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Evans hole and non linear optical activity in Bis(melaminium) sulphate dihydrate: A vibrational spectral study

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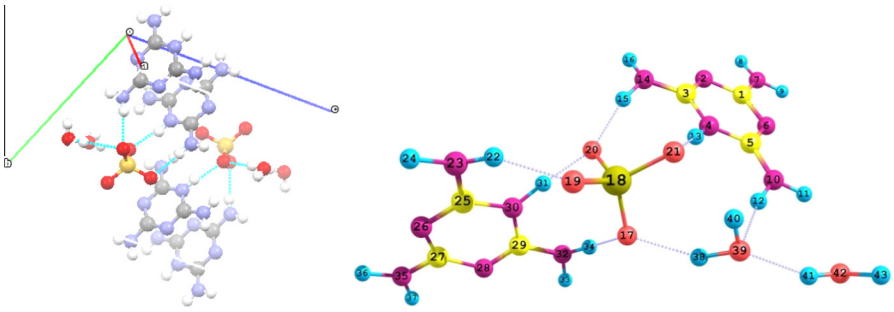
HIGHLIGHTS

- Spectral analysis of BMSD has been performed by FT IR and FT Raman techniques.
- Molecular geometry and vibrational spectra have been computed by B3LYP method.
- Evans hole analysis has been used to explain the band profile of IR spectrum.
- NBO analysis has been carried out to assess the strength of hydrogen bonding.
- The HOMO LUMO and MEP plots have been generated to explain NLO activity.

GRAPHICAL ABSTRACT

The crystalline network and the optimized geometry of Bis(melaminium) sulphate dihydrate.



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ABSTRACT

Bis(melaminium) sulphate dihydrate (BMSD), an interesting melaminium derivative for nonlinear optical activity, has been subjected to vibrational spectral analysis using FT IR and FT Raman spectra. The analysis has been aided by the Potential Energy Distribution (PED) of vibrational spectral bands, derived using density functional theory (DFT) at B3LYP/6-31G(d) level. The geometry is found to correlate well with the XRD structure and the band profiles for certain vibrations in the finger print region have been theoretically explained using Evans hole. The detailed Natural Bond Orbital (NBO) analysis of the hydrogen bonding in BMSD has also been carried out to understand the correlation between the stabilization energy of hyperconjugation of the lone pair of donor with the σ^* orbital of hydrogen-acceptor bond and the strength of hydrogen bond. The theoretical calculation shows that BMSD has NLO efficiency, 2.66 times that of urea. The frontier molecular orbital analysis points to a charge transfer, which contributes to NLO activity, through N–H...O intermolecular hydrogen bonding between the melaminium ring and the sulphate. The molecular electrostatic potential (MEP) mapping has also been performed for the detailed analysis of the mutual interactions between melaminium ring and sulphate ion.

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1. Introduction

Melaminium derivatives are the object of extensive chemical research for their role in living organism [1], self-assembly process in supra molecular architectures [2] and nonlinear optics [3]. A few hydrogen bonded complexes of melaminium, possessing second

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harmonic generation (SHG) activity, have been reported [4]. The recent toxicological and pharmacological investigations explore nephrotoxicity, crystal formation in kidney and renal toxicity induced by melamine or its derivatives [5,6]. Polyamide 6, one of the principal thermoplastics, used in the plastic engineering and in textile industries is prepared from Melaminium derivative [7]. The colour change induced by triple hydrogen-bonding enables on-site and real-time detection of melamine in raw milk and in infant formula, even at a concentration of 2.5 ppb without the aid of any advanced instruments [8]. The diverse applications of melamine and its derivatives offer tremendous scope for exploring structural and bonding features of BMSD and their role in its NLO activity, with the aid of Fourier Transform Infrared and Raman spectroscopy.

The present study focuses on geometry optimization and vibrational spectral analysis of Bis(melaminium) sulphate dehydrate (BMSD), a compound that potentially exhibits non-linear optical properties, using FT IR and FT Raman spectra aided by density functional theoretical computations at B3LYP/6-31G(d) level, along with the analysis of Evans hole and MEP mapping. NLO activity has been theoretically investigated using the computed hyperpolarizability tensor, supported by NBO and frontier molecular orbital analysis.

2. Experimental

2.1. Preparation

The starting compound Melamine (99%, Aldrich) and sulphuric acid (Merck) has been used for the present preparation. Melamine was dissolved in a 20% solution of H_2SO_4 at molar ratio 2:1, and the resulting solution was evaporated slowly. After several days, colourless crystals of the title salt appeared [9].

2.2. Spectroscopic measurements

The vibrational measurements were carried out at room temperature. The polycrystalline powders of BMSD were achieved by grinding in agate mortar with pestle. Samples, as suspensions in Nujol, were put between KBr windows. Infrared spectrum has been recorded with a Bruker IFS-88 spectrometer in the region 4000–80 cm^{-1} with a resolution of 2 cm^{-1}. The Fourier Transform Raman (FT Raman) spectrum of powder sample of BMSD was taken with FRA-106 attachment to the Bruker IFS-88 spectrometer equipped with Ge detector cooled to liquid nitrogen temperature. The signal to noise ratio was established by 32 scans, weak apodisation. Nd^{3+}:YAG air-cooled diode pumped laser, 1064 nm of power 200 mW was used as an exciting source. The scattered light

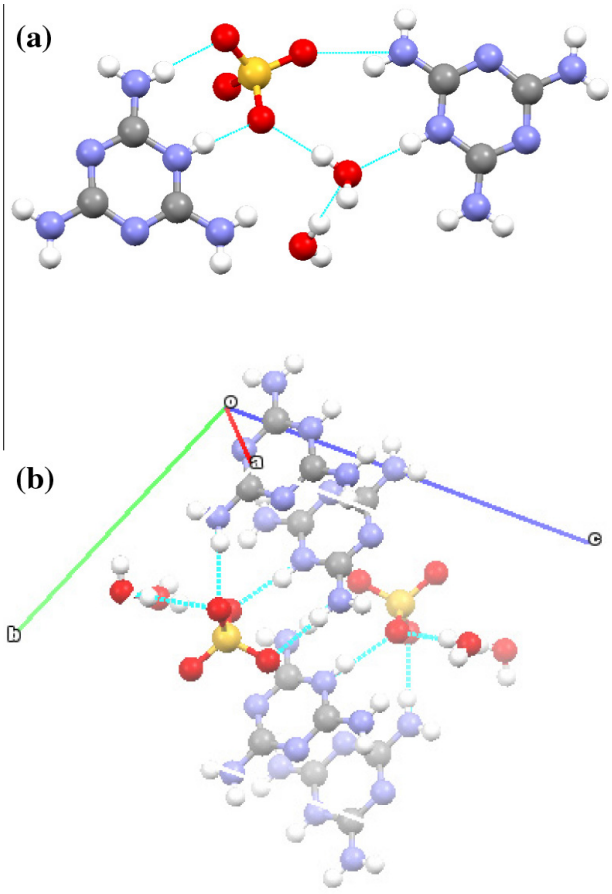

Fig. 2. (a) XRD showing formula unit with intermolecular hydrogen bonding. (b) The molecular arrangement in the unit cell showing the hydrogen bonding interactions.

was collected at the angle of 180° in the region 3600–80 cm^{-1}, resolution 2 cm^{-1}, 256 scans.

3. Computational

The computed results reported in this paper are obtained with the Gaussian '03 program package [9]. The geometry optimization was carried out by employing hybrid Becke's three-parameter Lee–Yang–Parr correlation functional (B3LYP), at 6-31G(d) level of theory, which can provide reliable results for energy data. The IR and Raman spectra were simulated from the optimized geometry of

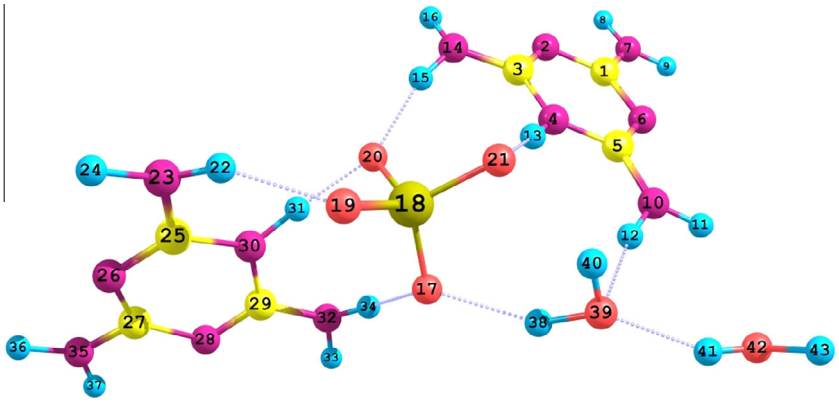

Fig. 1. Optimized geometry of BMSD at B3LYP 6-31 G(d) level.

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