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Crystal growth, vibrational, optical, thermal and theoretical studies of a nonlinear optical material: 2-Methyl 3,5-dinitrobenzoic acid

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ABSTRACT

Single crystals of 2-methyl 3,5-dinitro benzoic acid with reasonable size have been grown by slow evaporation solution growth method using ethanol as solvent. Quantum chemical calculation of 2-methyl 3,5-Dinitro benzoic acid was carried out by using DFT/B3LYP/6-31+G(d,p) method. The powder X-ray diffraction pattern was recorded and indexed. Both the experimental and theoretical vibrational spectrum validates the presence of functional groups. Polarizability, first order hyperpolarizability and the electric dipole moment values have been computed theoretically. The ^{1}H and ^{13}C NMR chemical shift of the molecule was calculated and compared with experimental results. TG/DSC analysis has been employed to understand the thermal and physio-chemical stability of the title compound. Frequency conversion property of the crystal was tested by Kurtz and Perry method. Optical absorption behavior of the grown crystal was examined by recording the optical spectrum and band gap energy was also estimated. The calculated HOMO and LUMO energy shows the charge transfer nature of the molecule.

1. Introduction

Single crystals play a significant role in the present era of rapid scientific and technical advancement where in the application of crystals has unbounded limits. New potential materials have received much attraction because of its usefulness in the field of device technology [1,2]. Many organic materials show extremely high nonlinear optical responses compared to its counterpart inorganic materials [3]. NLO property arises in the organic materials due to the electronic transitions which is faster than the distortions of crystal lattice which occurs in the inorganic materials. Most of the organic materials possess conjugated system which gives rise to a strong π-electron delocalization [4]. NLO properties of the materials depend on the polarizability nature of π-bond [5]. Delocalized π-electrons in the conjugated system can also be enhanced by adding the donor and acceptor groups. Most of the π-conjugated molecules with asymmetric electron donating and accepting group gives high values of hyperpolarizability [6]. Properties of the organic materials can be optimized by using molecular engineering and chemical synthesis. By means of modifying the molecular structure of organic materials, the SHG property of the materials can be tailored [7–9].

NLO properties of the crystals get affected due to the influence of hydrogen bonding on dipole alignment [10]. Among the available materials, nitro compounds receive much attraction because of its high NLO coefficients [11,12]. 2-Methyl 3,5-dinitrobenzoic acid (MDNBA) is an aromatic compound has both electron donor group (carboxyl) and electro acceptor groups (methyl & nitro-)hence there may be a possibility for the formation of hydrogen bonds in this system. This push-pull system with weak hydrogen bonds may show high value of NLO coefficients. In this manuscript, we report the experimental and theoretical studies on 2-methyl 3,5-dinitrobenzoic acid crystal.

2. Experimental details

2.1. Crystal growth

MDNBA compound was purchased from Sigma-Aldrich (U.S.A) with a stated purity of 99% and was used to grow the crystals. In the temperature range 30–50 °C, the solubility of the compound was tested gravimetrically in acetone, ethanol and methanol solvent. It is observed from the solubility test that ethanol is a suitable solvent to grow MDNBA crystals. Supersaturated solution of MDNBA was prepared in ethanol at the room temperature. The prepared solution was filtered and covered with pricked polythene paper and kept undistributed for slow evaporation. Good quality transparent yellow color plate shaped MDNBA crystals were obtained after 10 days and is shown in Fig. 1.

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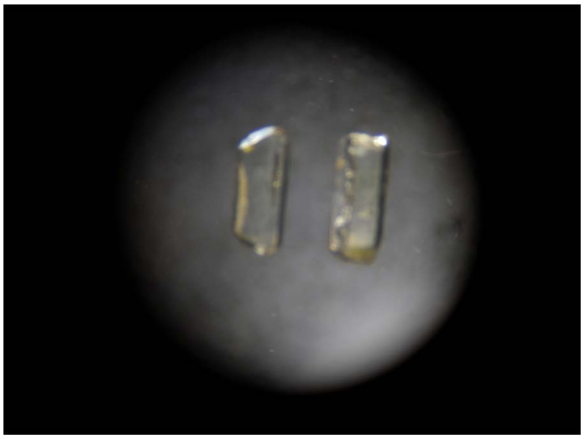

Fig. 1. As grown single crystal of MDNBA.

3. Computational details

Quantum chemical computational calculation is the effective tool for interpreting and predicting the vibrational spectra [13]. In order to study the consequence of charge transfer in MDNBA, its electronic property and the optimized structure were computed by using Gaussian09 package [14] and GaussView [15]. Density functional theory (DFT) methods received much attention since one can simulate the electronic structure of the molecules. Structural optimization were carried in B3LYP/6-31+ G(d,p) level [16,17]. The optimized molecular structure was used to simulate the IR, Raman and hyperpolarizability calculations. The GIAO method is one of the most common method for calculating the nuclear magnetic shielding tensors. ^{1}H and ^{13}C NMR isotropic shielding were calculated using $CDCl_3$ solvent effect by B3LYP/6-31+G(d,p) method.

4. Results and discussion

4.1. Powder X-ray diffraction

Unit Cell parameters of the grown MDNBA crystal were calculated by recording the powder XRD pattern using the PANalytical PW3040/60 X'pert PRO diffractometer with CuKα1, radiation of 1.54059 Å. The recorded pattern of XRD is shown in Fig. 2. The

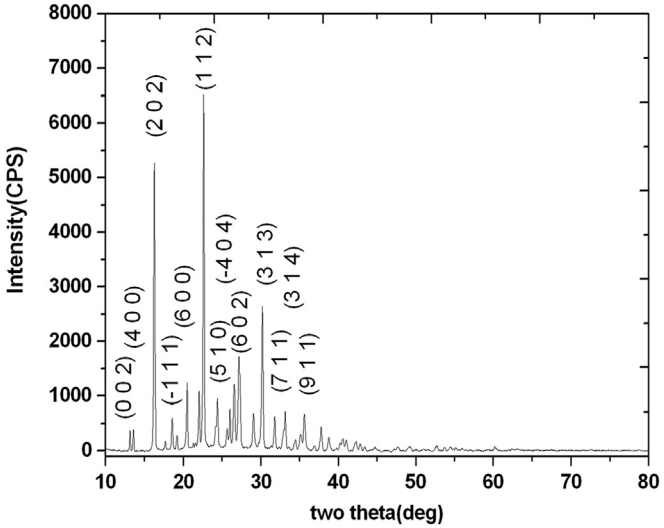

Fig. 2. XRD pattern of MDNBA crystal.

Table 1
Crystal properties of MDNBA.

Crystal property	Present investigation	Reported work [13]
Molecular formula	$C_8H_6N_2O_6$	$C_8H_6N_2O_6$
Crystal structure	Monoclinic	Monoclinic
Cell parameters		
a (Å)	26.839	26.844
b (Å)	5.113	5.104
c (Å)	13.879	13.885
β (deg.)	104.599	104.544
Volume (Å)^3	1843.007	1841.6

planes observed in the XRD pattern were indexed using XRDA program and it confirm that the crystal system of the title crystal is monoclinic. The derived crystallographic parameters of MDNBA are charted in Table 1. The calculated values of cell parameters are in good agreement with the reported literature [18].

4.2. Geometrical structures

Molecular geometry is one of the sensitive indicators of intra and inter-molecular interactions [19]. A complete geometrical optimization have been performed within the C_1 point group symmetry and the most stable optimized molecular structure of MDNBA is shown in Fig. 3. The optimized parameters such as bond lengths and bond angles for the geometry of MDNBA are presented in Table 2.

4.2.1. Hydrogen bonds

Hydrogen bond is one of the important types of non covalent interaction that is being present in many chemical and biological systems [20]. The strength of hydrogen bonding is determined by the molecular geometry and the donor, acceptor groups. Hydrogen bonds are formed by good donors (O–H, N–H) and good acceptors (N, O and halide) groups and are labeled 'strong'. MDNBA molecule has both electron donor (-carboxyl) and acceptor (-nitro & methyl) groups and forms a donor–acceptor bridge. Therefore, there is a possibility for the formation of larger number of hydrogen bonding in this system and these weak bonding helps to get high nonlinearity from the material. MDNBA has a molecular environment of adjacent carboxyl group and methyl group and also it

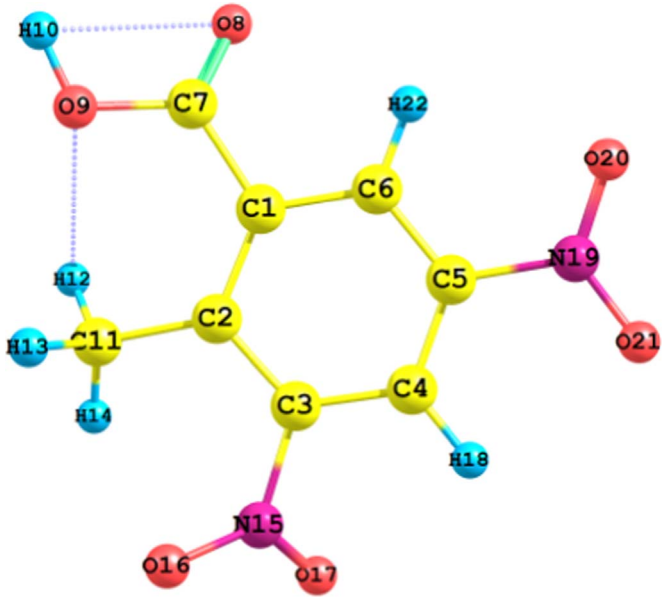

Fig. 3. Molecular structure of MDNBA.