Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Crystal Growth and Characterization of *N*-(5-Nitro-2-pyridyl)-(s)-phenylalaninol: A New Organic Material for Nonlinear Optics

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Crystals of N-(5-nitro-2-pyridyl)-(s)-phenylalaninol having good optical quality were grown from solution. The crystal structure and the linear and nonlinear optical properties were determined. Angle tuned phase matching was achieved with a d_{eff} = 31 *pm/V* and a conversion efficiency of 0.15% was obtained at the fundamental power of 50 kW/cm^2 using a 0.45-mm-thick crystal.

Keywords: nonlinear optical material, crystal growth, molecular structure, crystal structure, second-order nonlinear optical susceptibility, phase-matching

1. INTRODUCTION

Nonlinear optical crystals may be used as efficient frequency doublers and ultrafast light modulators for applications in optical memory and optical communication. In recent years, interest in using organic crystals with charge correlated and highly delocalized π-electron states has increased considerably, since very large nonlinear optical susceptibilities have been measured in several materials.[1–3]

In this paper, several important properties of a new organic nonlinear optical material, *N*-(5-nitro-2-pyridyl)-(s)-phenylalaninol (NPPA) are reported, including those of crystal growth, crystal structure, linear and nonlinear optical coefficients. This work was motivated by encouraging early results on NPPA[4] which reported a second-harmonic efficiency 130 times larger than that of urea using the powder method.

2. X-RAY MOLECULAR AND CRYSTAL STRUCTURES

An X-ray structural analysis of NPPA was carried out on single crystals obtained from a methanol solution. X-ray intensities were collected on a four-circle diffractometer using M_o-K_α radiation. A total of 2194 reflections were used for the structure determination. The structure was solved by the direct method using the program Multan 78,[5] and was refined by the least-squares method. The residual index, R, was 0.056. The space group is the monoclinic, non-centrosymmetric $P2_1$; the crystallographic parameters are listed in Table I.

The molecular structure drawn by Ortep[6] is shown in Figure 1. The benzene ring bends itself over the pyridine ring to form a scorpion-like structure. Figure 2 illustrates a part of the crystal structure showing a hydrogen bonded molecular layer parallel to the (0 0 1) plane. Intermolecular hydrogen bonds, N—H . . . O(OH) (N . . . O = 3.095 Å) and O—H . . . O(NO2) (O . . . O = 2.881 Å), hold the molecules in the layer tightly. The 2_1 axes along the b axis (upward) produce layers successively, and thus form the whole structure. The intramolecular charge transfer

TABLE I

Conditions of structural analysis and crystallographic data. Z is the number of molecules in the unit cell.

Formula	$C_{14}H_{15}N_3O_3$ (M = 273.29)
Melting point	Tm = 110°C
Diffractometer	RIGAKU four-circle automatical diffractometer
Radiation	M_o K_α (λ = 0.71069Å)
Scan limit, 2θ	60°
Number of reflections	
measured	2194
used [$\|F_o\| > 3\sigma(F_o)$]	1820
Crystal system	monoclinic
Space group	$P2_1$ (Z = 2)
Unit cell dimensions	a = 9.937(2) Å
	b = 6.017(1) Å
	c = 11.766(2) Å
	β = 100.56(2)°
Cell volume	V = 691.6(2) Å^3
Density	Dx = 1.3124 g/cm^3
	DM = 1.294 g/cm^3
Residual index	R = 5.6%

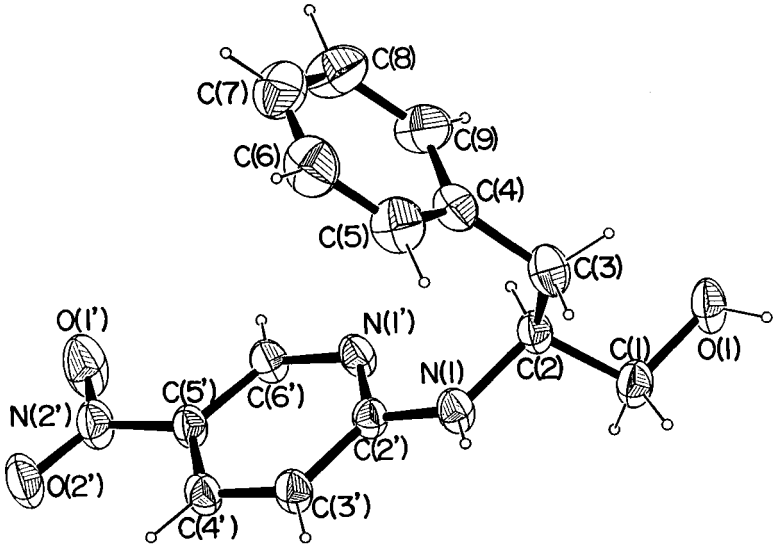


FIGURE 1 Molecular structure of NPPA. Thermal ellipsoids are scaled to include 30% probability except for the *H* atoms, which are represented by spheres of a fixed arbitrary radius.

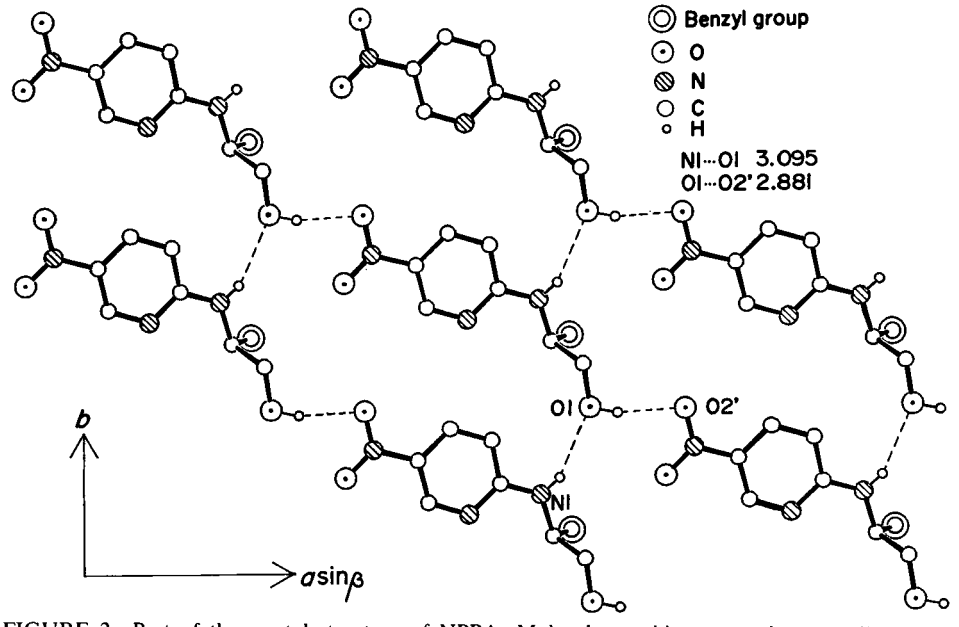


FIGURE 2 Part of the crystal structure of NPPA. Molecular packing on a plane parallel to the (0 0 1) plane is shown. The benzyl groups are represented by double circles at the CH_2 positions for clarity.

axis, taken as the line connecting $N(1)$ and $N(2')$, is at an angle of 74.9° with the polar 2_1 axis. This angle should be compared with that of 56.8° found in NPP.[7]

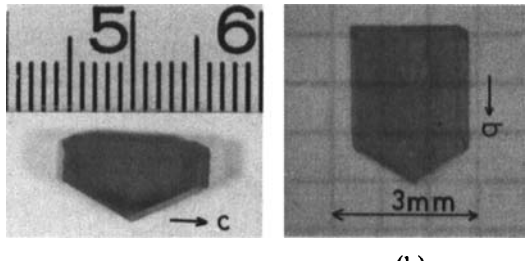
3. CRYSTAL GROWTH

The crude NPPA powder was purified by column-chromatography and recrystalization from several solvents. Seed crystals, which were thin pentagonal plates, were obtained from a methanol solution. Crystal growth was attempted by evaporation from a methanol solution. The temperature of the solution was maintained at 20 ± 0.05°C and the solvent was spontaneously evaporated at a rate of 1.4 ml/day. After 14 days, several good single crystals of good optical quality having dimensions as shown in Figure 3 were obtained.

4. OPTICAL PROPERTIES

The NPPA crystal was cleaved along a (0 0 1) plane (Figure 3 (b)), and the x and y dielectric axes were found to be in this plane from the conoscopic image. Figure 4 shows the optical transmission spectrum of a 0.34-mm-thick crystal for propagating along the c-axis. The cut-off wavelength was relatively short and was located around 0.48 μm.

Taking the $P2_1$ symmetry and the Kleinman's symmetry[8] into account, only four independent nonlinear optical coefficients, $d_{21} = d_{16}$, $d_{23} = d_{34}$, $d_{25} = d_{36} = d_{14}$, and d_{22}, remain. From the crystal structure, the magnitudes of the values of d_{ij} were considered to be $d_{21} > d_{22} > d_{23}$. The principal indices of refraction, n_x, n_y, and n_z, of which values were required to determine d_{21} and d_{22}, were measured by the Becke's line method[9] at a fundamental wavelength of 1.06 μm and at its second-harmonic wavelength. In the infrared region, the IR scope (Hamamatsu Photonix, C-2250) was used to see the boundary between the microcrystal and the immersion liquid. When the boundary disappeared, the refractive index of the crystal was determined to be equal to that of the immersion liquid. The results are indicated in Table II together with the nonlinear optical data.



a (b)

FIGURE 3 Photograph of NPPA crystals, (a) as grown, (b) cleaved along a (0 0 1) plane.

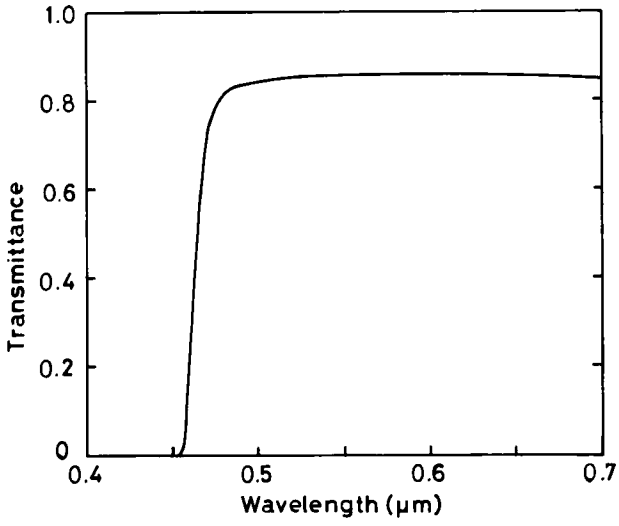


FIGURE 4 Optical transmission spectrum of a NPPA crystal (thickness: 0.34 mm).

The nonlinear optical coefficients, d_{21} and d_{22}, were measured using the Maker fringe method[10]. The light source was a Q-switched Nd: YAG laser operating at 1.06 μm (peak power $P(\omega) < 240$ kW, pulse duration $\tau = 25$ ns, repetition rate 10 Hz). The peak power incident on the crystal was 100 W: the beam waist $W_0 = 0.1$ mm (power density $I = 1.25$ MW/cm^2). A photomultiplier and gated integrator system detected the second-harmonic power and the coefficient, d_{33}, of lithium niobate was used as a reference. For the measurements, a crystal cleaved normally to the c-axis (thickness: 0.34 mm) was used.

TABLE II

Optical and nonlinear optical data of NPPA crystals

Refractive indices	n_x (1.06 μm) = 1.77 ± 0.02
	n_y (1.06 μm) = 1.68 ± 0.02
	n_y (0.53 μm) = 1.73 ± 0.01
	n_z (0.53 μm) = 1.55 ± 0.01
Nonlinear optical coefficients	d_{21} = 35 ± 15 pm/V
	d_{22} = 3.4 ± 1 pm/V
	d_{eff} = 31 ± 13 pm/V
Figure of merit for SHG	$\frac{d_{21}^2}{n^3} = 1.5 \times \frac{d_{33}^2\ (LiNbO_3)}{n^3}$

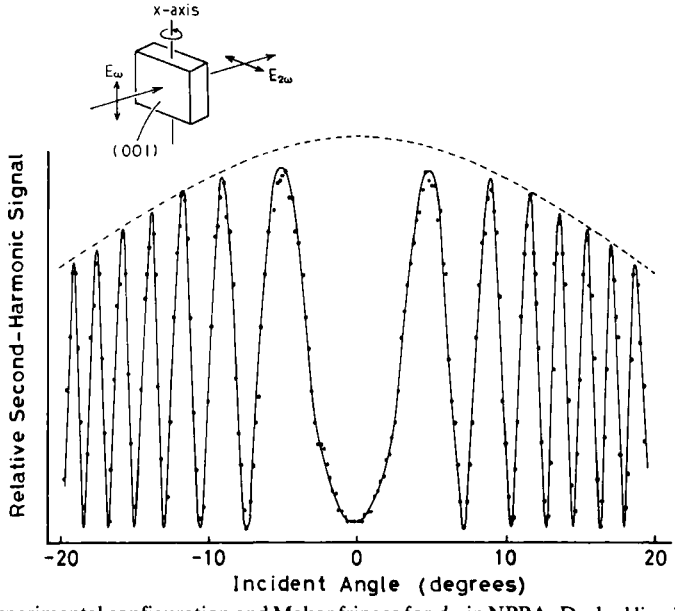


FIGURE 5 Experimental configuration and Maker fringes for d_{21} in NPPA. Dashed line is a theoretical envelope.

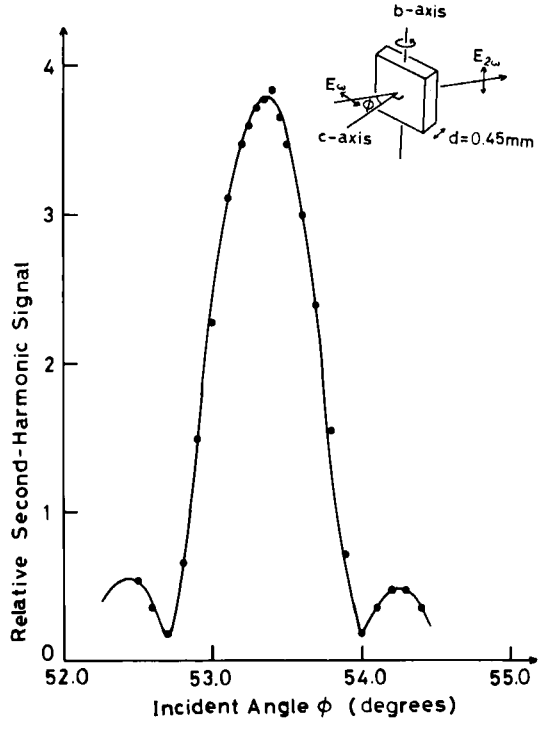


FIGURE 6 Measured SHG phase-matched signal for NPPA. Maximum second-harmonic power is observed at the incident angle of 53.35°.

The experimental configuration and Maker fringes for d_{21} are shown in Figure 5. The dashed line is the theoretical envelope in agreement with the experimental data. From the envelope, the nonlinear optical coefficients, $d_{21} = 35 \pm 15$ *pm/V* and $d_{22} = 3.4 \pm 1.0$ *pm/V*, were determined. Furthermore, the figure of merit, d^2/n^3, for the second-harmonic generation (SHG) is 1.5 times larger than that for d_{33} of lithium niobate.

Angle-tuned phase matching was obtained as shown in Figure 6. The maximum second-harmonic power was observed at the incident angle, $\phi = 53.35°$, and the conversion efficiency η was 0.15% at 50 kW/cm^2 with a beam waist $W_0 = 0.5$ mm using a 0.45-mm-thick crystal. Assuming n_z (1.06 μm) = 1.50 − 1.55, the effective nonlinear optical coefficient, d_{eff}, of 31 ± 13 *pm/V* was obtained. This value was comparable to that of DAN.[11]

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