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THE LINEAR ELECTRO-OPTIC EFFECT IN 4-NITRO-4'METHYL BENZYLIDENE ANILINE (NMBA) SINGLE CRYSTALS

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Abstract An assessment has been made of the linear electro-optic effect in single crystals of NMBA. Half-wave voltages of 1.1-2.8 kV have been determined in the spectral range 488-632.8 nm. Such low values are appropriate in a material which shows well aligned molecular dipoles in the crystalline state and define its potential for use as a modulator material.

INTRODUCTION

The observation that some acentric organic crystals show strongly non-linear optical behaviour has led to extensive experimental and theoretical studies of these materials.[1] One outcome of these examinations has been the realisation that the strength of the desirable properties is dependent on the relative orientation of the molecular dipoles in the crystal lattice.[2] Thus the linear electro-optic (Pockels) effect becomes strongest when the molecules are aligned so that they produce the maximum effect in one direction, in which the field inducing the effect can be applied.

NMBA approaches this ideal characteristic (Figure 1). The half angle between the molecular axes is about 18° and it is known from SHG experiments that there is a large second-order effect along the median axis.[3] We have tested the potential of this material as an efficient modulator by measuring the electro-optic effect along the polar axis and hence determining the half wave voltage and electro-optic coefficients in this direction at three wavelengths.

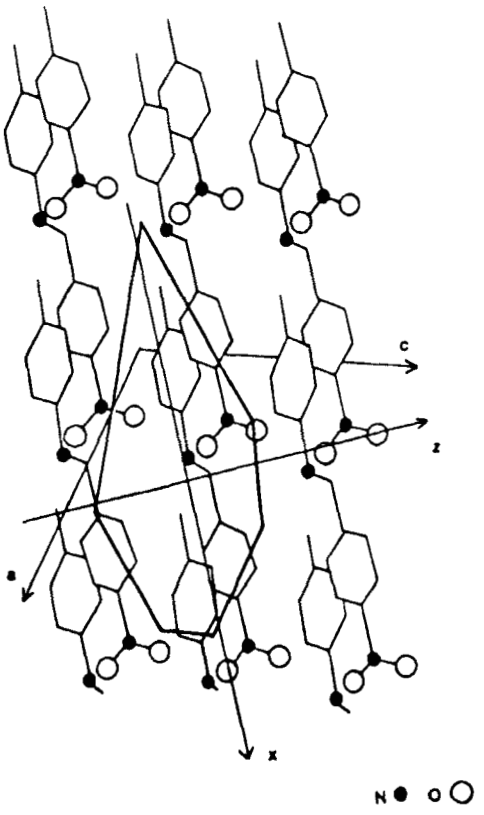

FIGURE 1 The relationship between the crystal morphology and the underlying crystal structure of NMBA. The positions of the dielectric axes are shown by x and z.

2. CRYSTAL PREPARATION

NMBA is reported to crystallise in two polymorphic forms; a centric form triclinic, space group P1, stable up to 338K and an acentric form, space group Pc stable from this temperature to the melting point (399K).[4] It was found impossible to obtain the centric form under a wide range of crystallization conditions. The acentric form could be prepared readily from the melt or by recrystallization from a wide range of solvents.[6] The monoclinic form has lattice parameters a = 7.445A; b = 11.675A; c = 7.852A with 2 molecules per unit cell.[5]

The growth of large crystals for orientation, cutting and polishing presented considerable problems. Attempts at growth from the melt yielded strained crystals of too low a quality for use. Growth from solution yielded small crystals, which in common with several other highly polar crystals, showed zero growth in some crystallographic directions. The result was that small seed crystals "capped out" until surrounded by these non-propagating faces without increasing significantly in volume. This problem was solved by developing long hair-like seeds (up to 10 cm long) prepared by evaporation of solutions in n-hexane and then growing these on as seeds from solutions of NMBA in ethyl acetate.[6] The final crystals were obtained in the form of rhombic tablets 7 x 5 x 0.5 cm^3 dimensions. The morphology of the crystal in relation to the crystal structure is shown in Figure 1.

3. SAMPLE PREPARATION

Following orientation by polarizing microscopy, goniometry and X-ray diffraction the crystals were cut on a solvent saw into rectangular specimens with two sets of opposite parallel faces for the electro-optic measurements.
One pair of faces of the rectangular specimen was cut, so that the normal was parallel to the polar axis of the system. The other pair of faces was cut to lie in the (010) plane. The two unpolished faces normal to the polar axis were electroded with silver epoxy and cured for 48 hours. The sample was then held under virtually zero stress between two brass electrodes mounted on a goniometer.

4. MEASUREMENTS

Measurements of the electro-optic effect were carried out with the crystal mounted between crossed polarizers using either a HeNe laser (λ = 632.8 nm) or a tunable argon-ion laser (λ = 514.8 nm and 488 nm) as light sources. The input light beam was directed along the b axis and was polarized at 45° to the x and z axes. A dc voltage was applied continually using a regulated power supply and the corresponding changes in intensity of the light transmitted through the analyzer were monitored using a photo multiplier

tube masked by a 25 μm pinhole and a narrow band pass interference filter. The half-wave voltages (V_π) were measured at the three wavelengths from the voltage differences between the adjacent maxima and minima.

During the experiments it was noted that variations in ambient temperature had a marked influence on the measurements. Care was therefore taken to maintain the temperature as constant as possible (±0.1K) during the procedure.

RESULTS

The half-wave voltage can be expressed by

$$V_\pi = \frac{\lambda}{r_{11} n_x^3 - r_{31} n_z^3}$$

Estimates of the relative values of the r_{31} and r_{11} components based on the orientation of the molecules and additivity of the molecular β values lead to the conclusion that the term in r_{11} will account for more than 90% of the value of the denominator in this equation. It can therefore be approximated by

$$V_\pi = (\lambda / r_{11} n_x^3)$$

Using values of the refractive index n_x determined by the prism method[7] gives the value of r_{11} recorded in Table 1.

TABLE 1

λ/nm*	n_x^7	V_π/kV	r_{11}/pm V^{-1}
632.8	2.078	2.8±0.2	25.2
514.5	2.216	1.3±0.1	36.4
488.0	2.283	1.1±0.1	37.2

* Absorption edge circa 460 nm

These values are closely similar to the best obtained with organic crystals. Their magnitude, plus the ease of preparation of good quality crystals and optical samples, makes NMBA a good candidate for development as an electro-optic (Pockels) modulator.

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