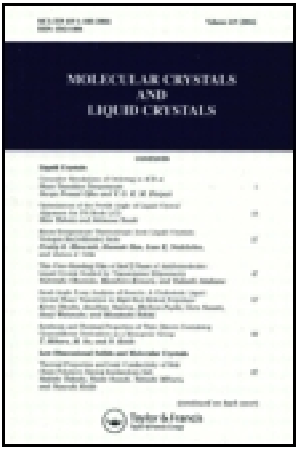

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Linear Optical Properties of the Organic Molecular Crystal (+)2-(δ-Methylbenzylamino)-5-Nitropyridine (MBA-NP)

R. T. Bailey [a] , G. Bourhill [a] , F. R. Cruickshank [a] , D. Pugh [a] , J. N. Sherwood [a] , G. S. Simpson [a] & S. Wilkie [a]

[a] Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 7XL, Scotland

Version of record first published: 24 Sep 2006.

To cite this article: R. T. Bailey , G. Bourhill , F. R. Cruickshank , D. Pugh , J. N. Sherwood , G. S. Simpson & S. Wilkie (1993): The Linear Optical Properties of the Organic Molecular Crystal (+)2-(δ-Methylbenzylamino)-5-Nitropyridine (MBA-NP), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 231:1, 223-229

To link to this article: http://dx.doi.org/10.1080/10587259308032508

Mol. Cryst. Liq. Cryst., 1993, Vol. 231, pp. 223–229
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

The Linear Optical Properties of the Organic Molecular Crystal (+)2-(α-Methylbenzylamino)-5-Nitropyridine (MBA-NP)

R. T. BAILEY, G. BOURHILL, F. R. CRUICKSHANK, D. PUGH, J. N. SHERWOOD, G. S. SIMPSON and S. WILKIE

Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

(Received September 22, 1992)

The linear optical properties of the organic molecular crystal (+)2-(α-methylbenzylamino)-5-nitropyridine (MBA-NP) are investigated. The specific rotation associated with this chiral molecule has been determined as +239.11°. The effective transparency range for nonlinear optical applications was found to be 465–1500 nm, with a 10 nm dichroism in the high frequency absorption edge position. MBA-NP displays angular dispersion to a larger extent than any other known organic nonlinear material, a 200 nm change in the wavelength of the incident light causing a 40° rotation of the dielectric axes. The linear refractive indices of MBA-NP have been determined using the minimum deviation technique, Maker fringe spacings and phase-matching directions. The principal refractive index dispersion curves are fitted with a Sellmeier equation and the coefficients of this equation are presented for the first time.

Keywords: linear optical properties, refractive index, organic crystal, nonlinear optics

INTRODUCTION

Materials with a large optical nonlinearity are of interest as frequency converters and modulators. They have a wide range of applications which include optical data storage, communications and optical computing systems.[1] Over the last few years, much interest has centered on conjugated organic molecules since they generally exhibit nonlinear optical properties which far surpass those of the commercially available inorganic materials.[2]

The organic material (+)2-(α-methylbenzylamino)-5-nitropyridine, MBA-NP, (Figure 1), was first reported as a potential nonlinear optical molecular crystal by Twieg and coworkers[3] when they were examining the powder second harmonic generation (SHG) efficiency[4] of various nitropyridine derivatives. They reported that fifteen different 5-nitropyridines derived from achiral amines were all inactive, whereas every chiral derivative exhibited nonlinear behaviour. Of this latter group, MBA-NP was the most outstanding material (SHG efficiency was 25 times a urea reference when using a fundamental wavelength of 1064 nm).

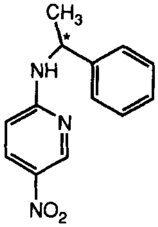

FIGURE 1 The molecular structure of MBA-NP.

Prior to characterizing a material's nonlinear properties, an intimate knowledge of the linear optical properties is required. To achieve this, single crystals of large size, from which oriented specimens can be cut, must be grown. MBA-NP single crystals of dimensions 5 × 3 × 2 cm^3 were grown in 12–18 days by temperature lowering a seeded supersaturated solution of methanol. A more detailed description of the growth process is reported elsewhere.[5]

One problem associated with the growth of organic nonlinear optical crystals is their tendency to crystallise in a centrosymmetric space group due to their large ground state dipole moments.[6] However, bulk crystals of MBA-NP did not crystallise in this undesirable (for three wave mixing processes) centrosymmetric manner since molecular crystals built from a single enantiomer of a chiral compound will necessarily exhibit a noncentrosymmetric structure. This strategy for achieving macroscopic noncentrosymmetry has also been used with the organic crystals NPP[7] and MAP.[8] The molecular structure of MBA-NP belongs to the monoclinic space group $P2_1$, point group 2, and has crystallographic parameters[9] $a = 0.5392$, $b = 0.6354$ and $c = 1.7924$ nm with $\beta = 94.6°$.

OPTICAL ACTIVITY

The optical activity of a single enantiomer of MBA-NP, purified to 99.98% by column chromatography, was measured. This involved making solutions of MBA-NP in ethanol, of various concentrations, and measuring the rotatory power of each solution in a standard polarimeter (Hilger & Watts Polarimeter Mark III), using a 2 dm path-length cell. The specific rotation[10] of an optically active material is given by

$$[\alpha]_D^{25} = \frac{\Delta\Theta}{cl} \tag{1}$$

where $[\alpha]_D^{25}$ is the specific rotation, $\Delta\Theta$ is the observed rotation in degrees, c is the concentration in g/ml and l is the cell length in dm. The gradient of a plot of $\Delta\Theta/l$ against concentration corresponds to $[\alpha]_D^{25}$ (Figure 2). The specific rotation of MBA-NP is +239.11°, where the '+' sign has the normal convention of representing a clockwise rotation of the plane of polarisation while looking towards the light source. The error associated with the measurement has been estimated as being ±1.2°.

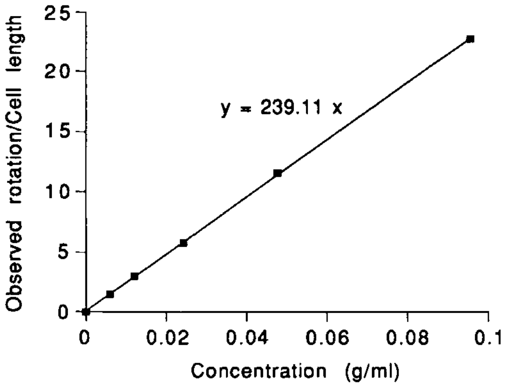

FIGURE 2 The specific rotation of MBA-NP. The squares represent experimentally measured points. The solid line is the best fit to these data.

ORTHOSCOPY

Orthoscopy consists of examining an optical blank of a material between the crossed polarisers of a microscope, with a parallel beam of light incident on the sample. It is used to determine the position of the principal dielectric axes. Monoclinic crystals necessarily have the *y* principal dielectric axis parallel to the *b* crystallographic axis. However, the *x* and *z* principal dielectric axes are not fixed by symmetry constraints and are free to lie anywhere in the crystallographic (010) plane. Since in this case the *x* and *z* dielectric axes are not determined by the crystal symmetry but by the physical properties of the molecules, they may have different orientations at different frequencies. This is known[11] as angular dispersion.

The crystallographic (010) plane was relatively easily obtained from a bulk crystal of MBA-NP as it is mutually orthogonal to both the (001) cleavage plane and the naturally occurring (100) facet.[12] The (010) plane was cut from a bulk crystal using a solvent saw and the orientation checked by X-ray Laue techniques. The sample was placed on the rotating stage of a polarising microscope. One of the edges of the sample was cut parallel to the crystallographic *a* axis and this axis was aligned parallel to the polarisation plane of the incident light. As the crystal was rotated it was found that there was no position for full extinction of the incident polychromatic light. In fact, as the crystal was rotated the analyser passed a different wavelength of light i.e. MBA-NP exhibited angular dispersion and the position of the *x* and *z* dielectric axes had therefore to be found as a function of wavelength. It is interesting to note that *N*-(4-nitro-2-pyridinyl)-phenylalaninol, which is structurally very similar to MBA-NP, also displays angular dispersion.[13]

Figure 3 shows the position of the *z* principal dielectric axis of MBA-NP relative to the *c* crystallographic axis as the wavelength of the incident light changes. It should be noted that the principal dielectric axis nearest the *c* crystallographic axis was labelled *z*, and that nearest the *a* crystallographic axis was *x*. This is in contrast to the normal convention[14] in which the principal dielectric axes are labelled according to their respective refractive index values such that $n_z > n_y > n_x$. It can be seen from Figure 3 that the *z* dielectric axis rotates almost 40° with a 200 nm

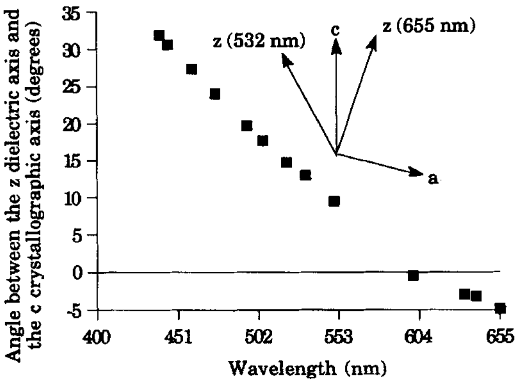

FIGURE 3 Angular dispersion of the z principal dielectric axis relative to the c crystallographic axis. The squares represent experimentally measured angles.

change in the incident light wavelength. This rotation is far larger than that reported for any other organic nonlinear molecular crystal. At approximately 600 nm, the z dielectric axis and the c crystallographic axis are coincident.

It has been calculated from X-ray data reported by Twieg and Dirk[9] that the projected charge transfer axis (from the nitro to amino group) in the (010) plane lies at 41.5° in an anti-clockwise direction from the c crystallographic axis while looking down the b crystallographic axis. Examination of Figure 3 reveals that as the frequency increases, the z principal dielectric axis rotates towards this projection of the molecular axis in the a-c plane. It has been proposed by Bailey *et al.*[15] that this behaviour would be anticipated on the grounds that the charge transfer transition is expected to make an increasing contribution to the polarisability as resonance is approached. At longer wavelengths however, the contribution of the nitro-amino dipole may be less significant and the dielectric axis will lie parallel to the average of all the molecular dipoles.

TRANSPARENCY

The spectrum of a 5×10^{-4} molar solution of MBA-NP in ethanol was recorded. This revealed that the onset of optical absorption (absorption edge) in MBA-NP occurs at approximately 435 nm. To obtain a spectrum of an MBA-NP single crystal, a (001) plate less than 0.6 mm thick was cleaved from an unpolished bulk sample. Spectra were recorded for the incident light polarised parallel to the y dielectric (b crystallographic) axis and the x-z principal dielectric plane (a crystallographic axis). These spectra are presented in Figure 4, where Fresnel reflection corrections have not been included.

The absorption edge for light polarised parallel to the y dielectric axis appears at 465 nm whereas for light polarised parallel to the x-z principal dielectric plane, the absorption edge occurs at 455 nm. This 10 nm dichroism in the high frequency absorption edge position may be due to the close alignment of the molecular dipoles along the y principal dielectric axis.[9] The bathochromic shift in the optical absorp-

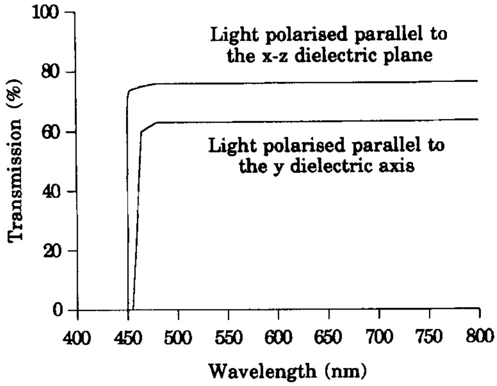

FIGURE 4 The transparency of an 0.6 mm thick unpolished (001) face of MBA-NP.

tion edge in the solid-state spectra compared to that in solution may have been pre-empted on the grounds that interactions between dipolar molecules in the solid-state may lower the energy of the electronic absorption. The first near infra-red absorption band in MBA-NP has been reported[16] as being at 1500 nm. Hence the transparency range of MBA-NP is between 465 and 1500 nm.

REFRACTIVE INDEX DETERMINATION

A vital prerequisite to understanding the nonlinear behaviour of materials e.g. phase-matching, is an accurate knowledge of their linear refractive indices. Due to the availability of large, high quality, single crystals of MBA-NP, the method chosen to evaluate the refractive indices was the minimum deviation technique.[17] In order that all three principal refractive index dispersions could be determined, two prisms were cut, each having the *y* principal dielectric axis parallel to the prism axis. Both the prisms were taken from low dislocation density volumes imaged using X-ray topography.[12] The input and output faces of each of the prisms was polished to a flatness of better than λ/2 of Na light using a Logitech PM-2 polishing machine, fitted with a polytron covered cast-iron lapping plate. The polishing abrasive used was 0.3 μm alumina dispersed in paraffin.

The *y* principal refractive index dispersion curve was determined between 465 and 680 nm using the monochromated output of a quartz-halogen lamp. There was excellent agreement (±0.002) between the *y* refractive indices determined from each prism. The maximum error in the *y* refractive index values was calculated as ±0.0015.

One of the prisms had an output face which was parallel to the (100) crystallographic plane. Light incident on this prism was polarised perpendicular to the prism axis (the *y* dielectric axis). The resulting refractive index constituted a mixture of n_z and n_x. This effective refractive index in the horizontal plane is denoted n_{xz}. This is obtained using Snell's law and the relationship

$$\tan \theta_r = \frac{\sin \theta \sin \alpha}{\sin(\theta_d - \theta + \alpha) + \sin \theta \cos \alpha} \tag{2}$$

where θ is the angle of incidence, α is the prism apex angle, θ_d is the measured deviation angle and θ_r is the angle of refraction. θ and α were measured using a back-scattering technique. The effective refractive index n_{xz} is related to the principal refractive indices by

$$\frac{1}{n_{xz}^2} = \frac{\cos^2\phi}{n_x^2} + \frac{\sin^2\phi}{n_z^2} \tag{3}$$

where ϕ is the angle between the refracted beam and the z principal dielectric axis. This angle is obtained using

$$\phi = (90 - \alpha) + \gamma + \theta_r \tag{4}$$

where γ is the angle between the z dielectric axis and the c crystallographic axis, which is known from orthoscopy (Figure 3). It is clear that it is not possible to evaluate n_z and n_x from (3) using only one angle of incidence. The effective refractive index n_{xz} was therefore evaluated at two angles of incidence and simultaneous equations, constructed from (3), solved.

It was found that the prism with the (100) output face gave accurate n_z values (± 0.003) but did not yield n_x values to an appreciable accuracy. The other prism had an output face parallel to the crystallographic (001) plane. In a similar manner this prism was used to obtain the x principal refractive index dispersion curve to an accuracy of ± 0.005. The x and z refractive indices were evaluated between 460 and 680 nm.

The y principal refractive indices at 1000, 1064 and 1300 nm were determined from Maker fringe spacings with the x and z refractive indices at these wavelengths being determined from phase-matching directions.[18] The index dispersions of MBA-NP were best represented by a Sellmeier equation of the form

$$n_i^2 = A + \frac{B\lambda^2}{\lambda^2 - C} - D\lambda^2 \tag{5}$$

where $i = x, y$ or z and λ is the wavelength in μm. The coefficients of the Sellmeier equation are presented for the first time in Table I, where δn is the average residual refractive index. Figure 5 shows the Sellmeier fit to the experimentally measured refractive indices.

Kondo and coworkers[16] have also determined the y principal refractive index of MBA-NP. Our n_y values are consistently lower than Kondo's by approximately

TABLE I

MBA-NP Sellmeier Coefficients

Index	A	B	C	D	δn
x	1.84369	0.79567	0.06624	0.02440	0.0013
y	2.37539	0.55690	0.14067	0.02855	0.0006
z	2.60872	0.22255	0.16002	0.00000	0.0008

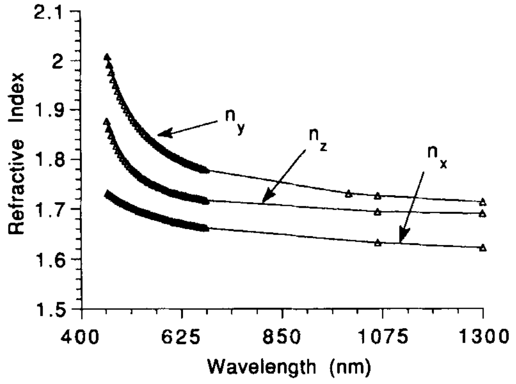

FIGURE 5 Sellmeier fit (solid line) to experimental refractive indices (triangles).

0.02. They quote an error of ±0.008 in n_y. Since we obtained n_y values to within 0.002 of each other from different prisms, the discrepancy between our data and that presented by Kondo cannot be adequately explained but may be due to differences in crystal quality.

Acknowledgment

The authors would like to thank E. Shepherd for crystal growth and the Science and Engineering Research Council for funding this work.

References

1. D. S. Chemla and J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, Volumes 1 and 2, (Academic Press: New York), (1987).
2. A. F. Garito and K. D. Singer, Laser Focus with Fiberoptic Technology, **18**(2), 59 (1982).
3. R. Twieg, A. Azema, K. Jain and Y. Y. Cheng, *Chem. Phys. Lett.*, **92**(2), 208 (1982).
4. S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, **39**(8), 3798 (1968).
5. J. N. Sherwood, Organic Materials for Nonlinear Optics, Edited by D. Bloor and R. A. Hann, (Royal Society of Chemistry Publication No. 69, Kent), 71 (1989).
6. J. F. Nicoud and R. J. Twieg, Nonlinear Optical Properties of Organic Molecules and Crystals, Vol. 1, Edited by D. S. Chemla and J. Zyss, (Academic Press, New York), 227 (1987).
7. I. Ledoux, C. Lepers, A. Perigaud, J. Badan and J. Zyss, *Optics Comm.*, **80**(2), 149 (1990).
8. J. L. Oudar and J. Zyss, Physical Review A, **26**(4), 2016 (1982).
9. R. J. Twieg and C. W. Dirk, IBM Report RJ5237(54077), 1 (1986).
10. R. L. Shriner, R. C. Fuson and D. Y. Curtin, The Systematic Identification of Organic Compounds, 4th Edition, (Chapman & Hall, New York), 55 (1956).
11. N. H. Hartshorne and A. Stuart, Practical Optical Crystallography, (Edward Arnold, London), 92 (1964).
12. P. J. Halfpenny and J. N. Sherwood, Phil. Mag. Lett. **62**(1), 1 (1990).
13. K. Sutter, G. Knopfle, N. Saupper, J. Hulliger, P. Gunter and W. Petter, *J. Opt. Soc. Am. B.* **8**(7), 1483 (1991).
14. M. V. Hobden, *J. Appl. Phys.* **38**(11), 4365 (1967).
15. R. T. Bailey, F. R. Cruickshank, P. Pavlides, D. Pugh and J. N. Sherwood, *J. Phys. D, Appl. Phys.*, **24**, 135 (1991).
16. T. Kondo, R. Morita, N. Ogasawara, S. Umegaki and R. Ito, *Jap. J. Appl. Phys.*, **28**(9), 1622 (1989).
17. D. Tentori and J. R. Lerma, *Optical Engin.*, **29**(2), 160 (1990).
18. G. Bourhill: Ph.D. Thesis, Strathclyde University, (1991).