

Preparation and electro-optic properties of 1-formyl 2(4-nitrophenyl) hydrazine

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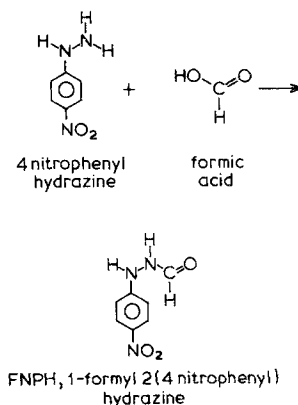
The chemical preparation and crystal growth of 1-formyl 2(4-nitrophenyl) hydrazine are described. Its refractive indices, optical absorption coefficients and electro-optic half-wave voltages at zero and 1 MHz frequencies are reported. The method used for the determination of the half-wave voltage at 1 MHz was extremely sensitive, and could provide a useful test for optical non-linearity in small crystals.

1. Introduction

Several authors have recently reported the occurrence of anomalously high non-linear optical susceptibilities in organic molecular crystals [1-3]. One such material, *m*NA, has been evaluated in terms of its second harmonic generation coefficients and its electro-optic coefficients [4] and its device potential as a filled fibre electro-optic modulator has been demonstrated [5]. A previous paper [6] reports the discovery of strong second harmonic generation in 1-formyl 2(4-nitrophenyl) hydrazine (FNPH) and results are here reported from a more detailed investigation of its optical and electro-optical properties.

2. Preparation and crystal growth

FNPH was prepared by synthesis from 4-nitrophenyl hydrazine (1 mole) and an excess of formic acid (2 mole). The reactants were mixed then heated with an equal volume of ethyl alcohol until the mixture suddenly began to solidify. At this point more alcohol was added to disperse the orange crystals forming in the liquid. The crystals were filtered off and recrystallized from ethyl alcohol five times, using activated charcoal to absorb impurities, until pale yellow crystals, m.p. 183°C, were finally obtained. The reaction can be described as:



From an analysis of its infra-red spectrum and by reference to the chemical literature [7] the compound was identified as having the above structural formula.

The solubility of FNPH in methanol is shown in Fig. 1. 500 ml of a solution saturated at 45°C was placed in a thermostatic silicone oil bath. Six seeds were mounted with silicone rubber onto radial limbs of a glass stirring rod and the vessel was thereafter flushed with nitrogen saturated with methanol at the bath temperature. By lowering the temperature of the bath through 10°C at a rate of 0.2°C per day initially, then 0.4°C and 1°C per day, as the crystal surface area increased, the seeds were

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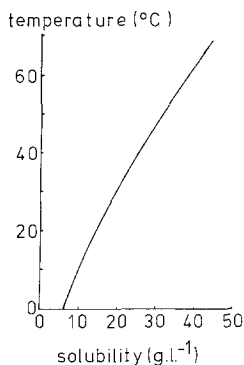


Figure 1 Solubility curve of FNPH in methanol.

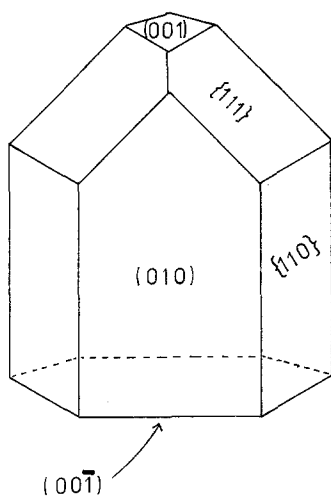


Figure 2 Typical habit of solution grown FNPH crystal.

grown into large (10 mm × 18 × 7 mm) crystals of the habit drawn in Fig. 2.

X-ray Weissenberg photographs on small crystals gave the following data: space group $Pca2_1$ $a = 10.3 \text{ \AA}$, $b = 9.5 \text{ \AA}$, $c = 8.0 \text{ \AA}$. Goniometric measurements of interfacial angles were in good agreement

with values calculated from the X-ray data with the above indexing.

The $\langle 001 \rangle$ axis showed an unusually high degree of asymmetry during growth: the (001) face was fast growing, its area being limited by the slower (111) facets; however, the $(00\bar{1})$ face was slow growing and left behind it a trail of inclusions as shown in Fig. 3. $(11\bar{1})$ faces were absent.

3. Optical properties

3.1. Absorption spectrum

A 10 mg l^{-1} solution of FNPH in ethanol showed three bands as follows; $0.205 \mu\text{m}$, $E_{\text{max}} = 0.8 \times 10^{-4}$; $0.225 \mu\text{m}$, $E_{\text{max}} = 1.0 \times 10^{-4}$; $0.347 \mu\text{m}$, $E_{\text{max}} = 1.6 \times 10^{-4}$. When viewed under a polarizing microscope single crystals showed the deep yellow colour characteristic of the $0.347 \mu\text{m}$ band only in y -axis polarized light.

3.2. Refractive indices

Since the optical system of point group $mm2$ is biaxial, three principal refractive indices are to be found. The method of immersion was used here, and two of the principal refractive indices were matched to mixtures of 2-bromonaphthalene and bromobenzene by the Becke line method [8]. The third index was higher than any suitable immersion liquid but was found indirectly from measurements of the non-principal refractive indices exhibited by crystals tilted with respect to the microscope axis. For example, if the crystal had its (010) face perpendicular to the microscope axis, and the polarizer was set parallel to $[001]$, disappearance of the Becke line occurred when the medium had a refractive index equal to n_z . Now, if the crystal was tilted through an angle θ about its $[100]$ axis, the Becke line disappeared when

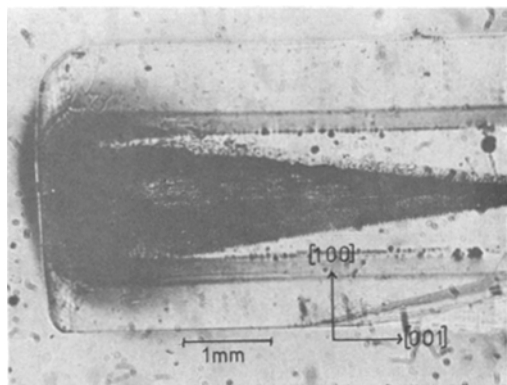


Figure 3 FNPH crystal showing an inclusion trail formed during growth along $[00\bar{1}]$ direction.

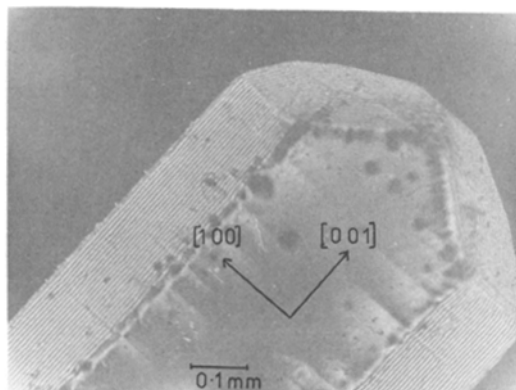


Figure 4 Birefringence fringes shown in the polarizing microscope.

TABLE I

Polarizer orientation	Beam direction	Half-wave voltage	Mode
45° to [0 1 0]	[1 0 0]	$\lambda(n_y^3 r_{23} - n_z^3 r_{33})^{-1}$	transverse
45° to [0 0 1]	[0 1 0]	$\lambda(n_x^3 r_{13} - n_z^3 r_{33})^{-1}$	transverse
45° to [1 0 0]	[0 0 1]	$\lambda(n_x^3 r_{13} - n_y^3 r_{23})^{-1}$	longitudinal

the refractive of the medium was $n\beta$, where,

$$n\beta^2 = n_z^2 \cos^2 \theta + n_y^2 \sin^2 \theta.$$

The principal indices were thus found to be:

$$n_x = 1.64, n_y = 1.9, n_z = 1.59 \quad \text{at } \lambda = 589.3 \mu\text{m}$$

(x , y and z indicate light polarized in [100], [010] and [001] respectively).

Fig. 4 shows the appearance of the crystal with its [010] axis upward and the polarizer and analyser crossed at 45° to [100]. The fringes on the {110} and {111} faces were due to the variation of optical retardation with crystal thickness. The optical retardation in the (010) plane may be defined as

$$\Gamma = \frac{2\pi l(n_x - n_z)}{\lambda_0}$$

where l = crystal thickness, λ_0 = observation wavelength. Polarized light enters the crystal and is resolved into components along (100) and (001) which emerge with a phase difference of Γ . Therefore, the emergent light is absorbed by the analyser when $\Gamma = 2n\pi$ and transmitted when $\Gamma = (2n + 1)\pi$. A geometrical analysis shown in Fig. 5 easily shows that the separation of the fringes is given by:

$$d = \frac{\lambda_0}{2(n_x - n_z) \tan \theta}.$$

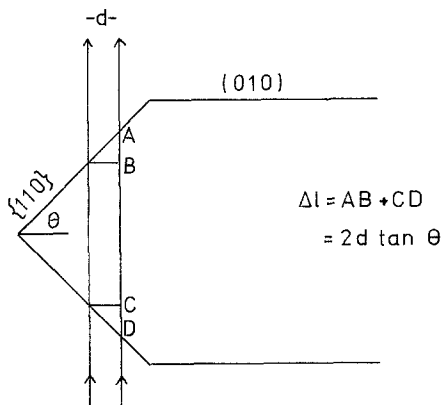


Figure 5 Geometrical diagram showing fringe spacing, d .

Thus an accurate value of $(n_x - n_z)$ was obtained:

$$n_x - n_z = 0.059.$$

4. Electro-optic half-wave voltages

The electro-optic tensor of FNPH can be represented by the orthogonalized matrix,

$$\begin{bmatrix} \cdot & \cdot & r_{13} \\ \cdot & \cdot & r_{23} \\ \cdot & \cdot & r_{33} \\ \cdot & r_{42} & \cdot \\ r_{51} & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix}$$

where

$$r = \frac{d}{dE} \left(\frac{1}{n^2} \right)$$

where E is the field.

To investigate the "diagonal" components r_{13} , r_{23} and r_{33} the field is applied along [001] and the electro-optic amplitude modulation of two of the propagation modes shown in Table I are measured. (Only two independent relations between the three coefficients may be gained by the amplitude modulation technique.)

The two transverse mode orientations were used here. A single crystal of FNPH was cut into a 2 mm plate by a wet string cutter using methanol as the solvent. The (001) and (00 $\bar{1}$) faces were coated with silver paste then {010} and {100} faces of fair optical quality were conveniently formed by mechanical cleavage. For each propagation mode, the modulation of the He:Ne laser was measured by a standard technique at zero frequency. Measurements of the modulation by a 1 MHz signal were made using a KD*P modulator in optical series with the crystal. A PIN diode detector was used and connected to a 1 MHz tuned low noise amplifier and the output was displayed on a C.R.O. A strong signal was observed on optimizing the optical bias by adjusting

TABLE II Half-wave voltages (kV)

	Zero Hz	1 MHz
$\lambda(n_y^3 r_{23} - n_z^3 r_{33})$	+ 16	± 12
$\lambda(n_x^3 r_{13} - n_z^3 r_{33})$	+ 30	± 12

(The sign of the d.c. half-wave voltage corresponds to (0 0 1) being electrically positive.)

a Babinet compensator placed in the laser beam. Half-wave voltages were found by comparison of the modulation indices shown when the field was applied to the FNPH and the KD*P respectively. Results are shown in Table II.

5. Discussion

A qualitative insight into the non-linear optical properties of crystals is given by the theory of the classical anharmonic oscillator [9]. The theory shows that second order non-linear optical effects arise if the transition controlling the optical properties is described as an electron in an asymmetric potential well. In the case of FNPH, the optical properties in the visible range are due to the band at 347 nm. Referring to an analysis of the 370 nm band in 4-nitroaniline [10] for which an electron transfer between the nitro group and the aromatic ring was held responsible, we may guess that a similar transition occurs in FNPH, its energy being increased due to the inductive effect of the carbonyl group. The FNPH molecule can then be represented by a one-dimensional oscillator as in Fig. 6.

The value of the non-linear susceptibility depends on the shape of the potential well, which is dictated by the crystal structure. The non-linear susceptibility should then be large given that:

(1) molecules in the crystal are packed with their dipole moments directed along [0 0 1], the only direction in which individual vector effects can reinforce each other;

(2) the electronic transition of Fig. 6 is also directed near to [0 0 1], so that the field vector

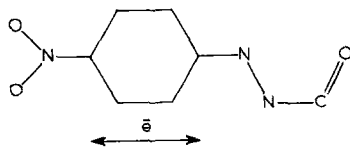


Figure 6 The FNPH molecule.

has a large component in the direction of the "oscillator".

The crystal growth and morphology showed a marked difference between the (0 0 1) and (0 0 $\bar{1}$) surfaces, i.e. a high degree of asymmetry of the [0 0 1] axis compatible with fulfillment of the first condition above. However, the dependence of the optical absorption and refractive index on polarization indicated that the transition was directed to [0 1 0]; therefore, the molecular packing in FNPH is not ideal with respect to the second condition.

Since the object of this work was to search for non-linear optical molecular crystals on a wide scale, the sensitivity of measurement of the electro-optic effect at high frequency deserves a further comment. Although up to 700 V peak to peak was applied in this work for reasons of accuracy, a response could be detected on application of only a few volts to the crystal. Therefore, we have a screening technique in addition to Kurtz and Perry's SHG test [11] which could be applied to small, imperfect crystals.

Acknowledgements

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