

Structural and Optical Characterization Studies on 2, 4- dinitrophenylhydrazine Single Crystal

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ABSTRACT

Single crystal of an organic nonlinear optical (NLO) material, 2,4-Dinitrophenylhydrazine (DNPH), was grown by slow cooling method. Powder X-ray diffraction (PXRD), Fourier transform infrared (FT-IR) FT-Raman and NMR studies have confirmed respectively the crystal structure and functional groups of the grown crystal. Crystalline perfection of single crystals was evaluated by high resolution X-ray diffractometry (HRXRD) using a multicrystal X-ray diffractometer and found that the grown crystals are nearly perfect. UV-Visible-NIR spectral analysis was used to determine the optical constants and band gap of DNPH. Fluorescence spectrum of DNPH was recorded.

Keywords: *X-ray diffraction, Growth from solutions, Single crystal growth, Nonlinear optic materials*

1. INTRODUCTION

The properties of hydrazides and hydrazones are of interest due to their biological activities and their use as metal extracting agents [1]. The hydrazone derivatives are used as fungicides, and in the treatment of diseases such as tuberculosis, leprosy and mental disorders. The complexes of

various hydrazones are reported to act as inhibitors of enzymes [2]. Many substituted hydrazides are employed in the treatment of psychotic and psychoneurotic conditions. Carboxylic acid hydrazides are known to exhibit strong antibacterial activities which are enhanced by complexation with metal ions. The study of biological activity on 2,4-dinitrophenylhydrazine (DNPH) proved that DNPH is an important material for biological applications. 2,4-dinitrophenylhydrazine is also an important constituent in various biomedical, pharmaceutical products and in toxicology [3, 4]. Single crystal 3-dimensional X-ray structure of DNPH was reported by Okabe et al. [5]. Wardell et al. [6] have analyzed the molecular and supramolecular structures of DNPH. Chis et al. [7] have reported a combined experimental and theoretical study on molecular structure of DNPH. Sundaraganesan et al. [8] have investigated the vibrational spectra of this molecule and identified the various normal modes of vibrations. In this chapter the growth of DNPH and its characterization is presented.

2. EXPERIMENTAL

2.1 Choice of Solvent and Solubility

The chemical structure of DNPH ($C_6H_6N_4O_4$) is presented in Fig. 1. Solvents offering moderate solubility-temperature gradient for a material and yielding prismatic growth habit will be considered as suitable solvents for growing crystal of that material. Another important factor influencing the habit of growing crystal is the polarity of the solvents and stirring the solution [9-11]. Acetone (electric dipole moment 2.88 Debye) was found to yield prismatic transparent crystals and hence it was selected as the suitable solvent to grow DNPH.

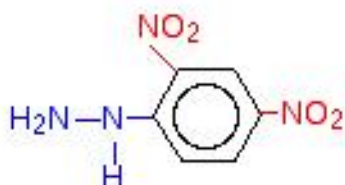


Fig. 1. The chemical structure of DNPH.

2.2 Growth of DNPH Crystal

Recrystallized salt of DNPH was dissolved in acetone to prepare the saturated solution at 30 °C. About 300 ml of this solution was taken in a beaker and placed in a constant temperature bath (CTB) having an accuracy of ± 0.01 °C. Crystals were grown by the slow cooling method by reducing the temperature from 30 °C at the rate of 0.1 °C per day. Single crystal of dimension $8 \times 4 \times 2 \text{ mm}^3$ was grown (Fig. 2) in a period of 7 days.

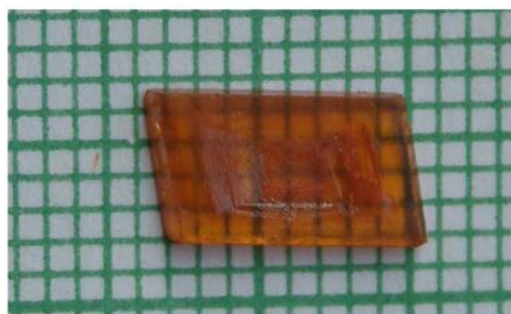


Fig. 2. As grown DNP.

3. STRUCTURAL ANALYSIS

3.1 Single Crystal X-Ray Diffraction

Single crystal X-ray diffraction study shows that DNP crystallizes in a monoclinic system. There is good agreement between the measured and the corresponding reported values [5] of cell parameter and are presented in Table 1. Also, the powder XRD pattern recorded are indexed and shown in Fig. 3.

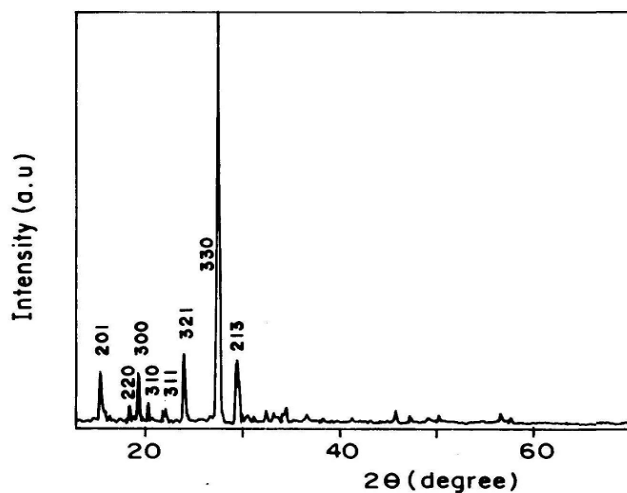


Fig. 3. X-ray powder diffractogram of DNP.

Table 1 Comparison of unit cell parameters

S.No.	a (Å)	b (Å)	c (Å)	β (°)	References
1.	4.7812	11.5923	14.0521	98.411	Present Work
2.	4.7917	11.5905	14.0496	98.372	[5]

3.2 HIGH RESOLUTION X-RAY DIFFRACTION

Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the DNPH crystal and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non-preferential etchant of water and acetone mixture in 1:2 volume ratio. Fig. 4 shows the high-resolution diffraction curve (DC) recorded for a typical DNPH single crystal specimen using (220) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with $\text{MoK}\alpha_1$ radiation. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled rectangles. On deconvolution of the diffraction curve, it is clear that the curve contains two additional peaks, which are 125 and 157 arc s away from the main peak. These two additional peaks correspond to two internal structural low angle (tilt angle ≥ 1 arc min but less than a degree) boundaries [12] whose tilt angles (misorientation angle between the two crystalline regions on both sides of the structural grain boundary) are 125 and 157 arc sec from their adjoining regions. The FWHM (full width at half maximum) of the main peak and the low angle boundaries are respectively 102, 96 and 170 arc sec. Though the specimen contains low angle boundaries, the relatively low angular spread of around 10 arc min of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good. The effect of such low angle boundaries may not be very significant in many applications, but for the phase matching applications, it is better to know these minute details regarding crystalline perfection [13].

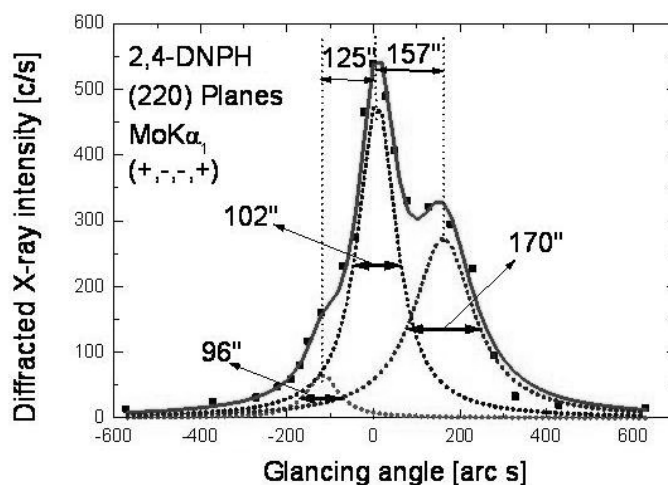


Fig. 4. High-resolution X-ray diffraction curve of DNPH single crystal.

3.3 Fourier Transform Infrared Raman Spectral Analyses

The FTIR spectrum of the grown DNPH recorded in the KBr phase in the frequency region 400 – 4000 cm^{-1} using Jasco Spectrometer FTIR, model 410 and Raman spectrum recorded for DNPH are shown in Fig. 5 and Fig. 6 respectively. The vibrational frequencies of various functional groups along with tentative frequency assignment are presented in Table 2.

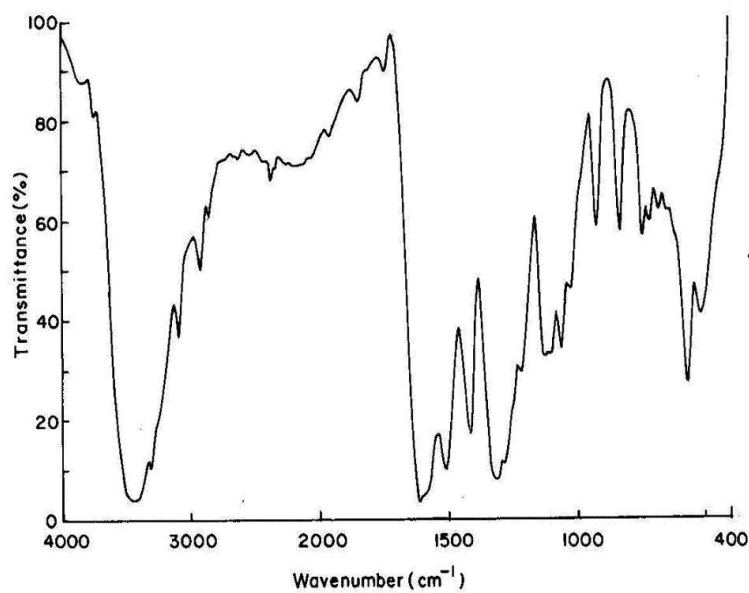


Fig. 5. FTIR spectrum of DNPH.

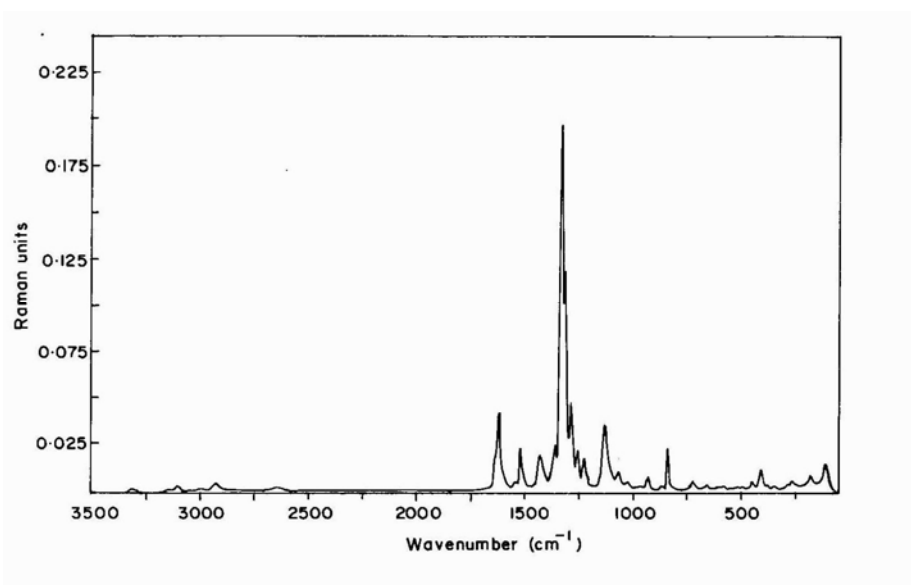


Fig. 6. FT-Raman spectrum of DNPH.

Table 2 Comparison of vibrational frequencies (cm^{-1}) of DNPH with tentative frequency assignment

IR (cm^{-1})		Raman (cm^{-1})		Assignments [14]
Present Work	Ref[8]	Present work	Ref[8]	
3312	3325	3318		N-H symmetric stretching
3099	3087	3101	3102	C- H stretching
1847 1614 1511	1860 1606 1518	1620 1521	1606 1530	C -C stretching
1420	1426	1431	1426	C- C stretching
-	-	1364 1333	1373 1335	N= O symmetric stretching C- N stretching
1314	1319	1316	1319	N- O symmetric stretching
-	-	1287 1257 1224	1280 1223	NH ₂ twisting N-H in-plane bending
1126	1130	1135	1135	C- H in-plane bending
1061	1061	1070	1066	C- C- C trigonal bending
922	923	931	923	C- C ring breathing
833	839	840	839	NO ₂ scissoring
744	744	729	716	NO ₂ wagging
718	716	-	-	C- C- C in-plane bending
682	692	662	-	C- C- C in-plane bending
569 516	530 508	453 412	453	C- C- C out-of-plane bending
-	-	271	225	C-NO ₂ out-of-plane bending
-	-	110	107	NO ₂ torsion

3.4. NMR Spectroscopy

The proton NMR spectrum of DNPH was recorded using JEOL GSX 400 model at 23 °C. Powder form of the DNPH crystal was dissolved in acetone. The chemical shift values of the protons are plotted on the X-axis and the intensity is plotted on the Y axis (Fig. 7). There are signals at 7.90 ppm (doublet), 8.35 ppm (doublet) and 8.90 ppm (singlet), indicating the presence of aromatic hydrogens at the positions 3H, 5H and 6H, respectively. A sharp singlet at 10.80 ppm is due to the presence of NH group proton. Also the NH₂ groups produce signal at 2.82 ppm. Appearance of additional peaks in the spectrum indicates that the compound is in the pure form.

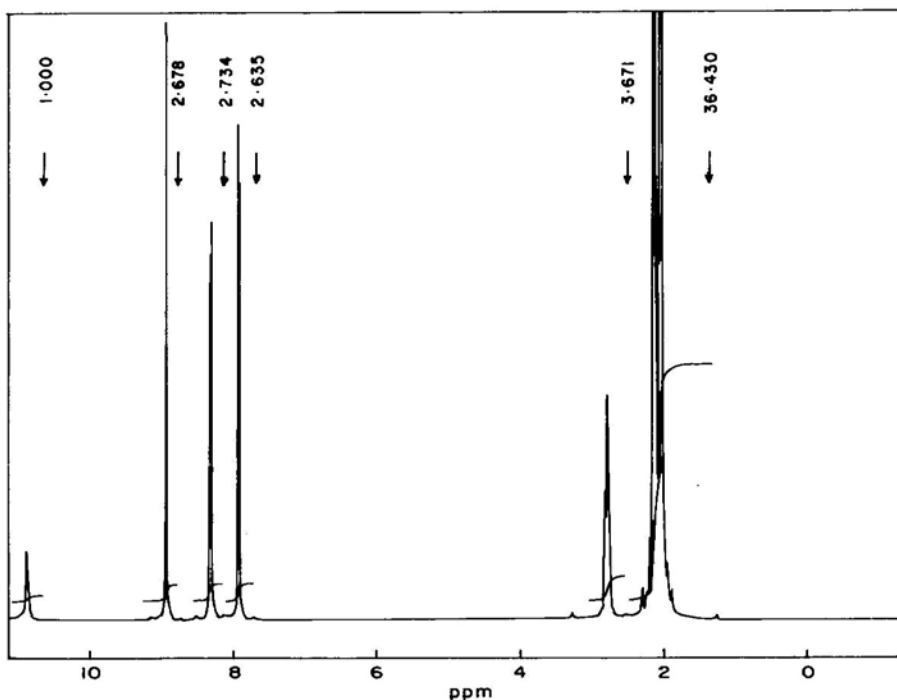


Fig. 7. NMR spectrum of DNPH.

3.5 Optical Transmittance

The optical transmittance spectrum of DNPH was recorded using Shimadzu model 1601 in the range of 300 – 1000 nm and is shown in Fig. 8. Optically clear single crystal of thickness about 2 mm was used for this study. There is no appreciable absorption of light in the entire visible range. The transmittance between 500 nm and 1000 nm is approximately 23 %. The short wavelength cutoff occurs at 400 nm.

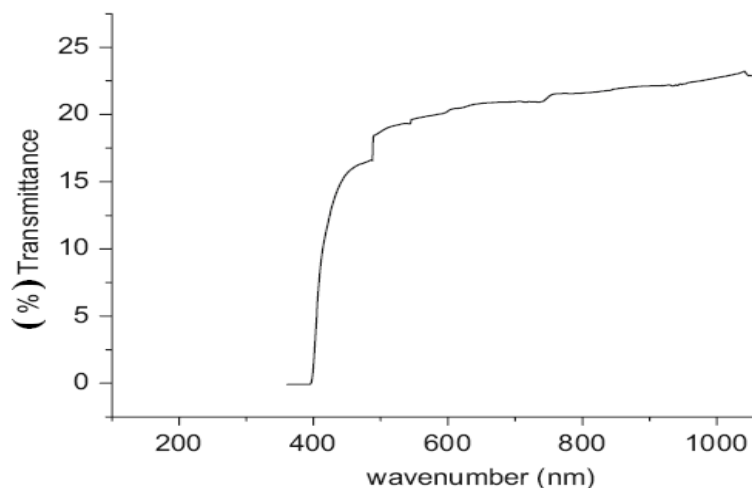


Fig. 8. UV-Vis-NIR spectrum.

3.6 Fluorescence Studies

Fluorescence may be expected generally in molecules that are aromatic or contain multiple conjugated double bonds with a high degree of resonance stability [15]. Fluorescence finds wide application in the branches of biochemical, medical, and chemical research fields, for analyzing organic compounds. It is also used as lighting in fluorescent lamps, LED etc. The emission spectrum for DNPH was recorded using FP-6500 Spectrofluorometer, in the range 320 – 520 nm (Fig. 9). It is observed that the compound was excited at 320 nm. The emission spectrum shows a sharp peak at 335 nm due to $\pi - \pi^*$ transition, and broad peak at 398 nm is due to $n - \pi^*$ transition [15, 16].

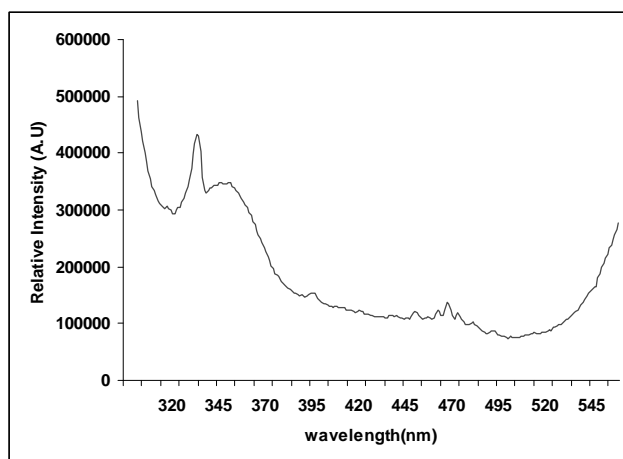


Fig. 9. Emission spectrum of DNPH.

4. CONCLUSION

DNPH single crystals of dimension 8x4x2 mm³ were grown by slow cooling method. The XRD studies confirm the structural identity of the grown crystals. The HRXRD study indicates that the grown crystal has very low angle boundary, which is due to the solvent incorporation into the crystal. FT-IR and FT-Raman spectra revealed the presence of various functional groups. NMR study confirms the placement of protons in DNPH molecule. The UV-Visible spectrum of DNPH showed that the crystal is transparent in the range 500 – 1000 nm. Fluorescence spectrum shows that DNPH fluoresces. A Z-scan technique analysis related to nonlinear optics may yield many interesting aspects of the title compound.

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