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Synthesis, spectral, structural, thermal and optical studies on dimethylammonium 4-nitrobenzoate – an organic charge transfer complex

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ABSTRACT

A new organic charge transfer complex, dimethylammonium 4-nitrobenzoate was crystallized by slow evaporation solution technique at room temperature. The stoichiometric ratio of the title complex was confirmed by elemental analysis. The crystal structure of the complex was determined by single crystal X-ray diffraction analysis to be monoclinic crystal system with space group $C2/c$. The cell parameters are $a = 40.123\ (3)$ Å, $b = 8.9533\ (7)$ Å, $c = 11.8240\ (9)$ Å, $\beta = 93.774^{\circ}\ (4)$ and $V = 4238.4\ (6)$ Å^3. The UV–visible absorption and transmittance spectra show the absorptions at 324 and 380 nm and the lower cut-off wavelength at 450 nm, respectively. The various functional groups were confirmed by Fourier Transform Infra-red (FTIR) spectrum. The thermal stability of the complex was studied by using thermogravimetric and differential thermal (TG–DTA) analyses and the compound was found to be stable up to 170 °C. Kurtz - Perry powder technique was used to find out NLO property of the grown crystal. The softness of complex was confirmed by Vicker's microhardness test.

1. Introduction

In recent years, great attention is given on adept organic non-linear optical (NLO) materials [1,2]. Organic charge transfer complexes have a plethora of applications in optical modulation, optical switching, telecommunication, laser technology and optical communications [3,4]. Generally, organic crystals have a high non-linear coefficiency compared to inorganic crystals. Organic crystals have high thermal and mechanical stabilities owing to the presence of intermolecular hydrogen bonding [5,6]. Charge transfer complexes also have high electrical conductivity which is widely used in solar cells and in the analysis of some drugs [7–9]. In recent years these organic charge transfer complexes are significantly used in pharmaceutical industries, micro-emulsion, organic semiconductors and in biological systems as antimicrobial activity and DNA binding [10,11]. These charge transfer complexes are formed by the interaction of an electron donor and an electron acceptor groups present in organic molecules. Charge transfer complexes are held together by weak intermolecular forces such as hydrogen bonding and van der Waals forces. The structure is formed by intermolecular hydrogen bonding, which plays a crucial role in charge transfer complexes. A new band appears in UV - visible spectrum at longer wavelength due to the transition of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor. This band is known as charge transfer band and due to the charge transfer in the complex the mechanical and thermal stabilities of the crystal are enhanced [12,13]. Organic charge transfer complex crystals exhibiting the non-linear optical properties should have a huge second order hyperpolarizability (β) which can be improved by intermolecular hydrogen bonding [14–16]. In this paper, the synthesis, spectral, thermal and optical studies on dimethylammonium 4-nitrobenzoate (DMNB) – an organic charge transfer complex is reported. The synthesized complex was characterized by elemental analysis, single crystal X-ray diffraction (XRD), UV–visible absorption and transmittance and FTIR spectroscopy, thermal analyses (TG–DTA), Vickers microhardeness test and SHG studies.

2. Experimental details

2.1. Synthesis of DMNB crystals

Single crystals of DMNB were grown by slow evaporation solution growth method at room temperature. Analytical reagent grade

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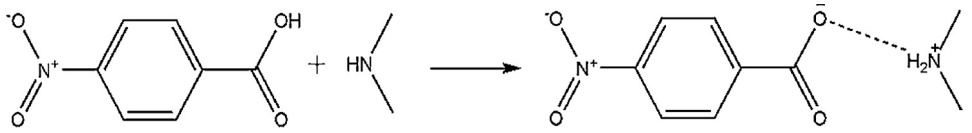

4-nitrobenoic acid dimethyl amine dimethylammonium 4-nitrobenzoate

Table 1
Elemental analysis data of DMNB crystals.

Element	Calculated (%)	Experimental (%)
Carbon	50.91	50.38
Nitrogen	13.2	13.18
Hydrogen	5.65	7.18

chemicals (E Merck: 98% assay) were used throughout this study without any further purification. The compounds 4-nitrobenzoic acid and dimethylamine were dissolved separately in tetrahydrofuran (THF) solvent in 1:1 stoichiometric proportions and the solutions were mixed together and stirred well for about 2 h to get a homogenous solution. The clear yellow colour solution obtained was filtered into a clean dry beaker through a Whatman 40 filter paper to remove any suspended impurities. The beaker was covered by an ordinary filter paper and kept in a dust-free environment without any mechanical shake for crystallization.

Under the experimental conditions bright, transparent and yellow colored crystals of DMNB were collected from the mother liquor within 25 days. Excellent quality crystals of DMNB were obtained by repeated recrystallization. The schematic representation for the formation of the DMNB crystal is given below.

2.2. Characterization techniques

The elemental analysis of the complex was carried out using an Elementar Vario EL III analyzer. The single crystal data was collected by using the instrument Bruker Kappa Apex II and the SHELXL-97 software was used to solve and refine the crystal structure of the compound. The electronic absorption and transmittance spectra of the title complex were recorded using Lambda 35 UV–visible spectrophotometer from 200 to 900 nm. The FTIR spectrum of the complex was recorded by using Thermo Nicolet, Avatar 370 FTIR spectrophotometer with KBr pellet technique at room temperature in the range 4000–400 cm^{-1}. The TG - DTA studies were carried out on a Perkin Elmer STA 6000 instrument at a heating rate of 10 °C/min in the temperature from 20 to 600 °C in nitrogen atmosphere. The second harmonic generation test on the complex was performed by the Kurtz powder SHG method. Microhardness test was performed using Leitz Weltzlar Vickers microhardness tester fitted with a Vickers diamond pyramidal indenter attached to an incident light microscope.

3. Results and discussion

3.1. Elemental analysis

The stoichiometric ratio of the complex was confirmed by elemental analysis. The elemental analysis shows that the compound contains, carbon: 50.38%, Nitrogen: 13.18%, Hydrogen: 7.18%. The experimental and calculated values are given in Table 1. The differences between the experimental and the calculated values are very close and within error limits. The calculated values were obtained from the molecular formula ($C_9H_{12}N_2O_4$) of the title complex.

Table 2
Crystallographic data and structure refinement for DMNB.

Empirical formula	$C_9H_{12}N_2O_4$	
Formula weight	212.21	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	$a = 40.123\ (3)$ Å	$\alpha = 90°$
	$b = 8.9533\ (7)$ Å	$\beta = 93.774°\ (4)$
	$c = 11.8240\ (9)$ Å	$\gamma = 90°$
Volume	4238.4 (6) $Å^3$	
Z	16	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F_{000}	1792	
Crystal size	0.25 mm × 0.30 mm × 0.35 mm	
Reflections collected	5076	
Number of parameters	276	
Theta range for data collection	2.7–28.1°	
R indices (all data)	*R*1 = 0.0523, *R*2 = 0.1972	
R_{int}	0.048	

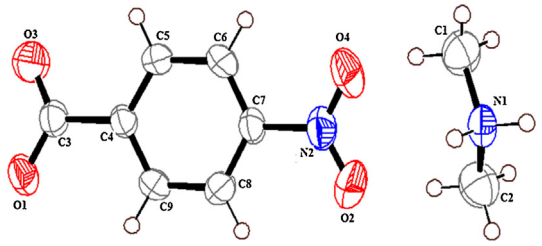

Fig. 1. ORTEP view of DMNB crystals.

3.2. Single crystal X-ray diffraction studies

The crystal structure of DMNB was resolute by diffraction technique by using appropriate crystals. The X-ray crystal data of 16160 reflections (5076 unique) were collected at 296 K using a Bruker Kappa Apex-II diffractometer with Mo *K*α radiation (λ = 0.71073 Å). The lattice parameters were determined by least-squares techniques of fine centered reflections in the θ range of 2.7° and 28.1°. The crystal structure was solved and the structure was refined by full-matrix least-squares method using SHELXS 97. After several refinement, the crystal has *R* value of 0.0523 and *wR*2 = 0.1972. Residual electron densities ranged from −0.25 to 0.19 $Å^3$. The crystal data collection and the structure refinement are given in Table 2. The DMNB complex belongs to monoclinic crystal system with space group *C*2/*c*. The unit cell parameters of DMNB are $a = 40.123\ (3)$ Å, $b = 8.9533\ (7)$ Å, $c = 11.8240\ (9)$ Å, $\alpha = 90°$, $\beta = 93.774°\ (4)$, $\gamma = 90°$ and $V = 4238.4\ (6)$ $Å^3$ with $Z = 16$. The ORTEP observation of the complex is shown in Fig. 1. In this complex, the lone pair of electrons present in the nitrogen atom of dimethylamine abstracts a proton from —COOH group of 4-nitrobenzoic acid and a charge transfer takes place between the two molecules through inter molecular hydrogen bonding. The hydrogen bonding parameters of DMNB crystals are given in Table 3. In the 4-nitrobenzoate anion, the bond distances of C4—C5 (1.386 Å) and C4—C9 (1.383 Å)