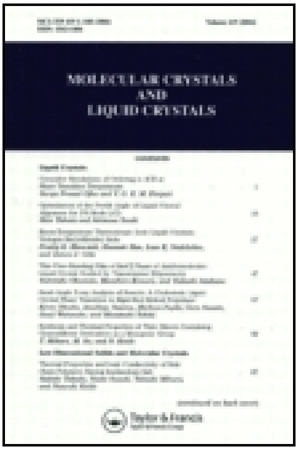

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Second Order Optical Non-Linearity and Phase Matching in 4-Nitro-4′- Methyl benzylidene Aniline (NMBA)

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Second Order Optical Non-Linearity and Phase Matching in 4-Nitro-4′-Methylbenzylidene Aniline (NMBA)

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Large single crystals (5 × 4 × 1 cm^3) of the noncentrosymmetric, monoclinic form of the organic crystal (NMBA) have been prepared by seeded growth from supersaturated solutions. Optically clear volumes permitted the preparation of polished specimens with faces parallel to the (100) and (010) directions. These were examined by the Maker fringe technique. The sections showed no dispersion of the dielectric axes with wavelength in the range 440–630 nm. The χ^2 elements d_{11} and d_{33} were found to be 4 and 143 respectively relative to quartz d_{11}.

Type II phase matching was observed using 1064 nm light at and near to normal incidence to the (100) plane with an efficiency of $\approx 10\%$ of that for a 2-(N,N-dimethylamino)-5-nitroacetanilide (DAN) crystal of the same thickness tested under identical conditions. Since the half angle between the molecular dipoles in the monoclinic NMBA crystal is 12°; a far from optimal angle for efficient phase matching, this lower efficiency was expected.

INTRODUCTION

The search for organic non-linear optical materials for use in optical devices has led to the prediction of potentially active molecular structures[1] and their synthesis and evaluation by powder techniques.[2] Semi-empirical rules have been developed relating the orientation of the molecular dipoles in the solid to its efficiency in phase matching.[3] Until now, there has been little opportunity to test these rules due to a lack of crystals of sufficient quality to permit comprehensive optical examinations. As part of a combined theoretical and experimental programme to assess and develop the properties of these solids, we have modified a wide range of well-proven techniques to extend their suitability to the preparation of highly polar organic crystals of ultra-high purity and low defect density.[4] The present paper describes preliminary results obtained on one material; 4-nitro-4′-methylbenzylidene aniline (NMBA).

NMBA crystallizes in two polymorphic forms.[5] One of these (triclinic P_1) is claimed to be stable at temperatures up to 338 K. This form is centrosymmetric and, consequently, exhibits no second order non-linear optical properties. The second form (monoclinic, space group Pc) is non-centrosymmetric and is stable to the melting point. Melting, re-freezing and cooling to room temperature gives this latter polymorph. It remains stable for at least 12 months without reverting to the triclinic form. The monoclinic form can also be recrystallized from solution at room temperature.

We have been unable to confirm reports that the triclinic form can also be prepared from solution in ethanol at room temperature.[5] Instead, we find that it can be generated only by rapid cooling of an undersaturated solution to temperatures below 273 K. When saturation is reached, the triclinic form precipitates. A detailed report on this phase behavior will appear later.[6]

In the monoclinic form, the molecules are planar and lie with the molecular dipoles 24° apart. It has been suggested that such molecular orientations should preclude efficient phase matching; the angle proposed for optimum performance being 54.74°.[3]

EXPERIMENTAL

NMBA (purity 98%) synthesized from 4-nitrobenzaldehyde and 4-amino-toluene was recrystallized three times from purified *n*-hexane and zone refined (120 passes of a 2 cm zone at 0.1 cm per hour) to reduce the impurity level to <150 ppm. Large single crystals grown from this material by a modified Bridgman technique were usually strained as a consequence of decomposition of the material in the melt and the subsequent incorporation of the resulting impurities in the crystal. Although this problem could be minimized by careful temperature control, growth from saturated toluene or ethyl acetate solutions yielded better quality crystals. The highest quality crystals obtained (see Figure 1) were grown from the latter solvent by the temperature lowering procedure at 0.1 K per day.[4] Specimens grew to typically $50 \times 30 \times 5$ mm^3 in a four week period.

Figure 2 shows, schematically, the typical growth morphology of the crystal. Although there is some doubt about the correct method of indexing this crystal, figure 2 defines unambiguously the orientation of the sections used to obtain the data discussed below.

In this indexing we have used the unit cell parameters; $a = 7.419$Å, $b = 11.679$Å, $c = 7.447$Å and $\beta = 110° \, 35'$.[6] The positions of the a and c axes in the crystal plane, (010) were carefully verified by Laue patterns of (100) and (001) sections.

OPTICAL CHARACTERIZATION

The monoclinic form of NMBA belongs to the point group m. The nonlinear polarization is of the form

$$P_x = d_{11} E_x^2 + d_{12} E_y^2 + d_{13} E_z^2 + 2d_{15} E_x E_z$$

$$P_y = 2d_{24} E_y E_z + 2d_{26} E_x E_y$$

$$P_z = d_{31} E_x^2 + d_{32} E_y^2 + d_{33} E_z^2 + 2d_{35} E_x E_z$$

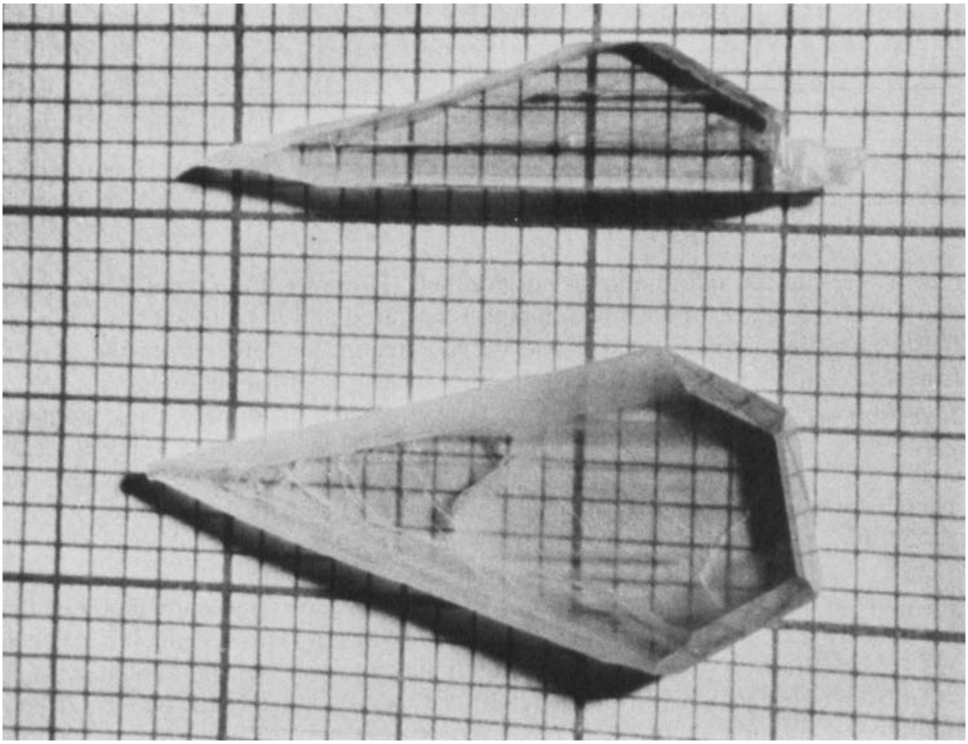

FIGURE 1 Crystals of NMBA.

Two samples were subjected to Maker fringe analysis in the equipment described previously.[2] These are indexed (010) and (100). Their positions in the original crystal are indicated in Figure 2.

All possible Maker fringes were collected from the (010) face; each input polarization being analyzed in both possible output polarizations. A full analysis of all the Maker fringe sets requires the refractive index tensors at 1064 nm and 532

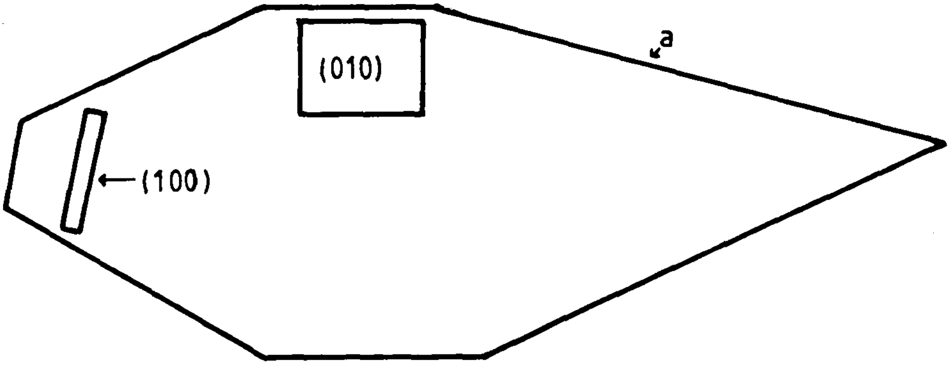

FIGURE 2 Typical growth morphology of monoclinic NMBA. The region where the (100) and (010) faced crystals were cut is indicated. The crystal edge marked 'a' is always rough and is helpful in orienting the crystal.

TABLE I

d_{11} and d_{33} for NMBA

	$n_{532\text{ nm}}$	$I_{532\text{ nm}}$	d_{ij}	l_c (μm)
d_{11}	1.86	80.5	4	1.7
d_{33}	1.735	2.1	143	7.6

nm. At present this information is not available. However, for d_{ij} where $i = j$ only one refractive index for each wavelength is required and it is possible to estimate these by setting a value for one and then evaluating the other from the Maker fringe separation. In NMBA there are two such d_{ij} coefficients (d_{11} and d_{33}). A value $n_{1064\text{nm}} = 1.7$ was chosen, being typical of such materials.[7] Table I shows the results. The relative second harmonic intensity ($I_{532\text{nm}}$) is given to allow recalculation of the d_{ij} values should an improved value of the refractive index become available. Coherence lengths (l_c) are also shown, together with the refractive indices at 532 nm, based on the above $n_{1064\text{ nm}}$. The d_{ij} values are ratioed against d_{11} of quartz.

No dispersion (±2%) of the dielectric axes was observed by examination under the polarizing microscope between 440 nm and 630 nm. The Z dielectric axis lies at 18° from the c crystallographic axis in an anticlockwise direction about b.

The Maker fringe signals from the (100) slice are dominated by the phase matched output. For rotation about the b axis, a single peak appears at normal incidence. Figure 3 shows this signal fitted to the theoretical function for the peak shape $\sin^2(\phi)/\phi^2$. The width of the curve is 0.8° (FWHM) demonstrating the high optical quality of the crystals. Two peaks are observed on rotation about the c axis ($-8°$ and $+4°$) but these are considerably less intense than the single peak observed for the b axis rotation. All phase-matching is type II. For rotation about the b axis,

$$e_{1064\text{ nm}} + o_{1064\text{ nm}} = o_{532\text{ nm}}.$$

However, for the c axis,

$$e_{1064\text{ nm}} + o_{1064\text{ nm}} = e_{532\text{ nm}}.$$

Assessment of the efficiency of the phase matched signal in this material was made by comparison with the main phase matched signal in DAN, which is presently considered to be a potentially outstanding non-linear material.[8] For the b axis rotation of NMBA the ratio of signals for NMBA:DAN was 1:10 for similar sample thicknesses and using identical experimental conditions. Further investigation on the phase matching locus may reveal more efficient phase matching directions for NMBA. This will be investigated by calculation when the refractive index tensor and full SHG matrix have been determined. Zyss has indicated that the ideal molecular alignment for efficient phase matching is when the half angle between the molecular charge transfer axes is 54.74.[3] In NMBA, this angle is 12° and therefore less efficient phase matching would be expected.

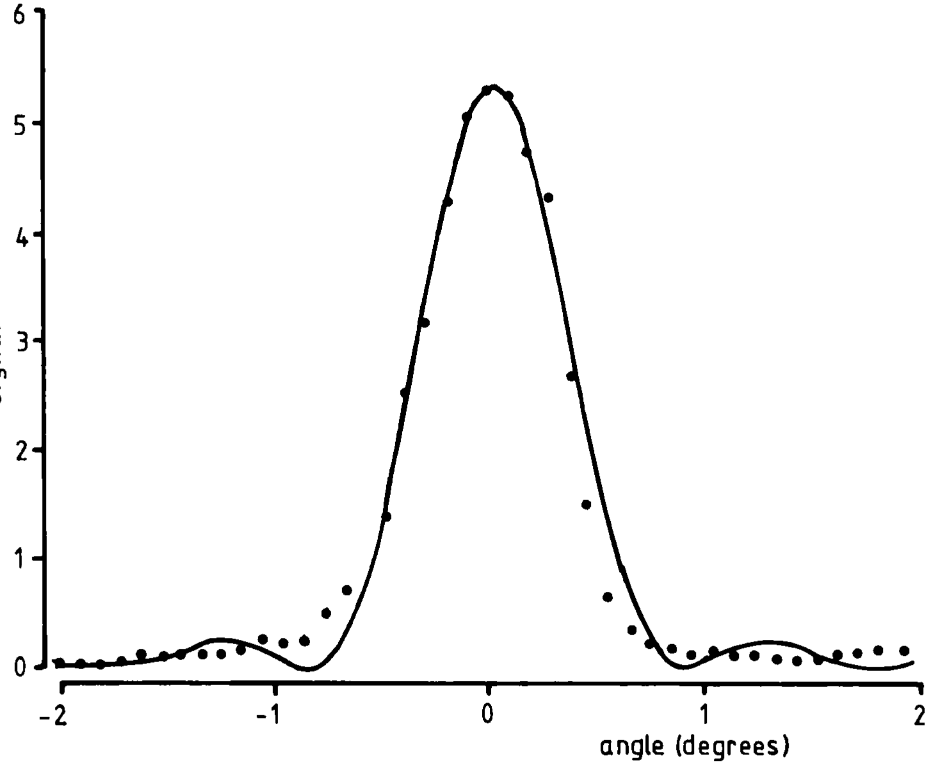

FIGURE 3 Phase matched signal for NMBA. The signal is in arbitrary units. Experimental points are indicated by the filled circles. The continuous line indicates the theoretical shape of the peak.

A fuller evaluation of the structural effects in operation in NMBA together with the current identification of the relationship between the piezoelectric and dielectric axes and the values of the $\chi^{(2)}$ elements d_{24} and/or d_{15} will be reported in due course.

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