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Synthesis, crystal growth, structural, thermal and optical properties of naphthalene picrate an organic NLO material

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Abstract

Crystalline substance of naphthalene picrate (NP) was synthesized and single crystals were grown using slow evaporation solution growth technique. The solubility of the naphthalene picrate complex was estimated using different solvents such as chloroform and benzene. The material was characterized by elemental analysis, powder X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and fourier transform-infrared (FT-IR) techniques. The electronic absorption was studied through UV–vis spectrophotometer. Thermal behavior and stability of the crystal were studied using thermogravimetric (TG) and differential thermal analysis (DTA) techniques. The second harmonic generation (SHG) of the material was confirmed using Nd:YAG laser.

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Keywords: Charge transfer; Solution growth; Naphthalene picrate; Nonlinear optical (NLO) materials

1. Introduction

Nonlinear optical crystals have been a great deal of interest in recent years due to their potential use in the fields like laser technology, optical communication, optical data storage and optical signal processing [1–3]. It is also contributing number of applications in the domain of optoelectronics and photonic technologies [4,5]. This induces the physicists, chemists, material scientists and crystal engineers to identify a new class of NLO materials which should fulfill the needs of the above fields. The search for finding the new and better NLO materials having high transparent window in visible region, high optical damage threshold and good optical frequency conversion efficiency have been engaged by several scientists. In this context, variety of organic and inorganic NLO materials has been proposed. Normally organic chromophores exhibit high and fast nonlinearities than their inorganic counterparts. This is because of their tendency to induce delocalization of π electron in their organic chromophores but in most of the inorganic materials the lacking of π electron delocalization makes them to possess only moderate optical nonlinearities. The major difficulty in inorganic materials is how to impart the acentric packing with large χ^2 value. Alternatively, the structural flexibility of the organic chromophores permits to easily modify the chemical composition in a precise manner to induce acentric packing which results in large hyperpolarizability (β) and remarkable second order NLO activity (χ^2) [6,7].

In our present work an attempt has been made to grow a new class of organic NLO crystal of NP which is an intermediate product of naphthalene and picric acid. The wide transparency window and lower cutoff wavelength in the visible region of this material attract greater attention for extensive investigations. The crystals which are composed of aromatic molecules with π electron donor and acceptor substitutions normally exhibit intermolecular charge transfer and leads to the required property of noncentrosymmetry and makes them good frequency conversion material. In this paper the synthesis, solubility, growth aspect, linear, nonlinear, optical and thermal properties of the title compound have been reported. It belongs to the monoclinic system with unit cell dimensions $a = 16.248(5)$, $b = 6.871(2)$,

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$c = 14.306(5)$ Å, $\beta = 96.62(5)°$, $V = 1586.47$ Å^3 and space group $P2_1/a$ have been already reported [8].

2. Experimental

2.1. Material synthesis

AnalaR grade naphthalene and picric acid were obtained from Merck, India. The title compound was synthesized by dissolving naphthalene ($C_{10}H_8$) and picric acid (PA) in benzene separately, in the ratio of 1:1 and the resulting solution was stirred well, a yellow precipitate of naphthalene picrate (NP) ($C_6H_3N_3O_7{\cdot}C_{10}H_8$) crystalline substance was obtained. The purity of synthesized compound was improved by successive recrystallization process. The reaction for the synthesis of NP is illustrated in Scheme 1.

2.2. Solubility

To grow good quality single crystals of considerable size the selection of the solvent is very important. For choosing the best solvent for crystal growth the valuable information are obtained through solubility test [9]. To carryout the crystal growth by solution method the solubility estimation has been studied by dissolving NP in different solvents. The solvents which dissolve NP were examined using chloroform and benzene. The solubility was measured by adding excess amount of NP in the solvent at constant temperature (30 °C) and it was continuously stirred using magnetic stirrer to achieve homogeneous concentration over the entire volume of the solution. On reaching saturation the content of the solution was analyzed gravimetrically. This process was repeated for different temperatures (30–50 °C) with the interval of 5 °C for chloroform and benzene. It is observed that NP exhibits high positive solubility temperature gradient in chloroform than in benzene and solubility almost increases linearly with temperature. Hence chloroform has been selected as solvent. The solubility curves are shown in Fig. 1.

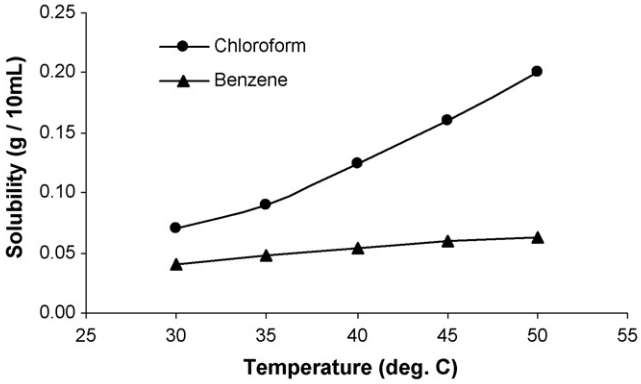
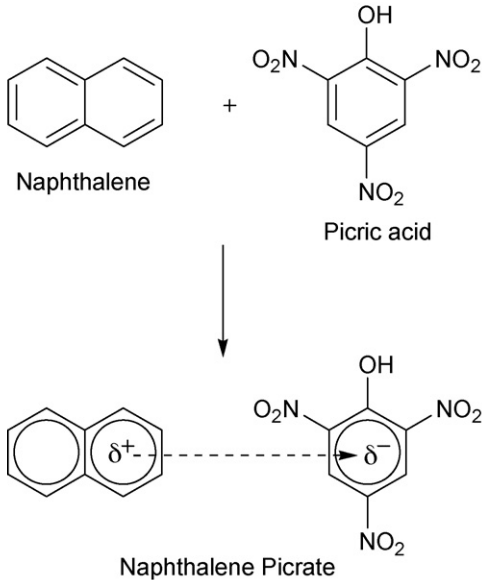


Fig. 1. Solubility temperature gradiant for naphthalene picrate in chloroform and in benzene.



Scheme 1.

2.3. Crystal growth

In accordance with the estimated solubility curve a saturated solution of NP in chloroform was prepared. The saturated solution was thoroughly stirred using magnetic stirrer for about 30 min to achieve homogeneous mixing of solvent. Suspended impurities from the solution were removed using high quality filter paper. This is kept in clean beaker for crystal growth. Throughout the experiment the supersaturation was maintained at the required level by selecting the room temperature i.e., about 30 °C as saturation temperature. This minimizes the temperature gradient of the solvent and also proper care was taken to free from the mechanical shocks. Then, the saturated chloroform solution of the synthesized complex has been kept for crystal growth by slow evaporation technique. In about 11 days well-defined, bright, transparent, good morphological yellow coloured crystals were harvested. The average size of the grown crystal is 8 mm × 4 mm × 2 mm. The photograph of the grown crystals is shown in Fig. 2.

2.4. Analyses

The elemental analysis was carried out using a PerkinElmer 2400 CHN instrument. The powdered sample had been subjected to X-ray diffraction studies using Shimadzu XRD 6000 diffractometer. The ^{1}H NMR spectrum was recorded using AMX 400 spectrometer in $CHCl_3$ with tetramethylsilane as internal reference. FT-IR spectrum was recorded by employing PerkinElmer FT-IR spectrometer using KBr pellet technique. Electronic absorption spectrum was recorded using Schimadzu 1601 UV–vis spectrophotometer. The thermal stability was identified by thermogravimetric (TG) and differential thermal analyses (DTA). The thermal analyses were carried out using Seiko Instruments between the temperatures 30–800 °C at a heating rate of 20 °C/min in air atmosphere.

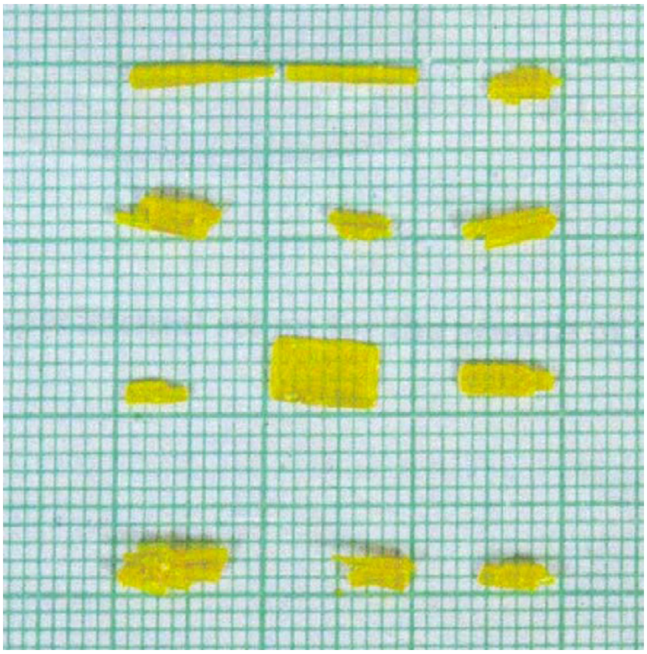


Fig. 2. Photograph of single crystals of naphthalene picrate.

3. Results and discussion

The purity of the synthesized compound was checked by the analysis of carbon, hydrogen and nitrogen present in them. The percentage composition of the elements present in NP are established as C = 52.83% (53.79%), H = 3.22% (3.10%), N = 12.37% (11.76%) and O = 31.62% (31.35%). It is observed that the calculated values given in parentheses are in good agreement with experimentally observed values. This result indicates that the NP was free from impurities also, confirm the absence of water molecules. It confirms the stoichiometry, hence the molecular formula of the complex crystal.

The powder X-ray diffraction pattern of the synthesized compound is shown in Fig. 3. The observed intensity of the peaks and its *d*-values are given in Table 1. The base peak appears at 2θ values of 12.03°, 12.47°, 17.66°, 26.52° and 27.14°. Many low intensity lines are also present. Among those the promising low intensity lines are at 13.30°, 15.73°, 21.94°, 22.28° and 23.12°. These sharp and well-defined Bragg peaks at specific 2θ angles confirm the crystalline nature of the synthesized compound.

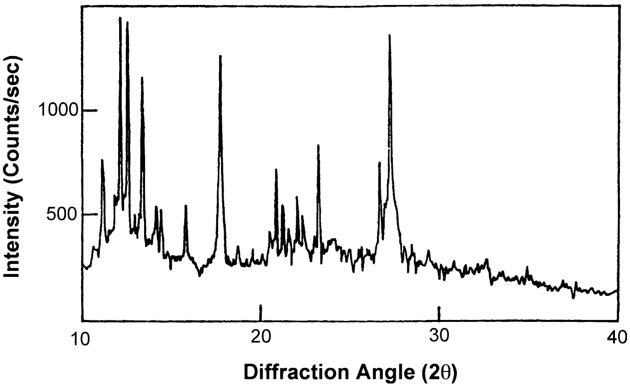


Fig. 3. Powder XRD patterns of naphthalene picrate crystals.

Table 1
X-ray powder diffraction data of naphthalene picrate crystals

Peak	2θ (°)	*d*-Value	*I* value
1	11.0111	8.0287	420
2	11.8000	7.4937	361
3	12.0323	7.3495	1140
4	12.4697	7.0927	1051
5	13.2975	6.6530	807
6	15.7281	5.6299	434
7	17.5200	5.0579	327
8	17.6560	5.0192	977
9	20.6710	4.2934	571
10	21.9435	4.0472	269
11	22.2800	3.9867	271
12	23.1211	3.8437	514
13	26.5210	3.3582	680
14	27.1433	3.2836	1385
15	27.4172	3.2504	2005

From the ^{1}H NMR spectrum (Fig. 4), the chemical shifts obtained at $\delta = 7.6$ and 7.9 ppm confirm the presence of two different kinds of protons in the naphthalene moiety and the signal observed at $\delta = 7.4$ ppm indicates the presence of two protons of the same kind in picric acid moiety. The peak at $\delta = 9.3$ ppm is assigned to the O–H proton of picric acid in NP whereas it was observed at $\delta = 11.94$ ppm [11] in the case of picric acid. This upfield shift is due to shielding of O–H protons by the π electrons of the naphthalene ring system confirming the charge transfer mechanism in this adduct.

The characteristic vibrational frequencies of the functional groups in the crystal lattices of NP are identified from the FT-IR technique and those are tabulated in Table 2. The formation of charge transfer complex during the reaction of naphthalene with picric acid is strongly evidenced through the realization of important bands of donor and acceptor in the resultant complex spectrum (Fig. 5). It is generally expected in acid–base interaction that there is a transfer of proton from the donor (acid) to acceptor (base) [10]. A similar activity is liable to expect in naphthalene and picric acid reaction also. This assumption is strongly evidenced through the appearance of a band

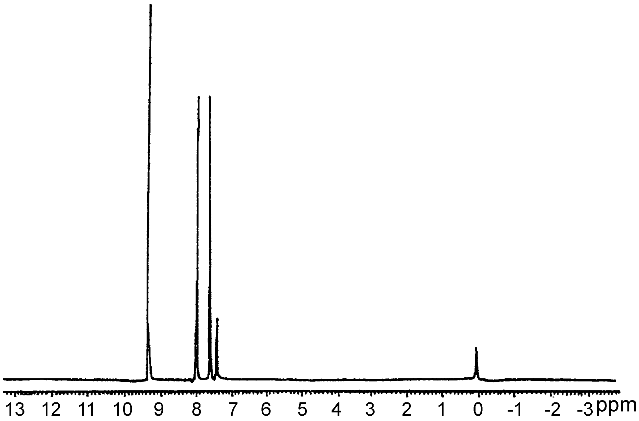


Fig. 4. ^{1}H NMR spectrum of naphthalene picrate.

Table 2
Characteristic infrared frequencies (cm^{-1}) and assignments for the naphthalene picrate crystals

Infrared frequencies (cm^{-1})	Assignments
3300	O–H stretching
3103	Asymmetric C–H stretching due to the aromatic ring
2850	Symmetric C–H stretching due to the aromatic ring
1632, 1543, 1436	C=C stretching due to the aromatic ring
1543	Asymmetric stretching of NO_2 group
1311	Symmetric stretching of NO_2 group
1280	C–O stretching

at 3300 cm^{-1}. This is due to the O–H stretching absorption which is normally expected at 3433 cm^{-1} for picric acid. This reduction in absorption has been attributed to the attraction of O–H protons by the π electron system of naphthalene moiety leading to an increase in O–H bond length. This confirms the expected symmetry and change in electronic structure through the formation of C–T complex. The absorptions at 1543 and 1311 cm^{-1} are confirming the anti-symmetrical and symmetrical stretching vibrations of NO_2 group, respectively. Usually the anti-symmetrical stretching vibration $\nu_{as}(NO_2)$ is sensitive for polar influences and the electronic states of the nucleus. Therefore one can realize that the shift to lower frequency of $\nu_{as}(NO_2)$ vibration (1543 cm^{-1}) in the complex spectrum compared with the free picric acid (1607 cm^{-1}) [11] is due to the large electron density on the picrate as a result of charge transfer interaction in the complex. The presence of C=C stretching vibration of aromatic ring is revealed from the absorption peaks at 1632, 1543 and 1436 cm^{-1} [12].

From the electronic absorption spectrum (not shown), the absorption maximum of naphthalene is at 312 nm and that for picric acid is at 210 nm. Whereas, a new distinct absorption maxima is observed at 380 nm for the complex. The longer wavelength (red shift) shift of complex from the reactants is the clear indication of charge transfer activity of the complex. As well, there is no significant absorption at 532 nm indicating that this is suitable material for second harmonic generation.

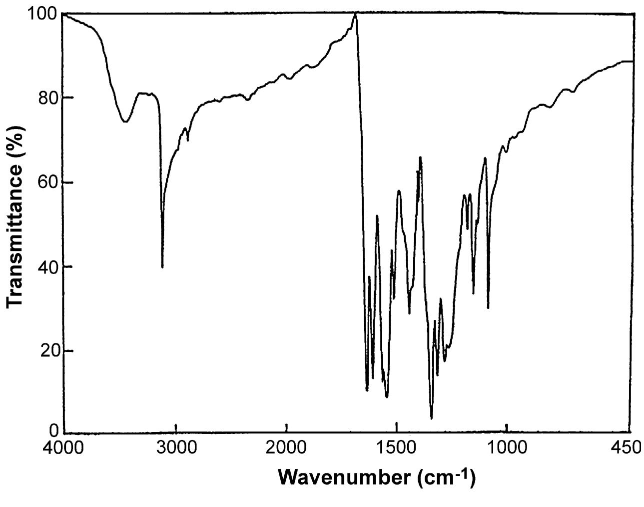


Fig. 5. FT-IR spectrum of naphthalene picrate.

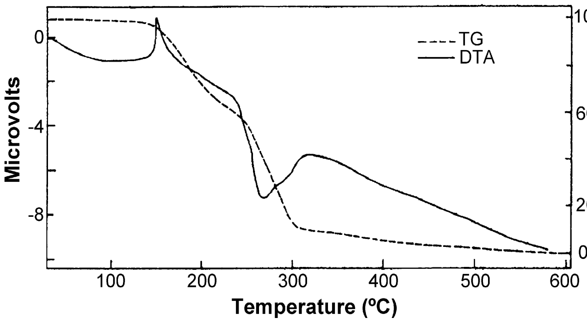


Fig. 6. TG and DTA thermograms of naphthalene picrate crystals.

$$C_{16}H_{11}N_3O_7 \longrightarrow C_{15}H_{11}O_2 + CO + 2NO + NO_2 \qquad \text{Eq. 1}$$

$$C_{15}H_{11}O_2 \longrightarrow C_{10}H_8 + CH_3^{\cdot} + 2CO + 2C \qquad \text{Eq. 2}$$

Scheme 2.

From the thermogravimetric curve (Fig. 6) it is noted that the decomposition of the title compound took place in two stages while the compound was heated from 189 °C to 413 °C. It is observed that the complex is very stable up to 151 °C after which the first decomposition starts and the second begins at 265 °C. The above reaction scheme (Scheme 2) is the most reasonable to account for the weight losses in the decomposition process.

The absence of weight loss around 100 °C confirms that there is no crystallization of water in the molecular structure. $C_{10}H_8$ is a mixture of different hydrocarbon gases which are evolved. Further, it is important to note that the compound has no phase transition till the material reaches the melting point which enhances the temperature range of the crystal for NLO applications.

The SHG property of as grown naphthalene picrate crystal was examined through modified Kurtz and Perry powdered technique. In this method powdered sample of randomly oriented crystallite particles were packed as a cell by sandwiching between glass slides. The sample was then subjected to the output of Q-switched Nd:YAG laser emitting a wavelength of 1064 nm with power 20 MW. The beam was well focused. It is observed that a signal of wavelength 532 nm was generated by the naphthalene picrate crystal. This reduction in wavelength of input radiation by half confirms the frequency doubling which strongly evidences the second harmonic generation of the naphthalene picrate crystal.

4. Conclusions

The NP complex was synthesized and single crystals were grown by slow evaporation solution growth technique. The solubility of synthesized compound was tested using benzene and chloroform. It was found that the complex compound was more soluble in chloroform than in benzene. The SHG nature of the crystal was tested through preliminary NLO testing which attributes to the noncentrosymmetry nature of the NP crystals. The formation of charge transfer complex has been confirmed through UV–vis spectrum. Elemental analysis, FT-IR and ^{1}H

NMR spectral studies confirm the molecular structure of NP crystals. The thermal analysis establishes the molecular formula of the compound and its thermal stability which indicates the suitability of the material for NLO applications.

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