SYNTHESIS, GROWTH AND CHARACTERIZATION OF BENZALDEHYDE 4-NITRO PHENYLHYDRAZONE CRYSTALS

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Abstract: An organic nonlinear optical (NLO) Single crystal of Benzaldehyde 4- nitro Phenyl hydrazone (BPH) was grown by slow evaporation solution growth technique. The grown crystal was characterized by various spectroscopic methods such as powder X-ray diffraction carried to find the structural properties of crystal, the vibrational studies are carried out by FTIR, FT-Raman and factor group analysis. The transparency of crystal was characterized by UV-VIS spectroscopy. Second harmonic generation (SHG) was investigated to inquire into its NLO properties.

Keywords: nonlinear optical, single crystal, transparency, SHG.

Introduction: Nonlinear optics (NLO) is a frontier of science and technology playing a major role in the emerging field of photonics, which involves the applications of photons for information and image processing [1,2]. The development of photonic and optoelectronic technologies rely heavily on the growth of NLO materials with high nonlinear optical responses and the development of new and more efficient materials. Organic NLO materials are generally more versatile than their inorganic counterparts owing to their more favourable nonlinear response, since these are often formed by weak Vander Waals and hydrogen bonds. Moreover organic materials offer flexibility of molecular design, virtually an unlimited number of crystalline structures and moderate damage resistance to optical radiation. Hence, these materials might make it desirable to replace electronic switching circuits in computing and telecommunication systems with purely optical devices [3].Due to their potential applications in photonic devices, the study of nonlinear optical properties of molecules,and their hyperpolarizabilities is considered as important for extensive research, and lot of efforts taken on the experimental [4,5] and theoretical aspects[6,7] on the bulk NLO properties as well as their dependence on the first order hyperpolarizabilities of molecules. In this present investigation we report the growth and characterization of Benzaldehyde 4- nitro Phenyl hydrazone (BPH) crystals.

Synthesis, Solubility and Crystal Growth of BPH: A mixture of 0.5 g of p-nitrophenylhydrazine, 0.5g of the aldehyde, 10-15 ml of ethanol and 2 drops of glacial acetic acid was refluxed for 10 minutes. The clear solution was cooled and p-nitrophenylhydrazone was filtered off. The reaction scheme is shown in Fig.1. The synthesized BPH was purified by repeated crystallization process before growth. The recrystallization was carried out in order to improve the optical quality as well as the size of the growing crystals.

The solubility of BPH in acetone was estimated as a function of temperature in the range 30-55°C. A thermostatically controlled vessel (100 mL) was filled with the solution of BPH with some undissolved BPH and stirred for 24 hour. On the next day, a small amount of the solution was pipetted out, and the concentration of the solute was determined gravimetrically. Fig. 2 shows the solubility curve for BPH. The title compound exhibits good solubility and a positive solubility temperature gradient (direct solubility) in the acetone.

The solution of recrystallized BPH was prepared at 35ºC using acetone as the solvent. The beaker containing the solution was covered at the top to prevent the evaporation of the solvent. The solution was housed in a constant temperature bath (+ 0.10C) and continuously stirred using Teflon coated magnetic stirrer. When the solution was subjected to slow cooling (0.5ºC/day), the temperature was achieved (320C) to initiate nucleation and the temperature has been thereafter reduced at a rate of 0.150C/day. The crystals were harvested after 10 days (Fig.3).
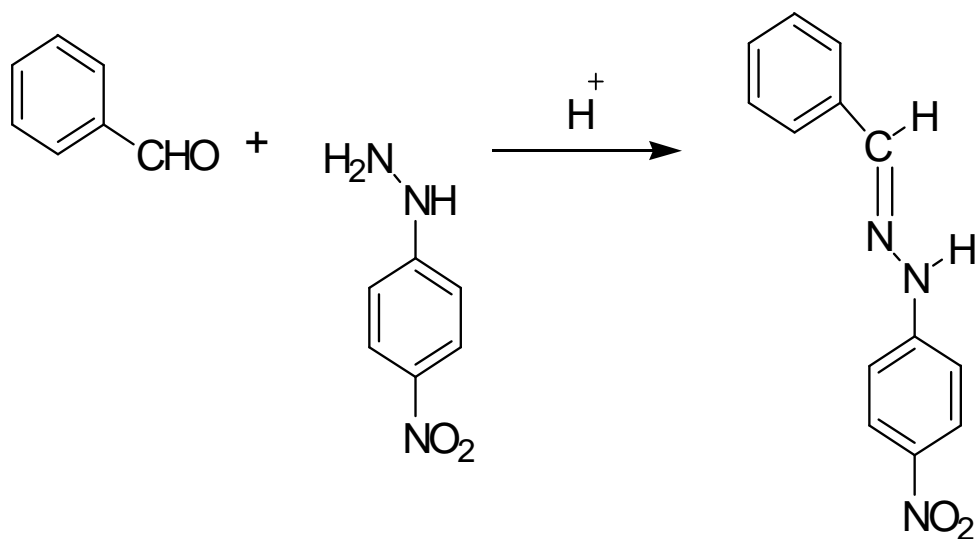
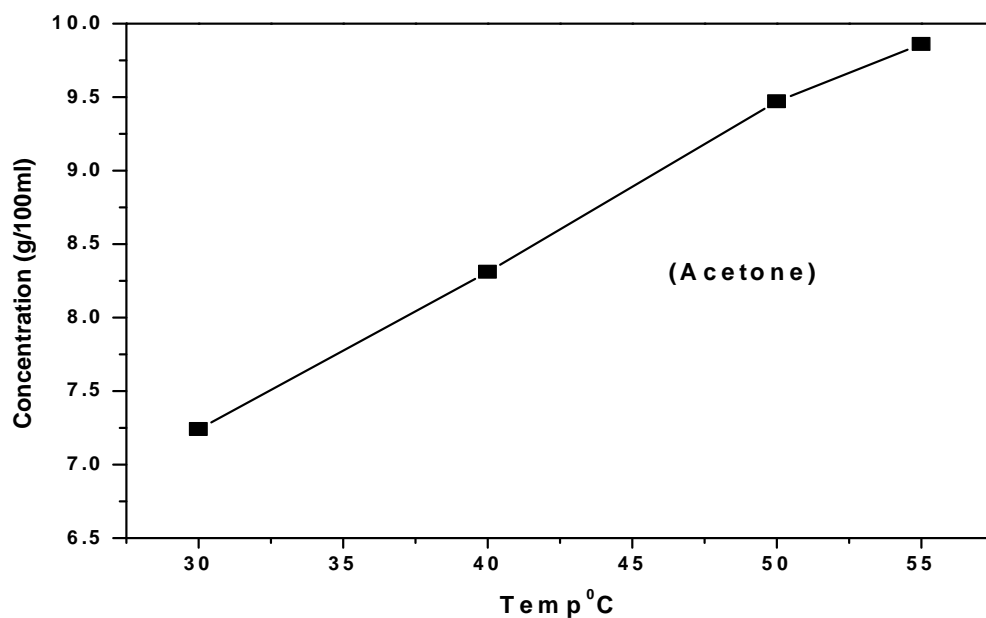Fig.1 shows the schematic diagram of BPH

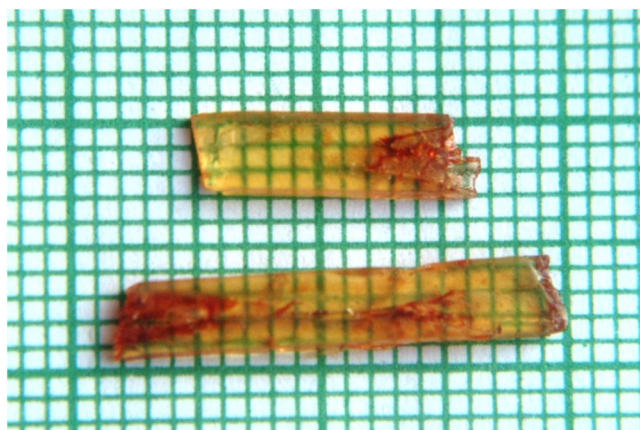Fig.2 Shows the Solubility diagram of BPH

Fig.3. Shows the grown crystals of BPH

Result and Discussion:

X-Ray Diffraction Studies: The structural properties of single crystals of BPH have been studied by Powder X-ray diffraction technique. The indexed X-ray diffraction pattern is shown in Fig.4. The lattice parameters were evaluated by using Powder X software. The evaluated lattice parameter are a=6.102 Å, b = 23.291 Å, c = 8.512 Å. The obtained values are in good agreement with the reported values (Brian Vickery and Willey 1985). The obtained and reported values of lattice parameters are stacked in Table1for the ease o f comparison.
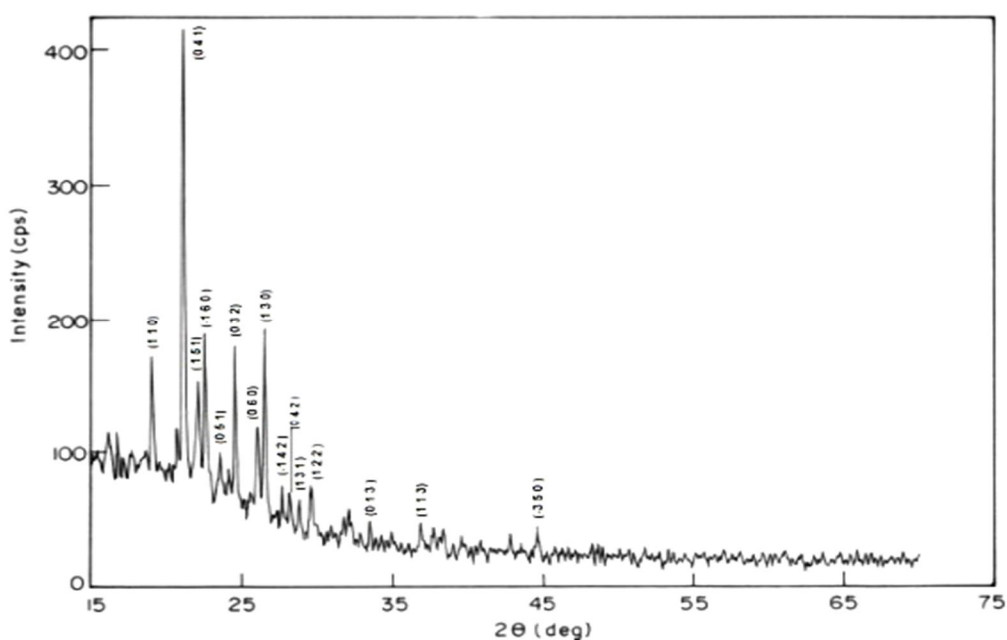

Fig.4 shows the Powder X-ray pattern of BPH

Table 1 Comparison of unit cell parameters of BPH						
a (Å)	b (Å)	c (Å)	α	β	γ	Volume Å³
6.049	23.320	8.506	90.0º	96.8 º	90.0º	1191.4
6.091	23.291	8.512	90.0º	96.4 º	90.0º	1207.5

Vibrational Studies OF BPH: The Fourier transform mid infrared spectrum was recorded using Perkin Elmer Spectrum RX1 spectrophotometer. the FTIR spectrum of BPH shown in Fig.5.
The FT Raman spectrum was recorded on a BRUKER IFS 66V model interferometer equipped with an FRA-106 FT Raman accessory. The experimental spectrum is shown in Fig. 6.

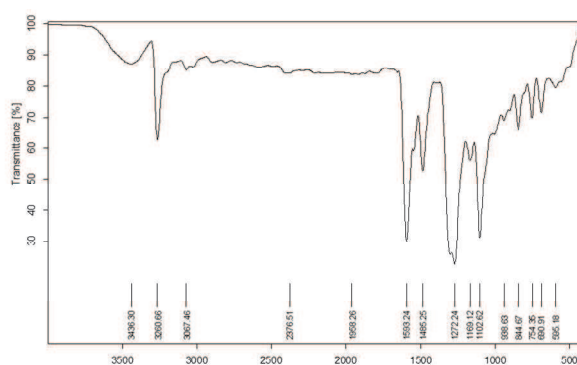Fig. 5. Shows the FTIR spectrum of BPH
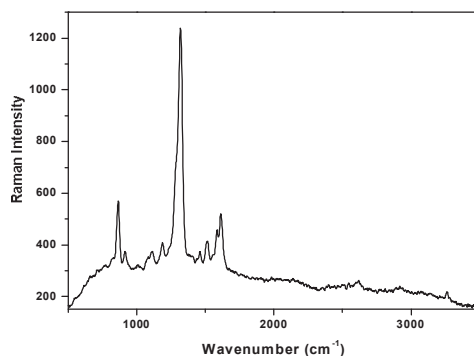
Wavenumber cm $^{-1}$

Fig.6. shows the FT Raman spectrum of BPH

Table 2. Observed IR and Raman bands of Benzaldehyde 4-nitro phenylhydrazone		
FTIR wavenumber (cm^{-1})	FT Raman wavenumber (cm^{-1})	Assignments
3436		υas(N-H)
3260		υas(N-H)
3067		υs(N-H)
2376		υ(C-H)
1958		υ(C-H)
	1612	δ(N-H)
1596		υ(C-C)
	1517	υas(NO2), υ(C-C)
1486	1457	ρ(N-H)
	1318	υs(NO2)
1271		δ(C-H)
1168	1184	υas(C-NO2)
1101	1114	φ ring
938	911	υ(C-C)
845	863	δ(C-H)
754		ω(NO2)
690		δring
595		τ(N-H)
υas- asymmetric stretching; υs-symmetric stretching; ρ - rocking; τ- torsion; ω- wagging; δ - deformation, φ -scissoring.		

The BPH crystallizes in the orthorhombic system, with Cc space group. As there are 29 atoms in the unit cell (Z=4), there are 348 branches to phonon dispersion curves. The representation of Γtotal of all vibrations can be decomposed according to the irreducible representation of the point group as Γ-total⊡=173A′+ 172 A″ apart from three acoustic modes (Γacou ⊡= A′ + 2 A″) are included that correspond to the block transitions of the crystal. The formal classification of fundamental mode predicts 324 internal vibrations which can be distributed as (162A′+ 162 A″) and 24 external modes such as (6A′+6A″) translational, (6A′+6A″) vibrational modes. The results of factor group analysis are presented in Table 3.

Table 3 Factor group analysis-Summary

Factor group species Cs		Benzaldehyde 4-nitro phenylhydrazone Cl site		C Cl site	H Cl site	N Cl site	O Cl site	Optical modes	Acoustic modes	Activity	
Internal modes		External modes		Benzaldehyde 4 nitro phenylhydrazone Cl site						IR	Raman
A′	162	6T, 6R		78	66	18	12	174	01	Tx, Ty	$\alpha xx, \alpha yy, \alpha zz, \alpha xy$
A″	162	6T, 6R		78	66	18	12	174	02	Tz	$\alpha yz, \alpha xz$
Total modes	324	12T, 12R		156	132	36	24	348	03		

The hydrogen bonding networks seem to tailor the molecular dipoles of the ionic species in similar direction. The presence of the hydrogen bond besides the columbic interactions between the ionic species helps in building up stable structures and is also one of the favorable factors to have high melting point and to grow single crystals with relative ease. The importance of hyperconjugative interaction and electron density transfer from lone electron pairs of the Y atom to the X-H anti-bonding orbital in the X-H...Y system have been analyzed. The intermolecular N-H...O hydrogen bonding is formed due to the overlap between n(O) and σ*(N-H) which results in intermolecular charge transfer causing stabilization of H-bonded systems. Thus the broad bands with complicated structures in thi region 3400–3000 cm⁻¹ corresponds to X-H stretching vibrations.

Generally N-H and O-H bands participate in hydrogen bonding, hence their stretching vibrations should be shifted to low wave number side and also they are asymmetric (νas). The symmetric stretching (νs) has no degeneracy. But the asymmetric stretching is doubly degenerate. This may be attributed to the lowering of symmetry in the crystal environment C₁ than that of the free ion. Because of this lowering of symmetry, the degeneracy of the asymmetric stretching is raised and so one can observe two bands corresponding to νasNH vibrations. Hydrogen bond vibration is clearly seen in IR than in Raman spectra. In IR, the band corresponding to this mode is observed at 3436 and 3261 cm⁻¹. Further in the present investigation, this N-H stretching wave number is red shifted in IR, which indicates the weakening of the N-H bond resulting in proton transfer to the neighboring hydrogen. The nature and the strength of the intermolecular hydrogen bonding can be determined by knowing the changes of electron densities (ED) in the vicinity of N-H... hydrogen bonds, which lead to the increase in ED of N-H anti bonding orbital. This causes concomitant red shift in N-H stretching wave number(Alabugin et al 2003). An interesting feature of these vibrations is that, through these intermolecular interactions charge transfer can take place inside the crystal. This mechanism enhances the hyperpolarizability value which in turn responsible for the propensity of the crystal to be NLO active.

The bands observed in the region 2900–3100 cm⁻¹ are assigned to the C-H stretching vibrations. In the present molecule the aromatic rings are asymmetrically disubstituted benzene derivatives. The bands corresponding at strong band 1596 cm⁻¹ in IR and around very weak bands 1517 cm⁻¹ in Raman are attributed to the Kekule C-C stretching mode. These

vibrations are expected to interact with C-H in plane bending hydrogen and its carbon moving oppositely but the substituents are nearly motionless (Spire et al 2000). The observed IR and Raman bands and their assignments are stacked in Table 2.

The region (1800-300 cm^{-1}) includes the stretching vibrations of amino groups and the bending vibrations of amino and methylene groups. The detailed vibrational assignments presented in Table 2 for various modes are self-explanatory. Since mixing of several groups is possible in this region it will be very difficult to distinguish the vibrations arising from various individual groups like C–C, deformation modes of N-H, C–H etc., and also functional group frequency correlation method will not work out for the accurate assignment of bands.

UV-VIS-NIR studies: When absorption is monitored from longer wavelength to shorter wavelength, the enhanced absorption is observed between 1500-2000 nm (Fig.7). The absorption in this region is due to overtones of some fundamental vibrations of nitro group. There is low absorption at the fundamental wavelength (1064 nm) of the Nd:YAG laser which contributes to its resistance to laser induced damage. Further there is very little absorption at the wavelength of 532 nm, which can improve the second harmonic throughput. Due to the weak inductive effects, the nitro group exerts a small shift in the absorption edge of BHP around 380 nm which recommends this as a better material for the fabrication of lased based spectral instruments and also good enough for the generation of higher harmonic light using IR lasers through NLO phenomena. Some absorption bands in the UV – visible region may be attributed to the colored centers within the forbidden gap of the material. It could pose some limits to the power handling capacity of this material.

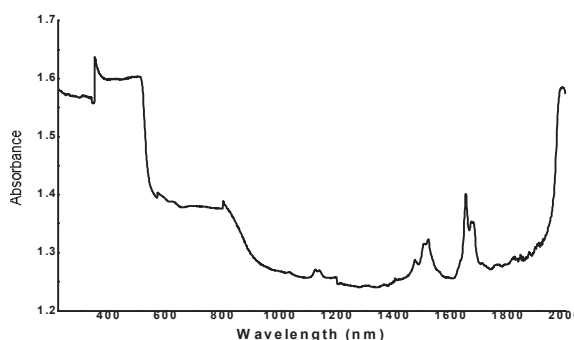Kurtz and Perry Powder Technique for SHG measurement:

Fig.7.Shows the UV-Vis-NIR Spectrum of BPH

The Table 4 shows the comparison of SHG signal energy output for the title compound BPH with that of standard KDP and Urea. The high efficiency of BPH crystal is higher than KDP and Urea counterparts.

Table 4 Comparison of SHG signal energy output			
Input power mJ/ pulse	KDP mV	Urea mV	BPH mV
1.9	9.0	----	162
3.0	---	100	213

Conclusion: A good optical quality crystal of BPH was obtained by slow evaporation solution growth method. The structural analysis of BPH was confirmed by powder x-ray diffraction analysis. The vibrational functional group of BPH was investigated and confirmed by FT-IR, FT-Raman and factor group analysis. In the transmittance spectra of BPH crystal has wide range transparency from visible to IR region. The SHG effect of BPH is higher than urea.

References:

1. D. A. Kleinman, "Nonlinear dielectric polarization in optical media," Phys. Rev. vol.126, pp.1977–1979, 1962.

2. L. Padmaja, T. Vijayakumar, I. Hubert Joe, C. P. Reghunadhan Nair and V. S. Jayakumar" Vibrational spectral studies and the non-linear optical properties of a novel NLO material L-prolinium Tartrate" J. Raman Spectrosc. vol. 37, pp.1427–1441, 2006

3. D.S.Chemla and J. Zyss, "Non-linear Optical Properties of Organic Molecules", Academic Press, Newyork, vol 1, 1987

4. A.A. Sukhorukov and Yu.S. Kivshar, "Nonlinear guided waves and spatial solitons in a periodic layered medium", J. Opt. Soc. Am. B, vol. 19, pp. 772-781, 2002.

5. G. Maroulis, "Static hyperpolarizability of the water dimer and the interaction hyperpolarizability of two water molecules", J. Chem. Phys. vol. 113, pp. 1813-1820, May2000

6. G. Maroulis, "Electric multipole moment, dipole and quadrupole(hyper)polarizability derivatives for HF ($X^1\Sigma^1$)" J. Mol. Struct. (Theochem). vol. 633, pp 177-197, 2003.

7. A.Schoonveld,.Wildeman, D.Fichou, P.A.Bobbert, B.J.Van Wees and T.M.Klapwijk, Nature, vol. 404, pp. 977, 2000.

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