



Synthesis, growth, optical, thermal and nonlinear optical studies of dimethylammonium picrate single crystal



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ABSTRACT

Dimethylammonium picrate (DMAP) was synthesized from dimethylformamide and picric acid as precursors and crystals were grown by the slow evaporation solution growth technique. Single crystal X-ray diffraction study revealed that DMAP crystallizes in orthorhombic system with space group $Pca2_1$. UV–Vis–NIR spectral study showed percentage of transmittance about 55% with a lower cut-off wavelength 475 nm. The relative second harmonic generation efficiency of grown crystal was found to be 3.1 times of KDP by Kurtz and Perry technique. From the TG–DT analyses, it is observed that the melting point is observed at 161.8 °C. The laser damage density of DMAP crystal was found to be 1.9 GW/cm² for 1064 nm Nd:YAG laser radiation.

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1. Introduction

Organic molecular compounds with a high degree of delocalized π -electrons have received a great deal of attention due to their more favorable nonlinear response [1–3]. Picric acid is known to have delocalized π -conjugation system and forms crystalline complex with organic and inorganic compounds. In the complex formation with picric acid, deprotonation of phenolic OH group facilitates hydrogen bonding interaction between picric acid and other molecules. Recently, picrate complexes have attracted material scientists due to their high second order nonlinear optical response [4–6]. Dimethylammonium picrate (DMAP) was synthesized using dimethylamine and picric acid as precursors and it crystallizes in orthorhombic system with space group $Pca2_1$ with the lattice parameters: $a = 9.995$ (3) Å, $b = 11.119$ (8) Å, $c = 21.326$ (7) Å and $\alpha = \gamma = \beta = 90^\circ$. Refinement of the crystal structure was carried out by the full-matrix least-squares method and the R value was 0.0542 [7]. Recently, the crystal growth, thermal stability (melting point: 158 °C), laser damage threshold (0.34 GW/cm²) and the second harmonic generation efficiency (2 times of KDP) of DMAP have been reported [8,9]. In the present investigation,

Dimethylammonium picrate (DMAP) was synthesized using *N,N*-dimethylmethanamide and picric acid as precursors. It is observed that DMAP crystal has good optical, thermal and laser damage threshold properties compared to already reported one.

2. Experimental

2.1. Synthesis and crystal growth

In the present work, the commercially available analytical grade dimethylformamide (DMF) and picric acid (Merck, 99%) was used for synthesis of dimethylammonium picrate. A mixture of acetone and distilled water (1:1) was used as a solvent. The purity of the synthesized salt was further improved by recrystallization process. The reaction scheme of DMAP is shown in Fig. 1. The prepared solution was allowed to evaporate at room temperature. After a period of 16 days well-defined, transparent, good morphological crystals were harvested. The average size of the grown crystal is 12 mm × 4 mm × 3 mm as shown in Fig. 2.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

In order to confirm the complex formation of DMAP, the intensity data were collected for a synthesized DMAP crystal using

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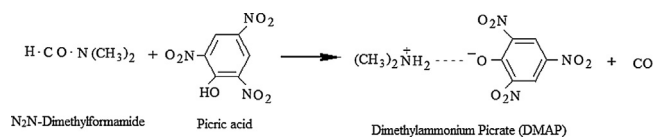


Fig. 1. Reaction scheme of DMAP.



Fig. 2. Photograph of the grown DMAP crystal.

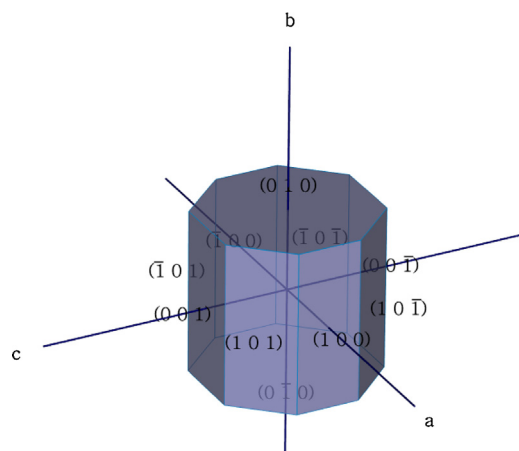


Fig. 3. Morphology of DMAP crystal.

a Bruker kappa APEXII single crystal X-ray diffractometer with graphite monochromatic MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K [10]. The structure was solved by the direct method and refined by the full matrix least-squares technique on F^2 employing the SHELXL 97 program package [11]. Crystallographic data for structure analyses of the title compound are listed in Table 1. The asymmetric unit of the title compound comprises of a *N*-methylmethanamine cation and picrate anion (Fig. 3). The crystal structure of DMAP along the crystallographic 'c' axis is depicted in Fig. 3. The chemical composition of the crystal is C₆H₂N₃O₇, C₂H₈N (DMAP). DMAP compound crystallizes in orthorhombic crystal system with space group Pca2₁. The cell parameters are $a = 9.9960(5) \text{ \AA}$, $b = 21.3323(12) \text{ \AA}$, $c = 11.1012(6) \text{ \AA}$ and volume $V = 2367.2(2) \text{ \AA}^3$. The lattice parameters for dimethylammonium picrate are comparable with the values reported in the literature. The *N*-methylmethanamine molecule exists as *N*-methylmethanaminium ion due to the protonation at the nitrogen atom (Fig. 4). The picrate anions adopt the keto form with C1–O1 and C7–O8 bond distance of 1.248(3) and 1.250(3) Å, C1–C2, C1–C6, C7–C8 and C7–C12 bond distance of 1.441(5), 1.451(5), 1.451(4) and 1.447(4) Å, respectively, which is longer than the other C–C bond lengths (between 1.374(5) and 1.460(4) Å) in the benzene ring. The bond angles C2–C1–C6 and C8–C7–C12 is 112.0(3) and 111.0(2)°, respectively, which

Table 1
Crystal data and structure refinement for DMAP.

Empirical formula	C ₈ H ₁₀ N ₄ O ₇
Formula weight	274.20
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pca2 ₁
Unit cell dimensions	$a = 9.9960(5) \text{ \AA}$; $b = 21.3323(12) \text{ \AA}$; $c = 11.1012(6) \text{ \AA}$
Volume	$2367.2(2) \text{ \AA}^3$
Z, Calculated density	8, 1.539 Mg/m ³
Absorption coefficient	0.137 mm ⁻¹
$F(000)$	1136
Crystal size	0.35 mm × 0.30 mm × 0.25 mm
Theta range for data collection	2.25–25.76°
Limiting indices	$-8 \leq h \leq 12$, $-21 \leq k \leq 26$, $-13 \leq l \leq 13$
Reflections collected/unique	12,050/4177 [$R(\text{int}) = 0.0265$]
Completeness to theta = 25.76	99.6%
Max. and min. transmission	0.9667 and 0.9038
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4177/5/363
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0435$, $wR2 = 0.1077$
R indices (all data)	$R1 = 0.0564$, $wR2 = 0.1175$
Absolute structure parameter	–0.3 (15)
Largest diff. peak and hole	0.261 and –0.228 e. Å ⁻³

is the case in some picrate complexes, while the corresponding bond angle of picric acid is 116.4(5)° [12]. In the picrate anion the deprotonated phenolate oxygen atom deviates slightly from the plane of the benzene ring (torsion angle O3–C1–C6–C5 = –175.8(3)° and O8–C7–C12–C11 = 176.4(3)°). The twist angles between the benzene rings (C1–C6 and C7–C12) and the *ortho* nitro groups (N1, N3, N4 and N6) are 22.6(2), 4.5(2), 5.5(2) and 19.6(2), respectively. The *para* positioned nitro groups are twisted by 1.6(2)° (N2) and 4.2(2)° (N5). The picrate ions are stacked head-to-tail, presumably as a result of charge-transfer interactions. In the crystal the cation and the picrate anions of crystallization are involved in N–H...O and weak C–H...O interactions, to form a three-dimensional supramolecular network (Table 2). The nitro group of the picrate anion interacts with *N*-methylmethanamine cation via a pair of bifurcated N–H...O [N(7)–H(7A)...O(1), N(7)–H(7A)...O(2), N(7)–H(7B)...O(8), N(7)–H(7B)...O(13), N(8)–H(8A)...O(1), N(8)–H(8A)...O(1), N(8)–H(8B)...O(8) and N(8)–H(8B)...O(9)] hydrogen bonds, forming a hydrogen bonded ring motif with graph-set notation $R_2^1(6)$ [13] and these motifs form a ring $R_2^2(8)$. The knowledge of morphology of crystal helps to grow the crystals in a required direction for device fabrication. The morphology of DMAP with ten well developed facets is shown in Fig. 5. It is observed that the growth rate is faster along *b*-axis than *a* and *c*-axes of the crystal.

3.2. Linear and nonlinear optical studies

Optical transmittance is an important parameter for NLO materials. UV–Vis–NIR spectrum of DMAP was recorded using a Varian Cary 5E spectrometer in the range 200 nm–800 nm as shown in

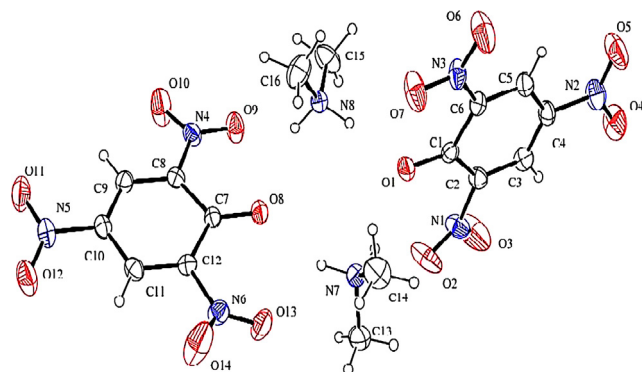


Fig. 4. Molecular configuration and atom numbering scheme for the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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