the protein synthesis in skeletal muscles [3,4]. The conformational behavior of Isoleucine has been investigated by Lesarri et al. [5]. In my present work MP2 and DFT-B3LYP calculations based on cc-pVDZ basis set has been found to interpret the vibrational spectra of Isoleucine. The DFT is cost effective procedures for exploring the physical properties of titled Isoleucine molecule [6].

Quantum chemical computational methods are advanced technique with most significant contribution towards interpreting and predicting the vibrational spectra to resolving the structure, functional groups and orbital interactions of the molecules [7]. Density Functional theory (DFT) incorporates the electron correlation and it is an important tool for the prediction of the molecular structure, IR intensities and Raman activities of the molecule [8]. However the spectroscopic measurement and detailed theoretical studies based on quantum chemical calculations for Isoleucine have not reported so for.

Experimental details

The compound under the investigation namely 2-Amino-3-methylpentanoic acid (Isoleucine) is procured from the reputed pharmaceutical company, Chennai, India, which is a spectroscopic grade and hence used for recording the spectra without further purification. The room temperature FT-IR spectrum of Isoleucine was recorded in the region 4000–400 cm^{-1} on BRUKER IFS 66 V spectrometer using KBr pellet with spectral resolution of ±1 cm^{-1}.

The FT-Raman spectrum was also recorded in the region 3500–50 cm^{-1} with BRUKER IFS 100/s Raman molecule equipped with Nd:YAG laser source operating at 1064 nm line width 150 mW power. The spectra were recorded with scanning speed of 50 cm^{-1} min^{-1} of spectral width 4 cm^{-1}. The reported wave numbers are believed to be accurate with in ±1 cm^{-1}. The UV–visible spectral measurements were carried out using a Varian carries 5E-UV-NIR spectrophotometer at sophisticated instrumentation Analysis Facility, IIT Madras, India.

Computational details

The optimized molecular structure, vibrational frequencies, thermodynamic properties, charge analysis, HOMO–LUMO energy, UV–visible and NMR spectra of the titled compound were calculated by ab initio-MP2 and DFT method adopting Becke3–Lee–Yang–Parr (B3LYP) combined with cc-pVDZ basis set using GAUSSIAN 09W program Package with molecular visualization program [9] on the personal computer at MP2 and B3LYP/cc-pVDZ calculation level [10–13].

The optimized geometrical parameters were used in the vibrational frequency calculation at MP2 and DFT levels to characterize all stationary points as minima, finally the calculated normal modes of vibrational frequencies provide thermodynamic properties through statistical mechanics. The calculation of the potential energy distribution (PED) and the prediction of IR were analyzed by VEDA-4 program [14].

Results and discussion

Geometrical parameters

The molecular structure of Isoleucine belongs to C_1 point group symmetry with 22 atoms composing the structure. Geometrical structure of the titled molecule along with numbering of atom scheme was shown in Fig. 1. The optimized geometrical parameters were obtained by MP2 and B3LYP with cc-pVDZ basis set. The comparative optimized values of bond lengths, bond angles and dihedral angles were presented in Table 1. The calculated geometrical parameters (bond lengths and bond angles) were compared with available experimental data [15]. The distance between the atoms C_2–C_3 was calculated as in the range of 1.540 Å and 1.550 Å by using MP2 and B3LYP methods respectively. All the C–H bonds were shown almost similar bond length values in both MP2 and B3LYP methods. The oxygen–hydrogen atoms (O_7–H_{17}) stands with the bond distance about 0.97 Å. N_9–H_{21} and N_9–H_{22} stand in the bond distance of 1.02 Å range by MP2 and B3LYP methods. The C_1–O_6 bond length calculated at 1.21 Å by both MP2 and B3LYP method is in good agreement with the literature data 1.208 Å [16–18]. The bond distance between C_1–O_7 is calculated about 1.36 Å in both methods, which is excellent agreement with literature data 1.36 Å [19].

HOMO and LUMO analysis

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters in quantum chemistry to determine the interaction of molecule with other species; thus, they are termed frontier orbitals. HOMO can be through the outermost orbital containing electrons tends to give these electrons such as an electron donor. On the other hand, LUMO can be through the innermost orbital containing free places to accept electron [20]. Owing to the interaction between HOMO and LUMO orbital of a structure, transition state transition of π^{-}–π^{*} type is observed with regard to the molecular orbital theory [21,22]. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures [23]. 3D plots of highest occupied molecular orbitals (HOMOs) and lowest an unoccupied molecular orbitals (LUMOs) with the energy value are presented in Fig. 2. As can be seen from the figure, the energy band gap $|(\Delta E)|$ of the optimized geometry was calculated to be about 0.24 au at B3LYP/cc-pVDZ level of theory. The highest occupied molecular orbitals are localized mainly in amine groups. On the other hand, the lowest unoccupied molecular orbitals are also localized mainly in carboxylic acid, 1-carboxyl and aliphatic groups.

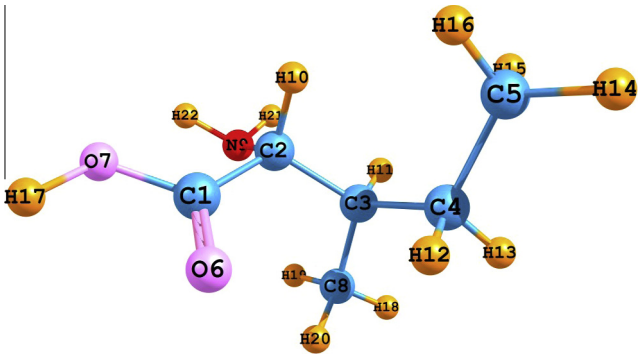

Fig. 1. Molecular structure of Isoleucine along with numbering of atoms.