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Density functional theory studies on molecular structure, vibrational spectra and electronic properties of cyanuric acid

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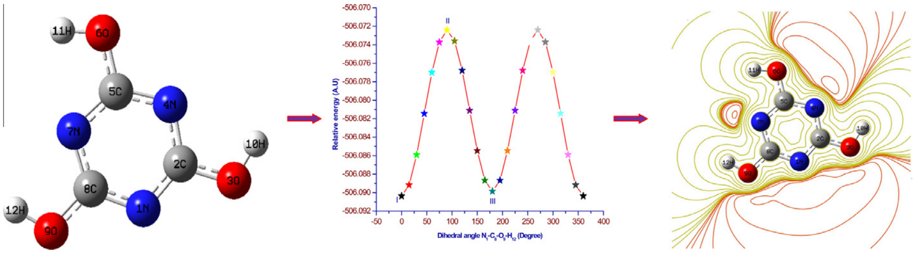
HIGHLIGHTS

- FT-IR and FT-Raman investigations of cyanuric acid were carried out.
- NBO analysis used to explain the interaction between electron donors and acceptors.
- The atomic charges on the various atoms of molecule were obtained by Mulliken population analysis.
- Thermodynamic parameters of the title molecule are reported.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work has been carried out a combined experimental and theoretical study on molecular structure, vibrational spectra and NBO analysis of cyanuric acid. The FT-IR (100–4000 cm^{-1}) and FT-Raman spectra (400–4000 cm^{-1}) of cyanuric acid were recorded. In DFT methods, Becke's three parameter exchange-functional (B3) combined with gradient-corrected correlation functional of Lee, Yang and Parr (LYP) by implementing the split-valence polarized 6-31G(d,p) and 6-31++G(d,p) basis sets have been considered for the computation of the molecular structure optimization, vibrational frequencies, thermodynamic properties and energies of the optimized structures. The density functional theory (DFT) result complements the experimental findings. The electronic properties, such as HOMO–LUMO energies and molecular electrostatic potential (MESP) are also performed. Mulliken population analysis on atomic charges is also calculated. The first order hyperpolarizability (β_{total}) of this molecular system and related properties (β, μ and $\Delta\alpha$) are calculated using DFT/B3LYP/6-31G (d,p) and B3LYP/6-311++G(d,p) methods. The thermodynamic functions (heat capacity, entropy and enthalpy) from spectroscopic data by statistical methods were also obtained for the range of temperature 50–1000 K.

Introduction

Cyanuric acid ($C_3H_3N_3O_3$) existing either in enol form (2,4,6-trihydroxy-1,3,5-triazine) or keto form (1,3,5-triazine-2,4,6-trione) is exhaustively applied in both day to day life and industries since late 1950s [1,2]. The notable properties of biodegradability by soil bacteria, it is used as a chlorine-stabilizer against the sun for the outdoor swimming pools and large industrial water system as it is non-toxic to human and aquatic animals [3]. Derivatives properties of the compound are also extensively applied as dyestuffs, optical bleaches, surface active agents and pesticides [1,4–6].

This organic compound was first identified over two centuries ago [1] and the crystal structure was reported for the first time in 1938 by Wiebenga and Moerman [7]. 1,3,5-Triazine or s-triazine

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ring present as the core structure, the compound is aromatic and slightly acidic in nature [1]. The presence of both the N-H and C═O motifs in the molecular structure provides functionality as both hydrogen bonding donor and acceptor [8]. The non-standard choice of crystallographic setting was selected allegedly by virtue of simplicity in explaining the crystal packing [9]. Single crystal structure determination, hydrothermal crystal growth and hydrogen bonding analysis of cyanuric acid have been reported previously [10].

It is reliably found that neither detailed quantum chemical calculations, nor the vibrational analysis study of cyanuric acid has been reported so far. FTIR spectroscopy has been extensively used in both qualitative and quantitative pharmaceutical analysis. Raman spectroscopy is now becoming widely applied in the pharmaceutical sciences too. Conventional applications of vibrational spectroscopy include the identification of drugs and raw materials, quality control, as well as characterization of polymorphs, salts and hydrates. A recent survey analyzed the pharmaceutical substances and formulated products by vibrational spectroscopy have been reported by Clark et al. [11]. Studies on polymorphs of drugs have also been addressed by Threlfall et al. [12]. *Ab-initio* HF, density functional theory (DFT) computations have become an efficient tool in the prediction of molecular structure, harmonic force fields, vibrational wavenumbers as well as the IR and Raman intensities of pharmaceutically important molecule.

Hence, the present work focuses with FT-IR, FT-Raman spectroscopic investigation of cyanuric acid employing the B3LYP method with 6-31G(d,p) and 6-311++G(d,p) basis sets. Vibrational spectral analyses have been carried out on the basis of calculated potential energy distribution (PED). The minimum energy conformational analysis was carried out with the help of potential energy surface (PES) scan. A comprehensive investigation of geometrical and electronic structure in the ground state and first excited state, dipole moment, polarizability, first static hyperpolarizability along with molecular electrostatic potential (MESP) surface and contour map lead to better understanding of structural and spectral characteristic of the cyanuric acid under experiment. The NBO analysis has also been carried out to elucidate information regarding the charge transfer within the molecule.

Experimental methods

Cyanuric acid with the stated purity greater than 99% was purchased from M/s. MERCK Chemical Co., Germany, and used without further purification for spectroscopic measurements to record the FTIR and FT-Raman spectra. The Fourier Transform Infrared Spectra of the cyanuric acid has been recorded in the 4000–400 cm^{-1} on a Perkin Elmer FTIR BX calibrated spectrometer using polystyrene bands. The FT-Raman spectrum has been recorded in the region 4000–100 cm^{-1} in pure mode using Nd-YAG laser of 200 mW, the spectra were recorded using BRUKER RFS 27 calibrated spectrophotometer using polystyrene bands. Liquid nitrogen cooled Ge diode was used as a detector. Spectra were collected for samples with 1000 scan accumulated for over 30 min duration. A correction according to fourth power scattering factor was performed, with no instrumental correction. The spectral measurements are carried out with Sophisticated Analytical Instruments Facility (SAIF), Indian Institute of Technology (IIT-M) – Madras, Chennai.

Computation details

An appropriate combination of theoretical method and basis set could be the best balance between accuracy and computing economy in computational chemistry. The entire calculations were carried out at density functional (DFT) levels on a Pentium IV personal computer using Gaussian 03W [13] program package invoking gradient geometry optimization [14]. The harmonic vibrational frequencies were calculated at the same level of theory for the optimized structures and obtained frequencies were scaled by 0.958 for DFT/B3LYP/6-31G(d,p) and 0.983 for B3LYP/6-311++G(d,p) [15]. Initial geometry generated from standard geometrical parameters were minimized without any constraint in the potential energy surface at DFT/B3LYP level, adopting the standard 6-31G(d,p) basis set. This geometry was then re-optimized again at DFT/B3LYP level using the 6-311++G(d,p) basis set. The optimized structural parameters were used in the vibrational frequency calculation at DFT levels to characterize all stationary points as minima. DFT/B3LYP approach has been used for the computation of molecular structure, vibrational frequencies and energies of optimized structures in the present work using GAUSSVIEW program with symmetry considerations along with available related molecules, vibrational frequency assignments were made with a high degree of accuracy. Then the spectra were analyzed in terms of the Potential Energy Distribution (PED) contributions by using the Vibrational Energy Distribution Analysis Program [16]. The natural bond orbital (NBO) calculations [17] were performed at the above said level using NBO 3.1 program as implemented in the Gaussian 03W package. In order to understand the various second order interactions between the filled orbital of one subsystem and vacant orbital of another subsystem. This is a measure of the inter-molecular and intra molecular delocalization or hyper conjugation.

Results and discussion

Molecular geometry

The optimized geometrical parameters of cyanuric acid is calculated by DFT/B3LYP level with the 6-31G(d,p) and 6-311++G(d,p) basis set are listed in Table 1. The molecular structure of cyanuric acid (Fig. 1a) and optimized structure of cyanuric acid obtained from B3LYP with basis sets 6-31G(d,p) are shown in the Fig. 1b. The values for all the bond lengths and bond angles have minor deviation with the experimental results calculated by 6-31G(d,p) and 6-311++G(d,p) basis sets. The theoretical calculations performed for an isolated molecule in gaseous phase and the experimental results for a molecule in solid state explains this minor deviation. This molecule has six C–N bond lengths, three C–O bond lengths and three O–H bond lengths. From the theoretical values, it is found that most of the optimized bond lengths are in good agreement with experimental bond lengths but bond angles are marginally longer and shorter than that of experimental values.

Conformational analysis

Potential energy surface is important because it aids in visualizing and describing the relationship between potential energy and molecular geometry [18]. The accurate determination of geometrical distortions is an important tool for investigating the nature of intra and inter molecular interactions. Conformational analysis performed in order to define the preferential position of cyanuric acid with respect to NH_2 rotation of the title molecule. The possible conformers of cyanuric acid depend on the rotation of amine group linked to the ring. The potential energy barrier obtained by the rotation of the amine group with dihedral angle N_1–C_8–O_9–H_{12} of cyanuric acid using B3LYP/6-31G(d,p) method is shown in Fig. 2. These bonds are responsible for the flexibility and conformational stability of cyanuric acid. Thus a search for low energy structure is performed, and it is relevant to coordinate the conformational flexibility within the molecule. During the calculation all the geomet-