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

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Version of record first published: 24 Sep 2006.

To cite this article: A. Seal , M. Mitra , S. Paul & R. Paul (1993): Orientational Ordering of a Nematogen from X-Ray Diffraction Studies, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 225:1, 355-360

To link to this article: http://dx.doi.org/10.1080/10587259308036239

Mol. Cryst. Liq. Cryst., 1993, Vol. 225, pp. 355–360
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Printed in the United States of America

Orientational Ordering of a Nematogen from X-Ray Diffraction Studies

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(Received December 1, 1991; in final form June 26, 1992)

In this paper we have reported the results of X-ray diffraction studies on the nematic phase of 4-ethoxyphenyl trans-4′-propyl cyclohexane carboxylate at different temperatures. We have analyzed the experimental data to determine the orientational distribution function and hence to calculate the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The experimental order parameter values disagree with the Maier-Saupe mean field theory, but are in excellent agreement with the continuum theory of T. E. Faber. The possible causes for deviation from mean field model have been discussed. The molecules also form association with apparent molecular length of about 1.5 times their actual length.

Keywords: nematogens, x-ray diffraction, order parameter, molecular association

1. INTRODUCTION

There are only a few experimental techniques that allow, at least in principle, the measurements of both the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in nematogens, e.g., Raman effect, neutron- and X-ray diffraction studies. The variation of $\langle P_2 \rangle$ is reported almost always to be in reasonable agreement with mean field theories[1,2] but the scantily reported $\langle P_4 \rangle$ values are always much lower than the values predicted by the mean field theories. However, the continuum theory of

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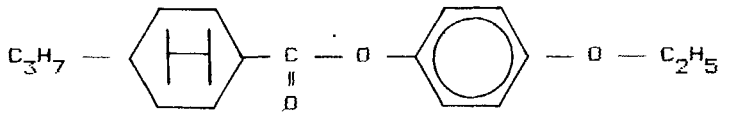
disorder in nematic liquid crystals, as formulated by T. E. Faber,[3] has recently been extensively tested against our experimental data,[4] showing good agreement. The object of the present investigation on 4-ethoxyphenyl trans-4′-propyl cyclohexane carboxylate by X-ray diffraction technique is to compare our experimental $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values with both Maier-Saupe and Faber's theories as an continuation of our previous studies. The results of three other members of this homologous series have already been reported by us.[4,5]

2. EXPERIMENTAL

Purified and recrystallized sample was obtained from Prof. S. B. Roy, Department of Optics, Indian Association for the Cultivation of Science, Calcutta. The structural formula of the compound is as given below:



The transition temperatures as found from the literature[6] are as follows:

$$\text{Solid} \xrightarrow{48^\circ\text{C}} \text{Nematic} \xrightarrow{78^\circ\text{C}} \text{Isotropic}$$

We have performed texture studies on the sample by using a polarizing microscope with a magnification 150X equipped with a hot stage (Mettler FP 80/82). The transition temperatures as observed by us are the same as the literature values but we have found supercooling in the nematic phase. According to our texture studies the transition temperatures are as follows:

$$\text{Solid} \underset{< 20^\circ\text{C}}{\overset{48^\circ\text{C}}{\rightleftharpoons}} \text{Nematic} \overset{78^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$$

The compound was used in the investigations without further purification.

2.1 X-ray Study

A detailed description of the experimental set-up for the X-ray diffraction study is given elsewhere.[7] Diffraction photographs were taken with a flat plate camera at different temperatures for aligned and unaligned samples. For alignment the sample was heated upto its isotropic state and then cooled down slowly to the desired temperature in presence of a magnetic field of about 6.0 KG. The specimen was sealed in a thin-walled glass capillary of 1 mm diameter. The temperatures were measured and regulated with an accuracy of $\pm 0.5^\circ$C with the help of a temperature controller (Indotherm 401).

In order to determine the various parameters, the photographs were scanned, both linearly and circularly, by an optical micro densitometer (VEB Carl Zeiss Jena, Model MD 100) equipped with an automatic recording facility. The measured

optical densities were converted to X-ray intensity values with the help of a calibration curve following Klug and Alexander.[8]

3. RESULTS AND DISCUSSIONS

3.1 Molecular Parameters

The molecular parameters which can be determined from X-ray diffraction photographs are the apparent molecular length (l) and intermolecular distance (D). The outer equatorial arc arises essentially from the intermolecular spacings perpendicular to the long axes of the molecules. We obtained the average intermolecular spacings using the formula[9] $2D \sin\theta = 1.117\lambda$. The apparent molecular length (l) has been obtained from the scattering about the meridional direction by using Bragg's equation. It was found that near solid-nematic transition temperature the experimental 'l' value is ~ 26 Å, whereas, the molecular length (L), determined from a stereo model unit, was found to be 17.3 Å. So it is clear that in the mesophase the molecules form associations, a phenomenon observed frequently in other polar nematic liquid crystals.[10-13] The polar part $C^+{=\!=}O^-$ of a molecule A induces dipole moment in the aromatic ring of the neighboring molecule B. Similarly $C^+{=\!=}O^-$ dipole of molecule B induces dipole moment in the phenyl ring of molecule A. Thus a pair of dipole-induced dipole interaction bind two neighboring molecules to form association. This process is enhanced since the phenyl rings are easily polarizable due to the delocalization of the TT-electrons in the system. The ratio of the model length of the dimer to that of monomer is ~ 1.50. The experimentally obtained ratio is also ~ 1.50, showing good agreement with the proposed interaction for molecular association. The reason for wide range of supercooled nematic phase may be due to the fact that the strong molecular associations retard the crystallization process. This type of behavior has also been found by us[5] for other two members of the same series.

While this dipolar association may seem appealing as the explanation for a smectic density wavelength about 1.5 times the actual molecular length, we should caution that many other esters do not show this effect. Another plausible explanation would be the effect of packing the bulky cyclohexane rings in adjacent molecules. Our experiments cannot distinguish between dipolar association and steric packing as the cause, and it may well be due to a combination of the two effects.

3.2 Orientational Order Parameters

The X-ray intensity $I(\theta)$ around the diffuse equatorial arc is related to the distribution function $f_d(\beta)$ as follows[14]

$$I(\theta) = C \int_{\beta=\theta}^{\beta=\pi} f_d(\beta)\sec^2\theta[\tan^2\beta - \tan^2\theta]^{-1/2} d(\cos\beta),$$

where $f_d(\beta)$ describes the distribution function of the directors of a local cluster of molecules which are assumed to be perfectly aligned within the cluster. However,

$f_d(\beta)$ can be expected to be almost the same as the singlet distribution function $f(\beta)$. The detailed procedure for the calculation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from $f(\beta)$ has been discussed earlier.[10]

Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ calculated for this compound at different temperatures are shown in Figure 1. The experimental uncertainties in both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are estimated to be ± 0.02. From this figure it is clear that the experimental $\langle P_2 \rangle$ values are in good agreement with Maier-Saupe[1] (MS) theoretical values. But $\langle P_4 \rangle$ values are significantly lower than the mean field theoretical values. Such behavior of $\langle P_4 \rangle$ has been observed by others.[10,11,16–18] Several possibilities have been proposed to explain the low values of $\langle P_4 \rangle$.[19–21] In Maier-Saupe theory the molecules are assumed to be cylindrical rigid rods; the interaction among molecules is due to only dispersive forces and there is no short range interaction force due to permanent dipoles in the molecules. In the present case, the central part is almost rigid but the end chains are flexible. Moreover, the molecules form associations in the nematic phase. Vibration of the end chain with temperature may also broaden the peak of the distribution function $f(\beta)$ thus lowering the $\langle P_4 \rangle$

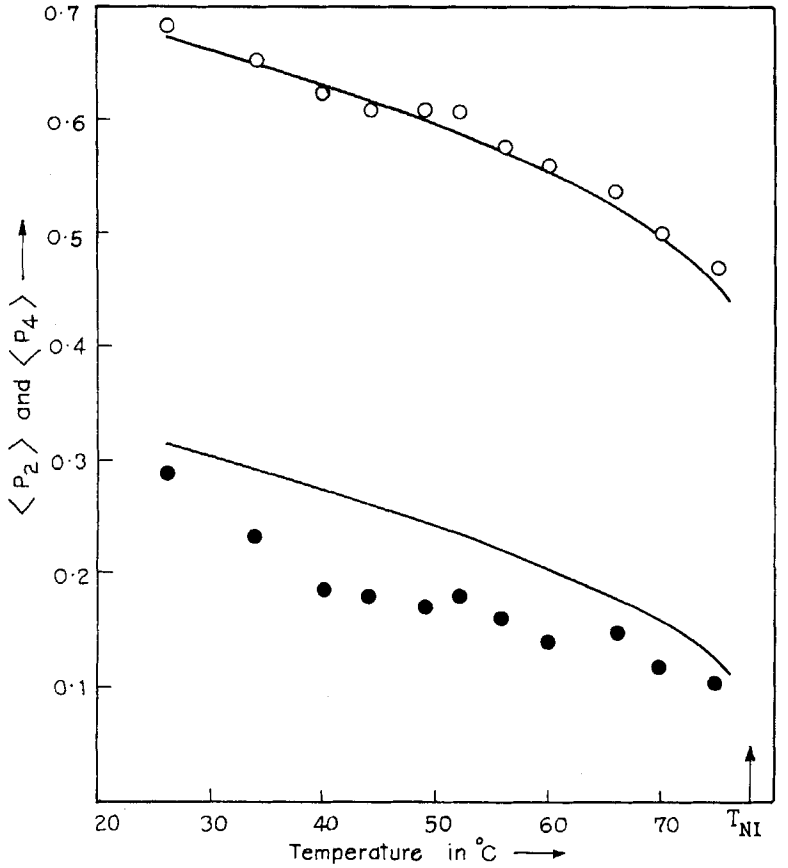


FIGURE 1 Variation of experimental $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values with temperature, solid lines show the Maier-Saupe theoretical curve.

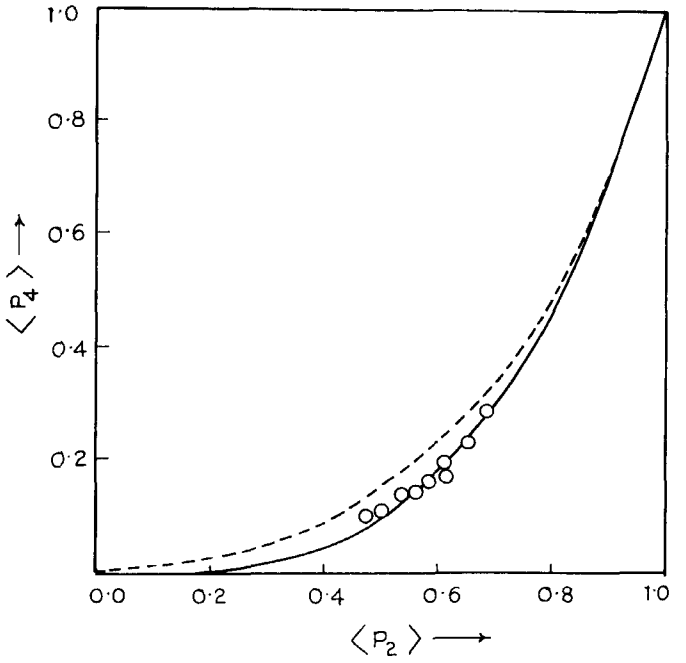


FIGURE 2 Comparison of experimental $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values (circles) with Maier-Saupe (MS) theory (dotted curve) and Faber's theory (solid curve).

values, although this effect will lower $\langle P_2 \rangle$ values as well. Mean field theory also neglects director fluctuations, which may contribute to the lowering of $\langle P_4 \rangle$ values.

Using the continuum theory of disorder in nematic liquid crystals, Faber[3] has derived a simple expression relating the two order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$, viz. $\ln\langle P_4 \rangle / \ln\langle P_2 \rangle = 10/3$. In Figure 2 we have shown our experimental $\langle P_4 \rangle$ and $\langle P_2 \rangle$ values as also the curves calculated from the theories of Maier-Saupe and Faber. It is clear from the figure that the agreement of Faber's theory with our experimental results is excellent, while Maier-Saupe theory is in disagreement. For the other three members of this homologous series we have arrived at the same conclusion.[4,5]

Acknowledgments

We are grateful to Prof. S. B. Roy, Department of Optics, Indian Association for the Cultivation of Science, Calcutta for suppling us with the liquid crystal sample used in the present work and to the University Grants Commission, New Delhi for financial assistance. The authors are also thankful to Mr. S. K. Sarkar for technical help. One of us (A.S.) thanks the authorities of Indian Association for the Cultivation of Science for financial support during her stay at North Bengal University for this experimental work and Prof. Siddharta Roy, Department of Solid State Physics, I.A.C.S., Calcutta for his constant encouragements.

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