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Molecular structure, vibrational spectra and nonlinear optical properties of 2,5-dimethylanilinium chloride monohydrate: A density functional theory approach

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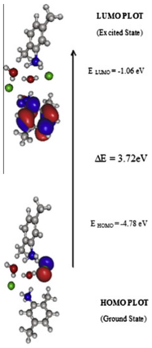
HIGHLIGHTS

- The complete assignments of 2,5-DACM were performed on the basis of PED.
- Nonlinear optical properties of 2,5-DACM were studied using DFT calculations.
- HOMO–LUMO energy gap explains the charge transfer interactions in the molecule.
- Stability of the molecule has been analyzed using NBO analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Single crystals of 2,5-dimethylanilinim chloride monohydrate were grown by slow evaporation at room temperature and were characterized by X-ray powder diffraction study to confirm the crystalline nature of the synthesized compound. The optimized molecular structure, vibrational spectra and the optical properties were calculated by the density functional theory (DFT) method using the B3LYP function with the 6-31G(d,p) basis set. Simulation of infrared and Raman spectra led to excellent overall agreement with the observed spectral patterns. The complete assignments of the vibrational spectra were carried out with the aid of potential energy distribution (PED). The stability of the molecule arising from hyper-conjugative interaction and charge delocalization has been analyzed using natural bond orbital (NBO) analysis leading to high nonlinear optical (NLO) activity. The lowering in the HOMO and LUMO energy gap explains the eventual charge transfer interactions that take place within the molecules.

Introduction

During the decade of crystal research, nonlinear optical (NLO) materials have been the subject of intense research to chemists, material scientist and optical physics owing to their potential application in various engineering technological fields [1–3]. Many investigations are being conducted to synthesize new organic materials with large second-order optical nonlinearities in order to satisfy day-to-day technological requirements [4]. They have innumerable potential applications in optical computing, telecommunications, optical data storage, etc. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power as compared to inorganic materials [5]. The basic structure of organic nonlinear optical (NLO) materials is

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based on the π bond system leading to an increased optical nonlinearity [6,7]. The key factor for material selection depends on the physical properties of the crystal and the prospect of the various applications. However, the implementation of single crystal of organic materials in practical application has been impeded by the inadequate transparency, poor optical quality and low laser damage threshold. The inorganic crystals have excellent mechanical and thermal properties, but they possess relatively modest nonlinearity because of lack of extended π electron delocalization [8]. To overcome these drawbacks, high optical nonlinearity of pure organic compound is combined with favorable mechanical and thermal properties of inorganic compound called semiorganic materials. 2,5-Dimethylanilinium chloride monohydrate (2,5-DACM) belongs to this large semiorganic NLO family. The crystal structure of this compound was elucidated by Smirani [9]. A literature survey reveals that to the best of our knowledge, neither vibrational spectra nor DFT wavenumber and structural parameter calculations of the title compound have been reported up to now. This inadequacy observed in the literature and the absence of center of symmetry of the studied compound encouraged us to make this theoretical and experimental vibrational spectroscopic research. In recent years, density functional theory (DFT) has been a shooting star in theoretical modeling. The development of better and better exchange–correlation functionals made it possible to calculate many molecular properties with comparable accuracies to traditional correlated ab initio methods, with more favorable computational costs [10]. Literature survey revealed that the DFT has a great accuracy in reproducing the experimental values in terms of geometry, dipole moment, vibrational frequency, etc. [11,12]. Vibrational spectroscopy is an efficient tool for the characterization of crystalline materials. It is effectively used to identify functional groups and determine the molecular structure of synthesized crystals. It can also provide deeper knowledge about the relationships between molecular architecture, non linear response and hyperpolarizability, and support the efforts towards discovery of new efficient materials of technological applications. The combination of infrared Fourier transformation (TF-IR) and Raman spectroscopy with quantum chemical computations have been used as effective tools in the vibrational analysis of complex organic molecular systems [13–16]. The natural bond orbital (NBO) analysis can be employed to identify and substantiate the possible intra- and intermolecular interactions between the units that would form the H-bonded network [17]. The present work deals with the growth and detailed vibrational spectral investigation of the crystal 2,5-DACM to elucidate the correlation between the molecular structure, NLO properties, charge transfer interaction and hydrogen bonds, aided by using the scaled quantum mechanical force field (SQMFF) technique based on density functional theory (DFT) computation.

Experimental

Crystal growth

Single crystals of 2,5-dimethylanilinium chloride monohydrate (2,5-DACM) were grown by the slow evaporation solution growth technique. The title compound was prepared by slow addition of an hydrochloric acid to an ethanolic solution of 2,5-dimethylaniline in a 1:1 molar ratio. A crystalline precipitate was formed. After adding distilled water, the resulting solution was mixed well using a magnetic stirrer to ensure homogeneous concentration in the entire volume of the solution. The obtained solution was left to stand at room temperature. The slow evaporation of solvent leads to the formation of colorless single crystals of 2,5-dimethylanilinium chloride monohydrate. Repeated recrystallization yielded to good quality crystals.

Powder XRD, IR and Raman measurements

Powder XRD measurements were carried out using a Phillips powder diffractometer PW 1710 with Cu Kα radiation (λ = 1.54187 Å) at the scan rate 0.02 s^{-1} for the 2θ angular range of 5.01–60.01° at room temperature in order to confirm the crystal identity. The Fourier transform infrared (FT-IR) spectrum of 2,5-DACM is recorded in the range 4000–400 cm^{-1} using PERKIN–ELMER FT-IR spectrometer. The resolution of the spectrum is ±2 cm^{-1}. The Fourier transform Raman (FT-Raman) spectrum of the same compound was recorded using Horiba Jobin-Yvon LabRAM HR 800 Dual Spectrophotometer. The incident laser excitation is 514.53 nm.

Computational methods

The density functional (DFT/B3LYP) at the 6-31G(d,p) basis set level was adopted to calculate the properties of the title molecule in this work using Gaussian 03 program [18]. An empirical uniform scaling factor of 0.97 was used to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity [19]. Vibrational analysis was performed including the calculation of vibrational modes and potential energy distribution (PED). These calculations were done with the VEDA 4.0 program written by Jamroz [20]. It should be noted that Gaussian 03 package does not calculate the Raman intensity. The Raman activities were transformed into Raman intensities using RAINT program [21] by the expression:

$$I_i = 10^{-12}(n_0 - n_i)^4(1/n_i) \cdot S$$

where I_i is the Raman intensity, S is the Raman scattering activities, n_i is the wavenumber of normal modes, and n_o denotes the wavenumber of the excitation laser [22]. The natural bond orbital (NBO) calculations [23] were performed using NBO 3.1 program as implemented in the Gaussian 03 package at the DFT/B3LYP/6-31G(d,p) level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which are a measure of the intramolecular delocalization or hyper conjugation. Various NLO properties such as dipole moment μ, polarizability α and molecular first hyperpolarizability β were computed. The electronic properties such as HOMO and LUMO energies were determined by time-dependent DFT (TD-DFT) approach.

Results and discussion

Characterization

X-ray powder diffraction was used for the identification of the synthesized compound. The indexed powder XRD pattern of the grown 2,5-DACM crystal is shown in Fig. 1. The XRD powder pattern has been indexed using CELREF programs. The title compound belongs to the monoclinic crystal system with the non-centrosymmetric space group $P2_1$ and the lattice parameters are evaluated as: a = 7.529(3) Å, b = 7.452(2) Å, c = 9.032(4) Å, $\alpha = \gamma$ = 90°, β = 102.830(4)° and V = 494.1 $Å^3$. The calculated lattice parameters from the powder XRD analysis agree well with the reported values [9]. From the single crystal XRD data, it is observed that the asymmetric unit of the title compound is built up from one chloride anion Cl^-, one 2,5-dimethylanilinium cation $[2,5\text{-}(CH_3)_2C_6H_3NH_3]^+$ and one water molecule. The crystal packing is determined mainly by N—H…O, N—H…Cl and O—H…Cl hydrogen bonds.