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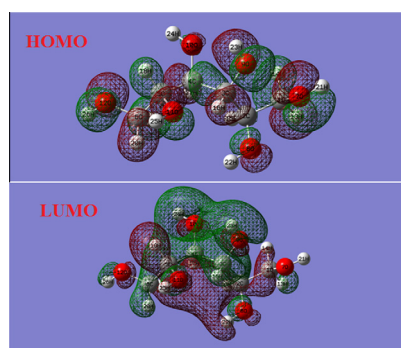
Quantum chemical density functional theory studies on the molecular structure and vibrational spectra of mannitol

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HIGHLIGHTS

- FT-IR, FT-Raman and UV-Vis spectra of mannitol was examined.
- The optimized geometry and vibrational wavenumbers were computed using ab initio and DFT(B3LYP) methods.
- Vibrational assignment made by TED calculation by VEDA program.
- Natural atomic analysis explained the intramolecular hydrogen bonding.
- First hyperpolarizability and HOMO, LUMO energy gap were theoretically predicted.

GRAPHICAL ABSTRACT



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ABSTRACT

A collective experimental and theoretical study was conducted on the molecular structure and vibrational spectra of mannitol. The FT-IR and FT-Raman spectra of mannitol were recorded in the solid phase. The molecular geometry, vibrational frequencies, thermodynamic functions and atomic charges of mannitol in the ground state have been calculated by using the ab initio HF (Hartree-Fock) and density functional methods (B3LYP) invoking cc-pVDZ basis set. The complete vibrational assignments were performed on the basis of Total Energy Distribution (TED) of the vibrational modes. The UV absorption spectra of the title compound dissolved in water. Natural bond orbital analysis has been carried out to explain the charge transfer or delocalization of charge due to the intra-molecular interactions. The ¹H and ¹³C nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by GIAO methods. The first order hyperpolarizability (β_0) of this novel molecular system and related properties (β , α_0 and $\Delta\alpha$) of mannitol are calculated using B3LYP/cc-pVDZ and HF/cc-pVDZ methods on the finite-field approach. By using TD-DFT calculation, electronic absorption spectra of the title compound have been predicted and a good agreement with experimental one is established. In addition, the molecular electrostatic potential (MEP) have been investigated using theoretical calculations, the calculated HOMO and LUMO energies shows that the charge transfer within the molecule.

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Introduction

Mannitol, chemically (2R,3R,4R,5R)-Hexan-1,2,3,4,5,6-hexol [C₆H₁₄O₆], is a polyol (sugar alcohol) considered as an important sweetener which is naturally found in variety of plants, fungi, marine algae and fresh mushrooms [1]. Polyols have low caloric values and have the ability to metabolize with nominal increase in the blood sugar which makes them important for food as well as pharmaceutical industry. D-Mannitol is white crystalline powder with granular form soluble in water, functionally used as sweetener, humectants, texturizer, stabilizer and bulking agent in food and has wide range of applications in pharmaceutical industries as inert osmotic control substance and as a facilitator for the transportation of medicines [2,3]. It is diuretic, used to force urine production in people with acute kidney failure. Increase the urine production and prevent the kidney from shutting down, and also speeds up elimination of certain toxic substances in the body.

Mannitol reduces the swelling and pressure inside the eye around the brain. It is an osmotic agent that causes a dehydrating effect on the airway epithelium leading to release of inflammatory mediators from inflammatory cells in the bronchial mucosa, and ultimately leading to airway smooth muscle contraction [4]. Mannitol has been promoted as a renal protective agent in patients at high risk of developing renal failure, such as those undergoing cardiac and vascular surgery, renal transplantation, and in patients with jaundice and rhabdomyolysis. It also acts as a free-radical scavenger and reduces the harmful effects of free radicals during ischemia–reperfusion injury.

Smith and associates [5] showed that mannitol clearance closely reflected glomerular filtration rate in man, there has been clinical attention in mannitol. With normal kidney function, after a single intravenous dose, the half-life of mannitol in the circulating plasma is 15 min [6]. However, the detailed theoretical studies based on DFT methods for mannitol have not been reported so far. This work deals with spectroscopic characterization and DFT studies of mannitol.

Experimental details

The compound under the investigation namely (2R,3R,4R,5R)-Hexan-1,2,3,4,5,6-hexol [mannitol] was procured from the reputed pharmaceutical company, Chennai, Tamil Nadu, INDIA, and which was used without further purification. The FT-IR spectrum of the compound was recorded in the 4000–400 cm⁻¹ region in evacuation mode on Bruker IFS 66 V spectrophotometer using KBr pellet technique (solid phase) with 4.0 cm⁻¹ resolution. The FT-Raman spectrum of mannitol was recorded on a BRUKER RFS 100/S model interferometer equipped with an FRA-106 FT-Raman accessory in the 4000–400 cm⁻¹ Stokes region using the 1064 nm line of Nd:YAG laser for excitation, operating at 150 mW powers. The reported wavenumbers are believed to be accurate within ± 4 cm⁻¹. The UV-Vis spectral measurements were carried out using a Varian Cary 5E-UVNIR spectrophotometer at Sophisticated Instrumentation Analysis Facility, IIT Madras, India. (1)H and (13)C NMR spectra have been recorded using BRUKER AVANCE III 500 MHz NMR at SAIF, IIT Madras, India.

Computational details

The combination of spectroscopic methods with DFT calculations are important tools for understanding the fundamental vibrational properties and the electronic structure of the compounds. The DFT–B3LYP correlation functional calculations have been carried out to provide complete information about the structural characteristics and the fundamental vibrational modes of

mannitol. The calculations of geometrical parameters in the ground state were performed using the Gaussian 09 W program [7]. DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee–Yang–Parr correlation functional (B3LYP) method. The geometry generated from standard geometrical parameters at (B3LYP) method by adopting split-valence polarized cc-pVDZ basis set. The 'cc-p', stands for 'correlation-consistent polarized' and the 'V' indicates they are valence-only basis sets. They include successively larger shells of polarization (correlating) functions (d, f, g, etc.). More recently these 'correlation-consistent polarized' basis sets have become widely used and are the current state of the art for correlated or post-Hartree–Fock calculations. Example of these are: cc-pVDZ – Double-zeta. For that we go with basis set of cc-PVDZ. The optimal geometry was determined by minimizing molecular symmetry constraints. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence with minima in the potential surface. At the optimized structure of examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The relative intensity of the most intense line appears to be theoretically overvalued by comparison with experimental IR and Raman bands. The vibrational modes were assigned on the basis of TED analysis using VEDA 4 program [8]. The total energy distribution corresponding to each of the observed wavenumbers shows the reliability and accuracy of the spectral analysis. The electronic properties such as HOMO and LUMO energies were determined by time-dependent DFT (TD-DFT) approach, while taking solvent effect into account.

Results and discussion

Geometrical parameters

The bond length between the atoms in mannitol molecule was theoretically calculated by both B3LYP and HF methods. The mannitol molecular structure comprised with 26 atoms and fitted to C₁ point group symmetry. Geometrical structure of the title molecule along with numbering of atom scheme was shown in Fig. 1. The optimized geometrical parameters were obtained by HF 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, bond angles and dihedral angles) were compared with available experimental data [9,10]. In the mannitol molecule all C–C and C–H bonds shows bond length 1.5 Å and 1.11 Å respectively on both B3LYP and HF methods, which is due to the attachment of electron withdrawing OH group on all carbon atoms. All C–O bonds were explored same bond length as 1.4 Å on both B3LYP and HF. The oxygen–hydrogen bonds were also provided similar bond

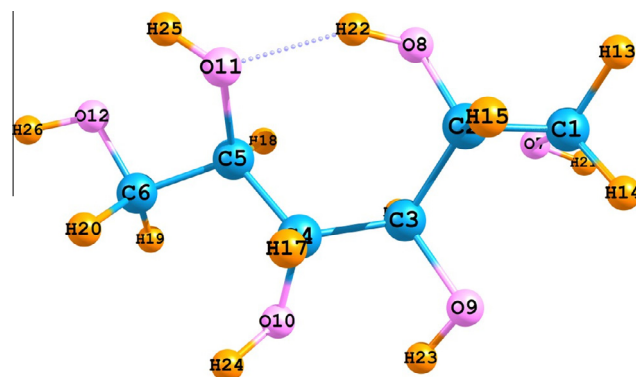


Fig. 1. Molecular structure of mannitol along with numbering of atoms.

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