Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: P. Mandal , M. Mitra , K. Bhattacharjee , R. Paul & S. Paul (1987): Nematic Order of APAPA from X-Ray Diffraction and Optical Studies, Molecular Crystals and Liquid Crystals, 149:1, 203-210

To link to this article: http://dx.doi.org/10.1080/00268948708082981

Mol. Cryst. Liq. Cryst., 1987, Vol. 149, pp. 203–210
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Printed in the United States of America

Nematic Order of APAPA from X-Ray Diffraction and Optical Studies

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(*Received July 17, 1986; in final form November 14, 1986*)

Anisylidene-p-aminophenyl acetate, a nematogenic Schiff's base, is studied by X-ray diffraction and optical methods. Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of magnetically aligned samples have been calculated from X-ray diffraction photographs. Order parameters $\langle P_2 \rangle$ have also been determined from refractive index measurements. $\langle P_2 \rangle$ values obtained from both the methods agree well with the MS values while $\langle P_4 \rangle$ values differ much. Average intermolecular distances and apparent molecular lengths have also been calculated.

Keywords: x-ray and optical study, nematogen

INTRODUCTION

Schiff's base compounds exhibit dynamic scattering effect which is used in liquid crystal display devices. Numerous studies were, therefore, performed on these compounds. We studied three Schiff's base compounds MBBA, BBBA and APAPA by X-ray diffraction and optical methods. Observations on MBBA and BBBA were reported earlier.[1,2] In this paper we report the experimental results on APAPA. Though this compound was studied by several workers by different methods,[3–9] no X-ray and optical studies have been reported so far.

EXPERIMENTAL

Material

Purified and recrystallised sample was supplied by Late Prof. M. Wada of Tohoku University, Japan. We checked the transition temperatures and no further purification of the sample was felt necessary.

Phase transitions

Phase transitions of the sample were studied by observing the textures under crossed polarizers with a polarizing microscope (150 ×) having a hot stage (Mettler FP82). Schlieren texture of nematic phase was observed both at the time of heating and cooling. It was found that APAPA could be supercooled in the nematic phase. Transition temperatures observed are as follows:

$$\text{Solid} \underset{\sim 74^{\circ}\text{C}}{\overset{83^{\circ}\text{C}}{\rightleftharpoons}} \text{Nematic} \overset{108.5^{\circ}\text{C}}{\rightleftharpoons} \text{Isotropic}$$

X-ray diffraction study

The specimen was sealed in a thin-walled glass capillary of about 1 mm diameter. Schiff's base compounds are very sensitive to atmospheric moisture so care was taken to minimise the exposure to atmosphere. A high temperature X-ray flat plate camera designed in our laboratory[10] was used to obtain X-ray diffraction photographs at different temperatures both in presence and absence of a magnetic field. The capillary containing the sample was inserted in a brass block. The temperature of the block was controlled within $\pm 0.5^{\circ}$C by a temperature controller (Indotherm 401). APAPA was aligned by a magnetic field of 6.1 K.Gauss using an electromagnet. Further details of the experimental procedures are given in our previous work.[11] The photographs were scanned both linearly and circularly by an optical microdensitometer (VEB Carl Zeiss, Jena, Model 100) equipped with auto recording facility. Measured optical densities were converted to X-ray intensities with the help of a calibration curve following Klug and Alexander.[12]

Optical study

Birefringence measurements were made using the techniques of Zeminder *et al.*[13] The thin prism was made by cutting a single microscopic slide. These glass plates were treated for surface alignment and thin hollow prisms of angle (1°–2°) were formed out of these. The liquid crystal sample was allowed to flow in by melting a few crystals at the top. The combination of rubbing and flow together with a magnetic field of strength 6 K.Gauss in the direction of rubbing produced a homogeneous nematic specimen with the optic axis parallel to the

edge of the prism. The prism was put in a brass thermostat heated electrically. The refractive indices were measured for two wavelengths using a mercury lamp. The densities of the sample at different temperatures were calculated from the data of Leenhouts *et al.*[9]

RESULTS AND DISCUSSION

Average intermolecular distance and apparent molecular length

X-ray diffraction patterns of aligned specimen were taken at different temperatures. The photograph with sample at 90°C is shown in Figure 1. The average intermolecular distance (D) and apparent molecular length (l) for oriented and unoriented samples have been calculated using the relation given by de Vries.[14] Variation of D with temperature is shown in Figure 2. We see that D increases slowly with temperature. Variation of "l" with temperature is shown in Figure 3. The value of l is found to be approximately 29 Å. The maximum molecular length measured on molecular model is approximately 17 Å, that is the repeat distance along the texture axis is 1.7 times the molecular length. This must result from strong molecular associations due to high dipole moments of APAPA. Such results have also been found in other nematogens.[11,15,16]

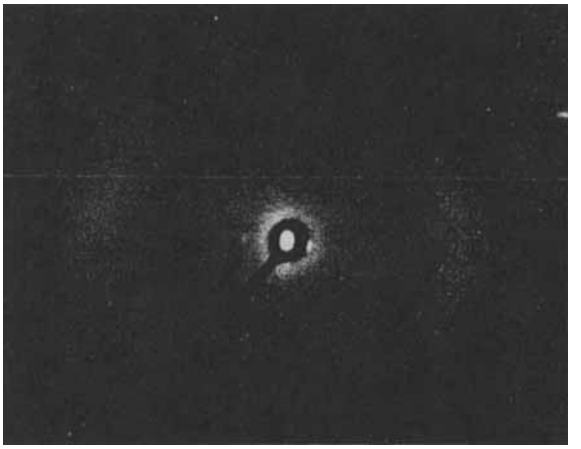

FIGURE 1 Photograph of oriented nematic phase at 90°C (Magnetic field 6.1 K. Gauss).

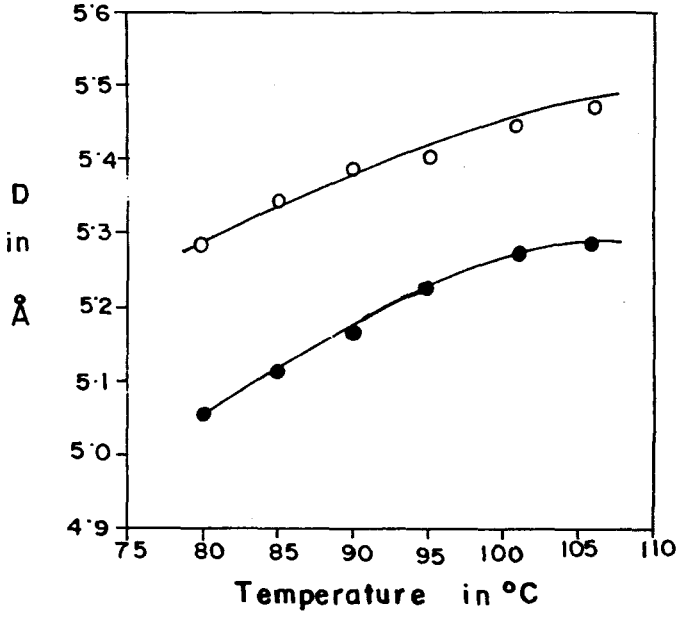

FIGURE 2 Variation of D with temperature.

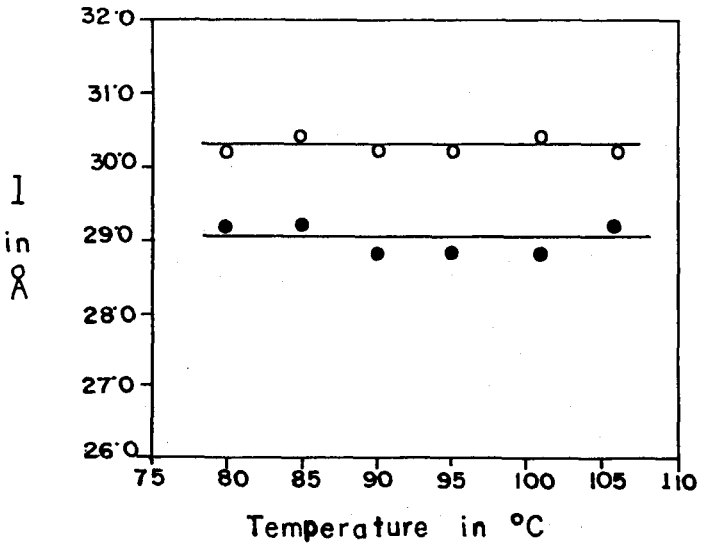

FIGURE 3 Variation of l with temperature.

Refractive indices and order parameters

The experimental values of refractive indices of APAPA for two wavelengths are shown in Figure 4. We make use of Vuks' formula[17] to calculate principal molecular polarizabilities (α_e, α_o) from refractive indices (n_e, n_o) and the order parameters were calculated using the relation,[18] $\langle P_2 \rangle = (\alpha_e - \alpha_o)/(\alpha_\parallel - \alpha_\perp)$ where $\alpha_\parallel$ and $\alpha_\perp$ are the polarizabilities parallel and perpendicular to the long axis. Because no solid phase data is available we could not calculate directly the values of $\alpha_\parallel$ and $\alpha_\perp$. The extrapolation procedure of Haller[19] was adopted for this purpose. We plotted log $(\alpha_e - \alpha_o)$ versus log

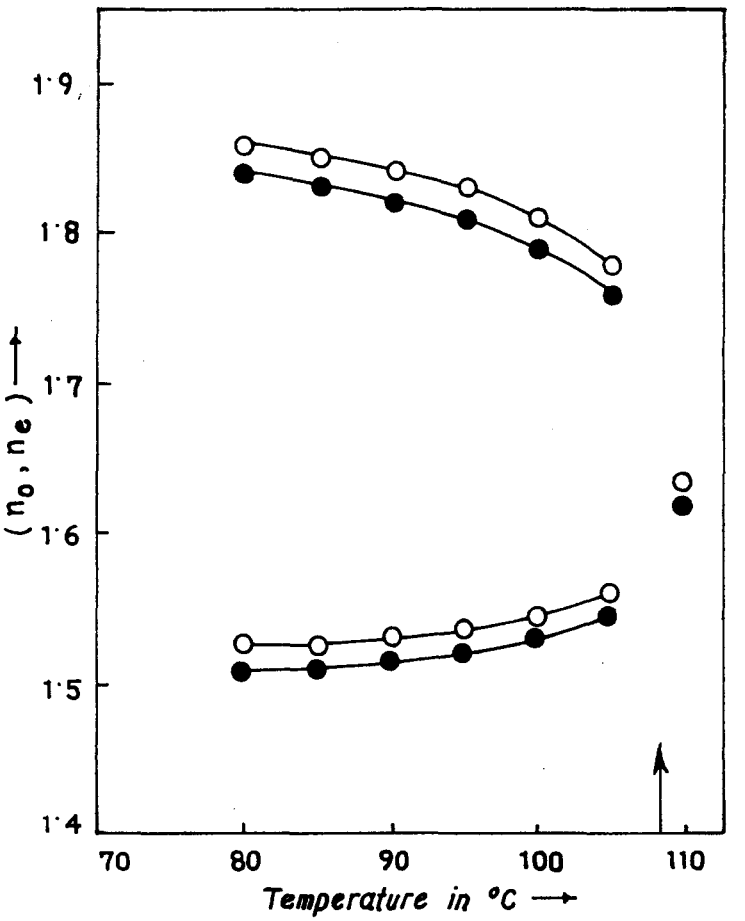

FIGURE 4 Variation of refractive indices with temperature. Open circles correspond to λ = 5461 Å and closed circles correspond to λ = 5780 Å.

$(T_C - T)$ giving a straight line which was extrapolated to log T_C. The limiting value of $(\alpha_e - \alpha_o)$ was assumed to correspond to $(\alpha_\parallel - \alpha_\perp)$. The densities, polarizabilities and order parameters are given in Table I.

Orientational distribution functions and order parameters

From the equatorial X-ray intensity distribution values $I(\psi)$ normalised orientational distribution function values $f(\beta)$ were calculated at different temperatures following a procedure described elsewhere.[11] The values are found, as expected, to be less peaked with increasing temperature. Only at 80°C (supercooled nematic region) the peak value is less than that at 85°C. Texture and X-ray studies, however, do not show any phase change between 80°C and 85°C.

Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ calculated from $f(\beta)$ values are shown in Figure 5. These values are compared with Maier-Saupe theoretical values. $\langle P_2 \rangle$ values determined from optical studies are also given in this figure. $\langle P_2 \rangle$ values obtained from X-ray diffraction studies and refractive indices measurements are in good agreement with the theoretical values except at one temperature. Moreover, these values agree well with those obtained from the anisotropies of diamagnetic susceptibility measurements.[9] $\langle P_4 \rangle$ values obtained from X-ray measurement, however, does not agree with the theoretically predicted values. Variation of the degree of ordering with the magnetic field have been calculated and it has been found that the degree of ordering increases in lower fields, gradually reaching a constant value at high fields. This is understandable, since with increasing field the number of domains decreases and individual domain directors tend to align along the magnetic field.

TABLE I

Density (ρ), polarizability (α) and orientational order parameter ($\langle P_2 \rangle$) of APAPA

Temp. (°K)	ρ (gm/cm³)	λ = 5780 Å			λ = 5461 Å		
		α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
353	1.1314	25.96	48.39	.6163	26.57	49.30	.6160
358	1.1265	26.15	47.98	.6000	26.76	48.90	.6002
363	1.1212	26.59	47.48	.5740	27.41	48.40	.5744
368	1.1155	27.05	46.99	.5493	27.67	47.92	.5488
373	1.1096	27.85	45.78	.4928	28.47	46.72	.4925
378	1.1033	29.00	43.86	.4084	29.63	44.81	.4115

α_o and α_e are in units of 10^{-24} cm³

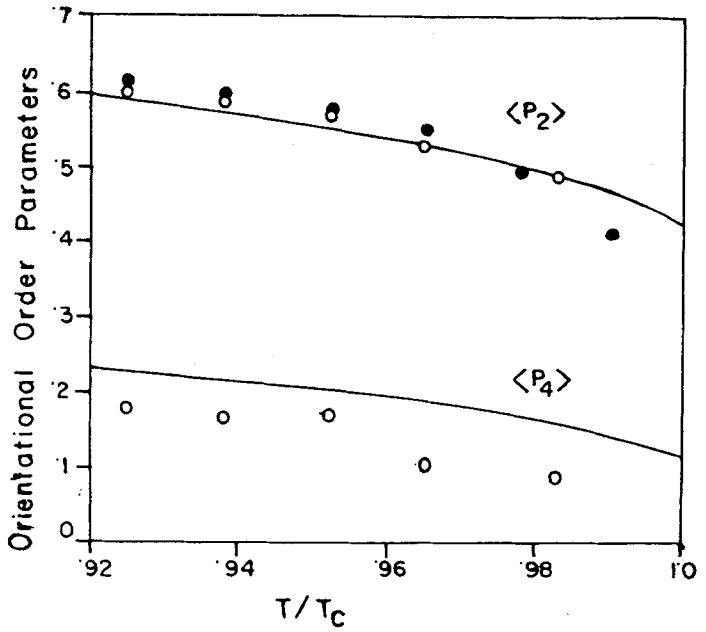

FIGURE 5 Variation of order parameters with T/T_C. Solid line corresponds to MS values, open circles to X-ray data and full circles to RI data.

Acknowledgment

We are thankful to University Grants Commission, India for financial assistance and a research fellowship (P. Mandal).

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