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Synthesis, experimental and theoretical Studies of 8-hydroxyquinolinium 3,5-dinitrobenzoate single crystal

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ABSTRACT

The 8-hydroxyquinolinium 3,5-dinitrobenzoate crystals were grown using slow evaporation solution technique. The structure was confirmed by single crystal X-ray diffraction and nuclear magnetic resonance analyses. The Fourier transform infrared and Raman spectral analyses were carried out to identify the various functional groups present in the title crystal. The optical properties were investigated by means of ultraviolet–visible spectroscopy and Kurtz–Perry powder method. Thermal properties were characterized by thermogravimetry, differential thermal analysis and differential scanning calorimetry. The mechanical strength of the crystal was investigated by Vickers microhardness tester. Additionally, first-order hyperpolarizability, nuclear magnetic resonance, molecular orbitals, electronic excitation and electrostatic potential were calculated theoretically by density functional theory using Gaussian 03 program package.

1. Introduction

One of the organic acids of interest is a strong acid, 3, 5-dinitrobenzoic acid (3,5-DNBA), which readily forms 3,5-dinitrobenzoate anion when crystallized with bases by transferring proton thereby forming a charge transfer complex. In these types of complexes, the trigonal 3,5-dinitrobenzoate anion has approximately a non-crystallographic $D_3h(2m)$ symmetry and is expected to act as a multiple acceptor of hydrogen bonds via the nitro and carboxylate groups [1]. Due to their biological activities, dinitrobenzoate derivatives are widely used in pharmacology and are effective in tumor treatment as radiation sensitizers. Moreover, some synthetic dinitrobenzoate compounds have shown useful properties in DNA and oligosaccharide synthesis [2]. A series of 3,5-dinitrobenzoic acid ester have been synthesized which have shown anti-creatinine properties [3]. Quinolines are interesting molecules which have enhanced noncentrosymmetry (essential property to exhibit NLO activity) due to their lack of rotational symmetry. In the molecular design of new nonlinear optical materials based on quinoline, the pyridine ring can function as an acceptor group and the benzene ring as a donor. The optical nonlinearities of this class of compounds can be improved by increasing the acceptor character of the pyridine ring and/or increasing the donor character of the benzene ring [4]. The 8-hydroxyquinolines (8HOQs) known as oxine have drawn significant attention due to good nonlinear optical property. 8HOQ has been found to be non-carcinogenic and is employed for in vitro assays as well as genetic toxicity [5]. Due to their ability to accept proton when added with acids, is an essential component for nonlinear optical applications. 8HOQ and its derivatives are well known for their antifungal, antibacterial and antiamoebic activities [6]. Aluminum (III) tris(quinolin-8-olate) (Alq3) is currently entering into the recent research interest especially after becoming a vital component for the development of organic light-emitting diodes (OLEDs), an important material currently used as electron injection, electron transport and emitting layer in flat panel display systems [7]. Amongst the bifunctional molecules, HOQs have been extensively studied from both experimental and theoretical view point. The 8HOQ molecule is planar and belongs to point group Cs [8].

Kim et al. reported a new acentric styryl quinolinium crystals which showed a large macroscopic optical nonlinearity with very efficient second harmonic generation (SHG) [9]. Smith et al. [10] reported a bis(8-hydroxyquinolinium 3,5-dinitrobenzoate) trihydrate structure which was grown with 95% ethanol and heated under reflux for about 90 °C. Based on this motivation, the

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authors have grown crystals devoid of water molecules using methanol as solvent at room temperature, with basic difference in structure from the reported one [10]. The devoid of water molecule in our structure shows considerable difference in the structure, cell parameters and melting point from the reported one. We have also grown the title crystal using ethanol and compared the cell parameters. The change of solvent had no impact in the cell parameters. Prince et al. [11] had reported two polymorphs of parental 3,5-dinitrobenzoic acid, one form was grown from benzene crystallized in $P2_1/c$ and another form which was grown from ethanol crystallized in C2/c. The HOQDNB single crystal was synthesized and systematic studies such as structural, optical, vibrational, nuclear magnetic resonance (NMR), thermal and mechanical have been done for the first time. Furthermore, DFT-B3LYP method was used to optimize the geometry and to determine the NMR chemical shift, molecular orbitals, first-order hyperpolarizability (β), electronic excitation and electrostatic potential calculations.

2. Experimental section

2.1. Synthesis

3,5-Dinitrobenzoic acid (Sigma-Aldrich, 99%) and 8-hydroxyquinoline (Merck, 99%) were used as supplied. The title compound was obtained by mixing 8-hydroxyquinoline (1.45 g) and 3,5-dinitrobenzoic acid (2.12 g) in methanol (100 ml) in 1:1 molar ratio. The reaction mixture was stirred for about 45 min at room temperature. The yellow solid was precipitated in 60% yield. The title crystal was obtained by recrystallization from methanol. Solvent evaporation was controlled by covering the beaker with porous aluminum foil. The pH value of the solution was found to be 5.41. The good quality transparent yellow color crystals were harvested after a period of four days. As-grown crystal having the dimension of $15 \times 5 \times 2$ mm^3 is shown in Fig. 1a. The theoretical morphology for the HOQDNB was determined by the Bravais, Friedel, Donnay and Harker (BFDH) method [12,13] with the help of Mercury software [14] by giving

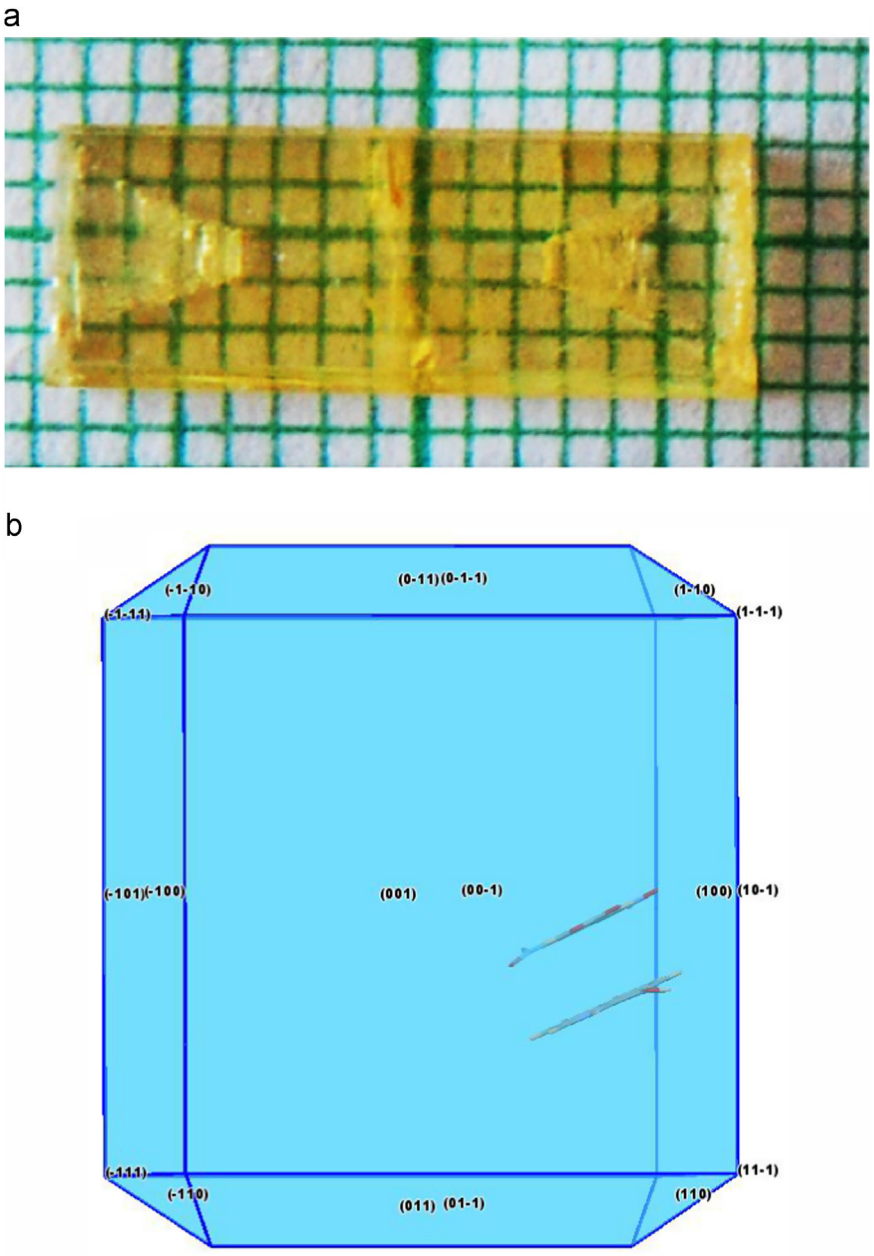

Fig. 1. (a) As-grown HOQDNB single crystal from methanol solvent. (b) BFDH surface morphology of HOQDNB crystal.