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Crystal growth and DFT insight on sodium *para*-nitrophenolate *para*-nitrophenol dihydrate single crystal for NLO applications

S. Selvakumar [a], Maria Susai Boobalan [b], S. Anthuvan Babu [c], S. Ramalingam [d], A. Leo Rajesh [a, *]

[a] Department of Physics, St. Joseph's College, Tiruchirappalli, 620 002 Tamil Nadu, India
[b] Department of Chemistry, St. Joseph's College, Tiruchirapalli, 620002 Tamil Nadu, India
[c] Department of Chemistry, Adhiyamaan College of Engineering, Hosur 635 109 Tamil Nadu, India
[d] Department of Physics, A.V.C. College, Mayiladuthurai, 609 305 Tamil Nadu, India

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ABSTRACT

Single crystals of sodium *para*-nitrophenolate *para*-nitrophenol dihydrate (SPPD) were grown by slow evaporation technique and its structure has been studied by FT-IR, FT-Raman and single crystal X-ray diffraction techniques. The optical and electrical properties were characterized by UV-Vis spectrum, and dielectric studies respectively. SPPD was thermally stable up to 128 °C as determined by TG-DTA curves. Using the Kurtz-Perry powder method, the second-harmonic generation efficiency was found to be five times to that of KDP. Third-order nonlinear response was studied using Z-scan technique with a He-Ne laser (632.8 nm) and NLO parameters such as intensity dependent refractive index, nonlinear absorption coefficient and third-order susceptibility were also estimated. The molecular geometry from X-ray experiment in the ground state has been compared using density functional theory (DFT) with appropriate basis set. The first-order hyperpolarizability also calculated using DFT approaches. Stability of the molecule arising from hyperconjugative interactions leading to its nonlinear optical activity and charge delocalization were analyzed using natural bond orbital technique. HOMO-LUMO energy gap value suggests the possibility of charge transfer within the molecule. Based on optimized ground state geometries, Natural bond orbital (NBO) analysis was performed to study donor-acceptor interactions.

1. Introduction

Semi-organic optical materials are reputed candidates for the device fabrication technology, owing to their large nonlinear efficiency, high laser damage threshold, good mechanical and thermal stability. Nonlinear optical materials with large second-order optical nonlinearities find wide application in the area of laser technology, laser telecommunication and in data storage devices [1–3]. The inorganic materials are widely used in these applications because of the high melting point, high mechanical strength and high degree of chemical inertness. The optical nonlinearity of these materials is poor. Organic compounds are often formed by weak Van der walls and hydrogen bonds and possess a high degree of delocalization. Hence, they are optically more nonlinear than inorganic materials [4,5]. The demerits of crystalline organic NLO materials found to be that, it is too difficult to grow in large with enough quality of optical crystalline nature. In order to overcome the above said drawbacks, a new class of materials has been developed and it is known as semi-organic material.

In recent days, an extensive study has been carried out on NLO crystals which have conjugation along with electron donor and acceptor substitutions. Due to the presence of delocalized electrons, these materials generally have high second-harmonic generation (SHG) efficiency. *Para*-nitrophenol matches with this criterion for its electron donor substituent namely hydroxyl group and electron acceptor substituent such as nitrogroup. Sodium *para*-nitrophenolate *para*-nitrophenol dihydrate (SPPD) is a kind of semi organic system which has noteworthy NLO activity [6]. The presence of hydroxyl group, nitrogroup and phenyl group forms a conjugated molecular configuration with remarkable electron transfer [7]. This SPPD compound has a metal complex of donor-acceptor substituted aromatic moieties [8]. Moreover, it can form a three-dimensional network of bonding with intermolecular and

* Corresponding author.
E-mail address: aleorajesh@gmail.com (A. Leo Rajesh).

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intramolecular hydrogen bonds. Consequently, it is responsible for the charge transfer that takes place on SPPD [9]. Similarly, the ionic bond along with extensive hydrogen bonding is responsible for the mechanical and thermal stability of target system [10]. All these chemical physics features of SPPD favor the NLO attributes and it is greatly acknowledged in terms of both experimental and theoretical scrutiny [11].

In the present scenario, the theoretical approaches include various analysis such as prediction of equilibrium geometry, frontier molecular orbital analysis, hyperpolarizability and natural bond orbital analysis [12–15]. The experimental plotform includes such as, single crystal studies, molecular vibrational analysis, optical activity examination, second harmonic generation, Z-scan technique, thermal, mechanical and electrical properties have been carried out. The hand-in-hand approach of both experimental and theoretical calculations can provide a new insight on the chemical physics of NLO active SPPD.

2. Experimental and theoretical approaches

2.1. Synthesis

The crystal growth of SPPD has been attempted by adopting two different solvents namely water and methanol. The performance of crystal growth on methanol solvent found to be more effective in comparison with water, since the size and quality of the grown crystal found to be more appreciative. The crystal growth procedure includes the following steps. The analytical grade *para*-nitrophenol and sodium hydroxide were taken in stoichiometric ratio of 2:1 and dissolved in methanol solvent. The purity of the synthesized salt was further increased by successive recrystallization process. The resultant solution was completely stirred to obtain a homogenous solution after which it was filtered and kept inside a constant temperature bath with a controlled accuracy of ±0.01 °C. A cooling rate of 0.1 °C per day was employed and supersaturation was achieved gradually to initiate nucleation followed by growth. The red-orange color single crystal of dimensions with $17 \times 11 \times 6$ mm^3 was obtained after a period of 20 days and the photograph of the as grown crystal is shown in Fig. 1. Though the synthesis of SPPD was reported in literature [16], the dimension and quality of the crystal is more in the present work. In addition, in order to improve the understanding on this crystal an intensified experimental and theoretical characterization has been reported in the present work and which was not reported in previous work.

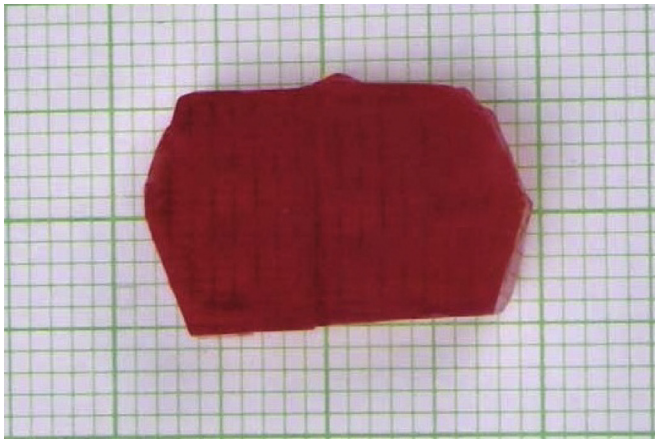

Fig. 1. The photograph of the as grown SPPD crystal.

2.2. Specification on computation

The computation on SPPD have been performed using Gaussian09 quantum chemistry program package [17] using B3LYP hybrid functional with 6–311++G(d,p) basis set. The electronic structure properties such as equilibrium geometry, molecular dipole moment (μ), energy gap, polarizability (α_o) and hyperpolarizability (β) were calculated. The optimized molecular geometry has been confirmed by the absence of imaginary frequencies that were obtained from a frequency calculation. The calculation of polarizability has been resulting from the following equation,

$$\alpha_o = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

The derivation of first-order hyperpolarizability (β) includes 10 components of $3 \times 3 \times 3$ matrix as β_{xxx}, β_{xxy}, β_{xyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{yzz} *and* β_{zzz} respectively, from which x, y and z components of β were calculated. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman Symmetry [18]. The first-order hyperpolarizability β_{tot} can be given by,

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

where,

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}, \beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The natural bond orbital calculation has been carried out using NBO 3.1 program. The numerical results were visualized using GaussView5.0.8 GUI.

2.3. Characterization

The single crystal data of the title compound was carried out using Enraf nonius CAD 4 X-ray diffractometer. The optical absorption spectrum was recorded between 200 and 1100 nm using lambda–35, UV-Vis-NIR spectrometer. The bonding between different atoms and chemical information of the crystals was collected by FT-IR spectrum (Perkin-Elmer RX1 spectrometer). Raman measurements were performed at room temperature between 50 cm^{-1}- 4000 cm^{-1} using Bruker RFS-27 FT-Raman spectrometer. The thermal stability was studied by thermogravimetric (TG) and differential thermal analysis (DTA) using a SDT Q V8.3 system in the temperature from 30 °C to 1200 °C at a heating rate of 20C/min in nitrogen atmosphere. The hardness of the crystal was measured using Riechert Polyvar 2met fitted with a Vickers diamond pyramidal indenter attached with a photomicroscope. The dielectric study has been carried out using the instrument of HIOKI 3532-50 LCR meter in the frequency range 5 Hz – 5 MHz. The electrical conductivity has been carried out using a versa tat impedance analyzer in the frequency range 1 Hz to 1 MHz by having the pellets held in between two silver electrodes. To find the NLO property, the grown crystal was subjected to second-harmonic generation studies by the Kurtz – Perry powder technique. The third-order nonlinear optical measurements were carried out by Z-scan technique using He-Ne laser at wavelength 632.8 nm.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The structure of the crystal was solved by the direct methods using SIR 92 program and refined by the full matrix least square method using SHELXL 97 program. The structure of SPPD is consisting of *para*-nitrophenol molecules, *para*-nitrophenolate anions