Experimental and theoretical studies of 2,5-dichloroanilinium picrate

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HIGHLIGHTS

- The second harmonic generation efficiency was found to be 0.8 times that of KDP.
- The first-order hyperpolarizability (β) was found to be 5.50321×10^{-30} esu.
- NMR study confirms the molecular structure of the title compound.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Organic 2,5-dichloroanilinium picrate crystal was grown by using slow evaporation solution technique. The lattice parameter was estimated by powder X-ray diffraction. The absence of absorption at around Nd:YAG fundamental wavelength was confirmed by ultraviolet–visible absorption study. The vibrational analyses confirm the various functional groups present in the grown crystal. The NMR study confirms the presence of chemical environment of hydrogen in the title crystal. The thermogravimetric (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) traces reveals the thermal stability of the compound. The second harmonic generation (SHG) of the crystal was confirmed by Kurtz Perry powder technique. The theoretical studies such as first-order hyperpolarizability (β), molecular orbitals, electronic excitation and electrostatic potential (ESP) were performed using Gaussian 03W software at HF/6-31G (d) level.

Introduction

Organic and semiorganic materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra-fast response time and good optical properties [1–4]. Organic materials have been found to exhibit second-harmonic generation (SHG) efficiencies that by far exceed those of inorganic materials. Picric acid (2,4,6-trinitrophenol) is an organic acid, which is used in the dyeing industry, munitions, bombs, rocket warheads and as an explosive. The presence of three electron withdrawing nitro groups makes it as a good π-acceptor for neutral carrier donor molecules [5–7]. Moreover, it is well-known as TNP which is an organic nonlinear optical crystal by its shorter cut-off wavelength, optical quality, sufficiently large nonlinear coefficient, transparency in UV region and high damage threshold [8]. Among the organic materials picric acid draws much more attention because of its tendency to form salts or charge transfer molecular complexes with many organic compounds particularly with aromatic amines, aliphatic amines, aromatic hydrocarbons, etc. [9]. An alternative approach to obtain a large NLO response is to device molecular systems in which a charge transfer occurs between non

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covalently bound chromophores, (i.e.), by intermolecular or 'through-space' charge transfer [10]. Picric acid has an activating —OH group and deactivating nitro groups in its structure. It is known that picric acid acts not only as an acceptor to form various π stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions [11]. Most of the complexes of picric acid encourage acentric packing which results in large hyperpolarizability (β) and remarkable second order NLO activity (χ^2) [12]. In our frame work of picrates, we have reported a new third order nonlinear optical material (hydroxyethylammonium picrate) [13]. Yoshio et al. performed ultraviolet–visible study to confirm the occurrence of charge transfer between 2,5-dichloroaniline and picric acid [14]. The structural information of 2,5-DCAP has been given by Meng et al. [15]. After that there are no reports in connection with the title compound in a full-fledged manner. In order to accomplish the complete investigations of the title compound, the authors have grown 2,5-DCAP and characterized using powder X-ray diffraction (XRD), UV–Visible spectroscopy, vibrational (Fourier Transform Infrared & Raman), Nuclear Magnetic Resonance (NMR), thermal analysis such as TG/DTA & DSC and second harmonic generation (Kurtz–Perry method). In addition, first-order hyperpolarizability, molecular orbitals (HOMO and LUMO), electrostatic potential, electronic excitation calculations and the simulation of IR and Raman spectra were also carried out on the optimized geometry using Gaussian 03W software with a view to have insights of the charge transfer mechanism.

Prediction of Raman intensity

The calculated Raman activities (S_i) have been converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [16,17]:

$$I_i = f(v_0 - v_i)^4 S_i / v_i [1 - \exp(-hcv_i/K_B T)] \quad (1)$$

where v_0 is the exciting frequency in cm^{-1}, v_i the vibrational wavenumber of the ith normal mode, h, c and K_B are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities. The simulated Raman spectra have been plotted using pure Lorentizian band shape with a bandwidth of full width and half maximum (FW–HM) of 10 cm^{-1}. The HF/6-31G (d) calculated frequencies were scaled by 0.8953.

Computational details

The computational approach allows the determination of molecular NLO properties as an inexpensive way to design molecule by analyzing its potential before synthesis and to determine the higher order hyperpolarizability tensors of molecule [17]. The quantum chemical computation was performed at Hartree–Fock level using Gaussian 03W program package [18], invoking gradient geometry optimization. The geometry was optimized using the Hartree–Fock level of theory employing 6-31G (d) basis set. Optimized structure was confirmed to be minimum energy conformation. An optimization is complete when it has converged, i.e., when it has reached a minimum on the potential energy surface, thereby predicting the equilibrium structure of the molecule. This criterion is very important in geometry optimization [19].

The dipole moment (μ), mean polarizability $\langle \alpha \rangle$, and the total first static hyperpolarizability (β_{tot}) in terms of x, y, z components were given by following equations:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{1/2} \quad (2)$$

$$\langle \alpha \rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{1/2}$$

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

$$(4)$$

The β components are converted to esu units from Gaussian output file (1 au = 8.3693×10^{-33} esu).

The electronic excitation of the title compound was calculated by CIS method keyword. This requests a calculation on excited states using single excitation. The number of excited states used in the calculation was ten ($n = 10$).

Experimental work

Synthesis and crystal growth

2,5-Dichloroanilinium picrate was synthesized by taking 2,5-dichloroaniline and picric acid in 1:1 M ratio and dissolved in distilled water and heated at 40 °C to have a complete dissolution of the solute in distilled water. The resultant solution was filtered and kept undisturbed for slow evaporation at room temperature. The pH of the 2,5-DCAP solution was varied for 2.48, 3.81, 6.20, 10.93, 11.57 and 12. Above all, the pH value 2.48 yielded transparent crystal. The transparent yellow[1] colored crystal was harvested after 2 months of evaporation. The pH of the solution after dissolving the grown crystal was found to be 2.43. The picture of the as-grown 2,5-DCAP crystal was shown in Fig. 1. The average size of grown crystal was found to be $9 \times 4 \times 2$ mm^3.

Solubility

Thermodynamically, the chemical potential of the pure solid is equal to the chemical potential of the same solute in the saturated solution. Also the growth rate of the crystal depends on its solubility and temperature. Hence solubility is one of the most important factors for bulk crystal growth [20]. The solubility of the synthesized 2,5-DCAP salt was checked in ethanol, methanol, toluene, acetone, benzene, acetonitrile and mixed solvents. The solubility was found to be moderate in water. The solubility was done for four temperatures (30 °C, 40 °C, 50 °C and 60 °C). Water was taken as a solvent and then the synthesized 2,5-DCAP salt was added to it little by little until a point where it gets supersaturated. The solution was stirred constantly using magnetic stirrer until it becomes fully soluble. The solution was poured into the Petridish. The solvent was completely evaporated by drying the solution. The amount of the salt present in the solution was measured by subtracting the empty Petridish weight. Following the same procedure, the amount of DCAP salt dissolved in water at 40 °C, 50 °C and 60 °C were determined. The solubility curve for 2,5-DCAP was shown in Fig. 2. It was observed from Fig. 2, that the solubility increases with rise in temperature. As a result, the solubility curve in the present study of 2,5-DCAP exhibits positive temperature coefficient.

Results and discussion

Powder X-ray diffraction and morphology studies

The 2,5-DCAP crystal was subjected to powder XRD study using Panalytical xpert pro MPD X-ray diffractometer with Cu Kα = 1.5405 Å radiation. The monoclinic crystal system was

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[1] For interpretation of color in Figs. 1, 9 and 10, the reader is referred to the web version of this article.