Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Order parameters and densities in the smectic C, smectic A and nematic phases of a liquid crystal mixture

R. Paul[a]; B. Jha[a]; D. A. Dunmur[b]
[a] Department of Physics, University of North Bengal, Siliguri, West Bengal, India [b] Department of Chemistry and Centre for Molecular Materials, University of Sheffield, Sheffield, England

To cite this Article Paul, R. , Jha, B. and Dunmur, D. A.(1993) 'Order parameters and densities in the smectic C, smectic A and nematic phases of a liquid crystal mixture', Liquid Crystals, 13: 5, 629 — 636
To link to this Article: DOI: 10.1080/02678299308026336
URL: http://dx.doi.org/10.1080/02678299308026336

LIQUID CRYSTALS, 1993, VOL. 13, NO. 5, 629–636

Order parameters and densities in the smectic C, smectic A and nematic phases of a liquid crystal mixture

by R. PAUL, B. JHA and D. A. DUNMUR*†
Department of Physics, University of North Bengal,
Siliguri, West Bengal, India, PIN-734430
† Department of Chemistry and Centre for Molecular Materials,
University of Sheffield, Sheffield S3 7HF, England

(*Received 20 November 1992; accepted 29 January 1993*)

Measurements of the orientational and translational order parameters for the nematic, smectic A and smectic C phases of a commercial liquid crystal material are reported. The order parameters have been obtained by analysis of the angular distribution of the intensity of X-rays scattered by a sample aligned by a magnetic field. Results are presented as a function of temperature, and it is found that the apparent orientational order parameter in the smectic C phase decreases with decrease in temperature. This is explained using a model of random tilt. The experimental order parameters are compared with those calculated from a mean field model.

1. Introduction

Many commercial display devices now use liquid crystals as the active element because of their low power consumption, relative ease of manufacture and light weight. To produce displays of the best quality, the liquid crystal material must have optimum physical properties in the required operating temperature range of the device, and so mixtures of pure compounds are used, the compositions of which are adjusted to obtain the desired performance. Hence the study of mixtures having mesomorphic properties is an essential part of the design of new improved materials for applications. Properties of importance for devices depend on the structure of the liquid crystal molecules and the extent of their organization, and the anisotropies of dielectric, optical, elastic and viscous properties are determined by the order parameters. These in turn are characteristic of the orientational distribution function, which can in principle be obtained from various theoretical models. Thus experimental measurements of order parameters are useful for comparison with theory, and as an aid in the design of suitable materials for applications. In this paper we report values for the order parameters from X-ray diffraction intensities and densities measured for the nematic, smectic A and smectic C phases of a commercial liquid crystal mixture.

2. Experimental

The material studied was mixture 6040 supplied by Merck Ltd, U.K. (formerly BDH Ltd), and is a mixture of fluorinated alkyl-alkoxy-fluorophenyl benzoates having the following mesophase behaviour:

$$S_C\ 54{\cdot}8^{\circ}C\ S_A\ 67{\cdot}5^{\circ}C\ N\ 101^{\circ}C\ I.$$

---

* Author for correspondence.

Densities were determined in the temperature range 20°C to 70°C using an Anton Paar precision digital density meter (model DMA602HT) with an accuracy of about $5 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$. The temperature of the substance during the density measurements was kept constant within +/−0·05°C. All experimental values reported in this paper are the average of at least three independent measurements.

Small angle X-ray diffraction photographs from magnetically aligned samples were taken using a modification of a system employed previously [1]. Nickel-filtered Cu–K_α radiation was used, and alignment achieved with a permanent magnet having a field strength of about 1500 G. The sample was kept in a thin-walled lithium glass capillary of 1 mm diameter, and the temperature of the sample holder was kept constant within +/−0·2°C for short exposure times (about 30 min) and +/−0·5°C for longer exposures (4 h). X-ray diffraction photographs were taken at regular intervals from room temperature (~20°C) for smectic C phases to above 101°C for the isotropic liquid phase. Some photographs for the smectic phases were taken with a sample to film distance of about 12 cm, otherwise a distance of ~6 cm was maintained. The X-ray films were scanned by using a Zeiss micro-densitometer (model MD 100) and the optical density values were converted to X-ray intensity data following a standard procedure [2].

3. Results and discussion

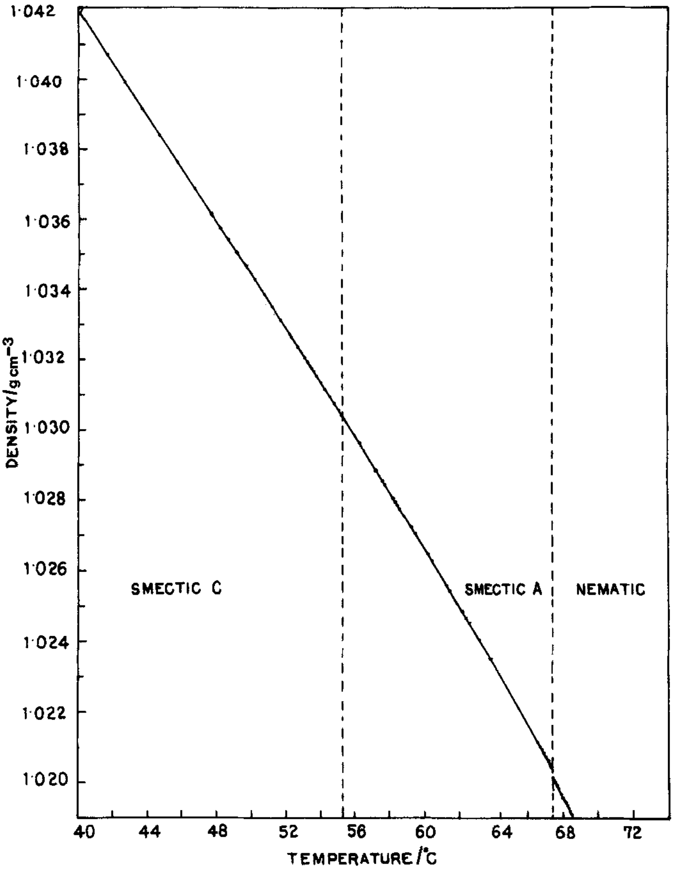
3.1. *Density measurements*

Figure 1 (*a*) shows the variation of the density of 6040 over the temperature range 40°C to 70°C. The experimental values close to the smectic A–nematic phase transition are shown in figure 1 (*b*), and these clearly indicate that this transition is first order. On the other hand, the smectic A to smectic C transition (see figure 1 (*c*)) seems to be second order with no change in density within experimental uncertainty. However, the slopes of the density against temperature curve are slightly different on the two sides of this transition, and the corresponding coefficients of thermal expansivity are $1{\cdot}937 \times 10^{-3}$°C in the smectic C phase near the transition temperature, $1{\cdot}900 \times 10^{-3}$°C in the smectic A phase and $2{\cdot}583 \times 10^{-3}$°C in the nematic phase.

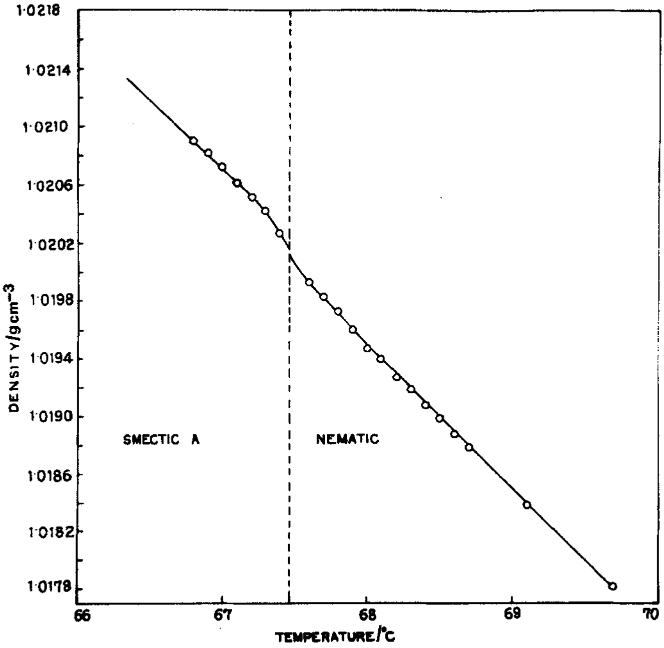
3.2. *X-ray measurements*

The X-ray diffraction photographs for the nematic and the smectic A phases were exactly as expected from well-aligned samples. However photographs of the smectic C phase were similar to those obtained from mono-domain smectic A samples. This indicates that in our samples the director is randomly oriented in a cone about the layer normal of the smectic C phase of 6040, which is the laboratory-fixed magnetic field direction [3]. It was not therefore possible to determine the tilt angle in the smectic C phase from the X-ray photographs directly. This angle can be calculated indirectly from the variation of the layer thickness in smectic A and C phases, which is determined accurately in the present case from the long distance X-ray photographs taken for these phases; tilt angles determined in this manner are illustrated in figure 2. The variation of the layer thickness with temperature is shown in figure 3. The layer thickness in the smectic A phase is 31·54 Å, which is the average of many measurements taken over the entire smectic A temperature range. Figure 2 shows the variation of the experimental tilt angles θ with temperature T fitted to a function of the following form:

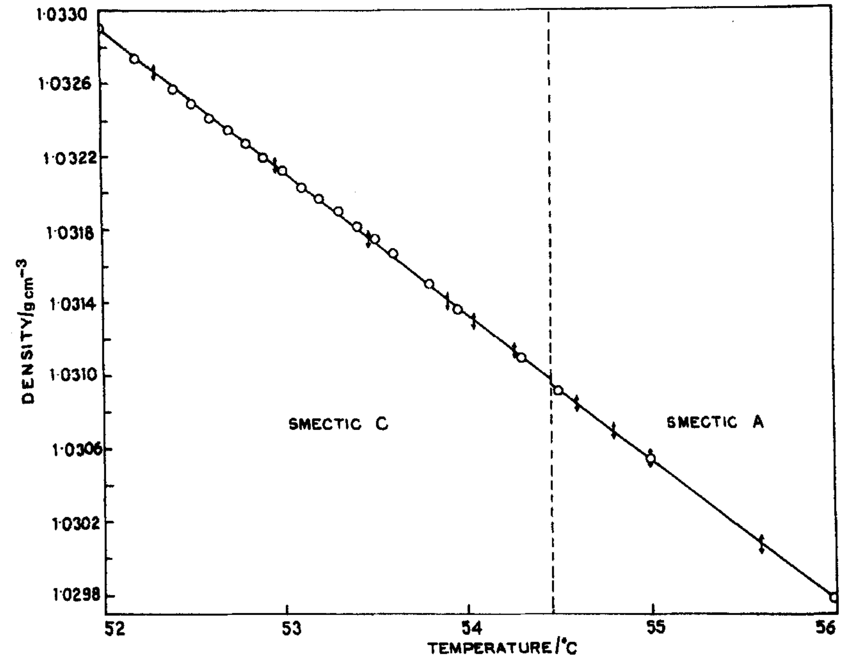
$$\theta = \theta_0 (T_{S_C S_A} - T)^\beta \qquad (1)$$


1·042
1·040
1·038
1·036
1·034
1·032
1·030
1·028
1·026
1·024
1·022
1·020
DENSITY/g cm^{-3}
40
44
48
52
56
60
64
68
72
TEMPERATURE/°C
SMECTIC C
SMECTIC A
NEMATIC

(*a*)


1·0218
1·0214
1·0210
1·0206
1·0202
1·0198
1·0194
1·0190
1·0186
1·0182
1·0178
DENSITY/g cm^{-3}
66
67
68
69
70
TEMPERATURE/°C
SMECTIC A
NEMATIC

(*b*)



(*c*)

Figure 1. The density of 6040 as a function of temperature. (*a*) over mesophase range, (*b*) close to the smectic A/nematic transition, (*c*) close to the smectic C/smectic A transition.

where $T_{S_CS_A}$ is the smectic C to smectic A transition temperature, taken to be 54·7°C; the best fit curve gives a value of $\theta_0 = 9{\cdot}44°$ and $\beta = 0{\cdot}25$. The critical exponent β for the smectic tilt angle has been found to be in the range 0·35 to 0·50 by several other workers [4–6].

The orientational distribution function $f(\theta)$ and hence the orientational order parameters were determined from X-ray intensity data using the method described previously [3, 7], and results for $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ are shown in figure 4. We have also calculated the translational order parameters using McMillan's potential [8]

$$\varepsilon(\cos\theta, z) = -\varepsilon_0[\delta\alpha\tau\cos(2\pi z/d) + \{\eta + \alpha\sigma\cos(2pz/d)\}P_2(\cos\theta)], \qquad (2)$$

where α and δ are two adjustable parameters, z is the displacement along the layer normal, d is the layer thickness, $\eta = \langle P_2\cos\theta)\rangle$, the orientational order parameter, while $\tau = \langle\cos(2\pi z/d)\rangle$ is the translational order parameter and $\sigma = \langle P_2(\cos\theta)\cos(2\pi z/d)\rangle$ is the mixed translational and orientational order parameter. Using this potential with values of $\delta = 0{\cdot}05$ and $\alpha = 0{\cdot}73$, the experimental nematic/isotropic and smectic A/nematic transition temperatures are reproduced, and a reasonable fit to the measured orientational order parameters in the nematic and smectic A phases is obtained (see figure 4). Experimental $\langle P_2(\cos\theta)\rangle$ values in the nematic phase are somewhat higher than the theoretical values, but this may be due to our inability to correct properly for the background X-ray scattering. We had to assume that the X-ray diffraction intensity along the outer halo was zero at a point 90° from the intensity maximum [3, 7], which obviously increases the magnitude of the order parameters. The error in the smectic A phase is negligible, since the above assumption is increasingly valid for the more orientationally ordered phases.

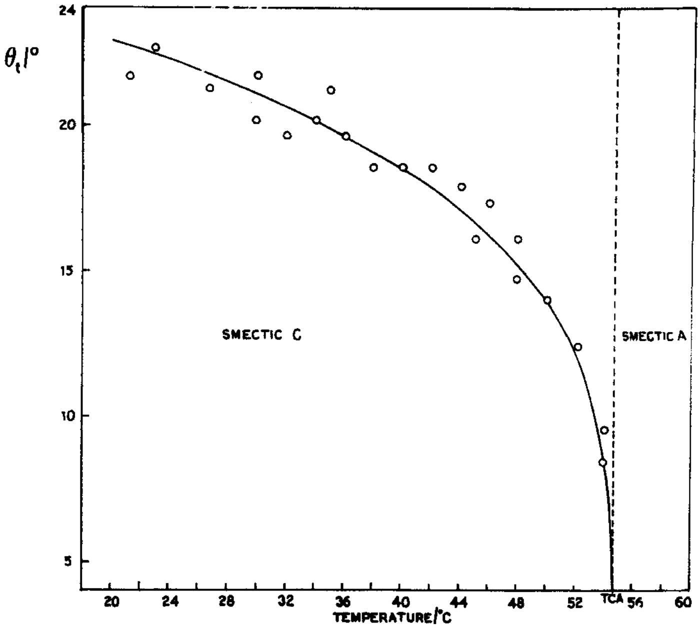


Figure 2. The measured tilt angles (○) for the smectic C phase of 6040; solid line is calculated from equation (1) (see text).

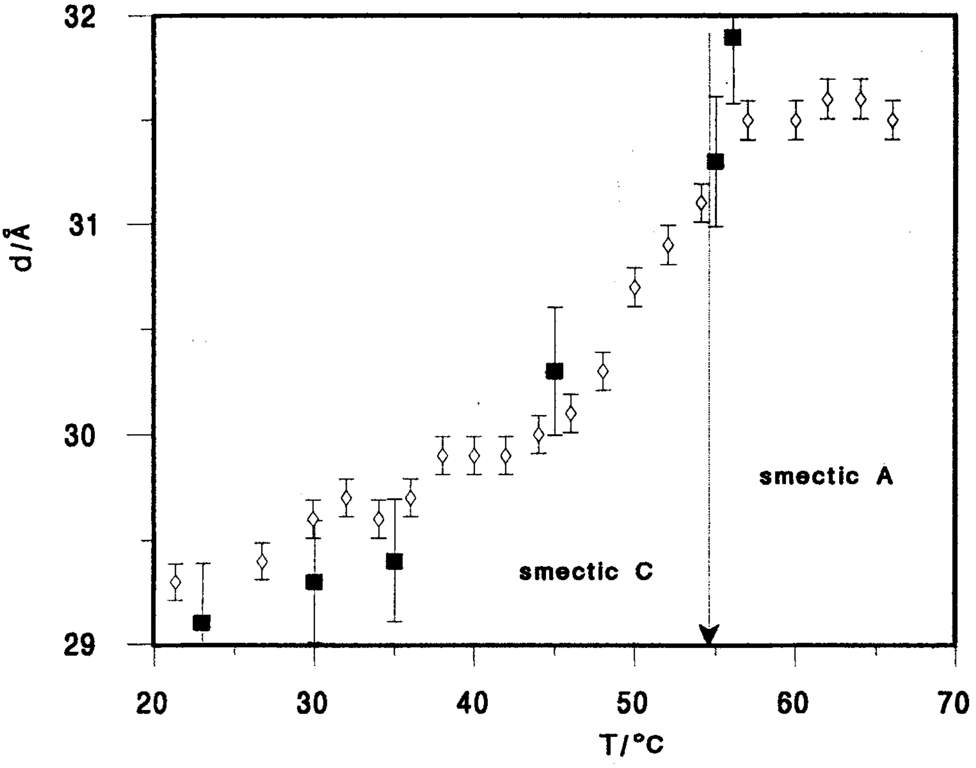


Figure 3. The layer thicknesses for 6040 in the smectic C and smectic A phases. ◇, from measurements at a film–sample distance of 12 cm, ■, measurements at a film–sample distance of 6 cm.

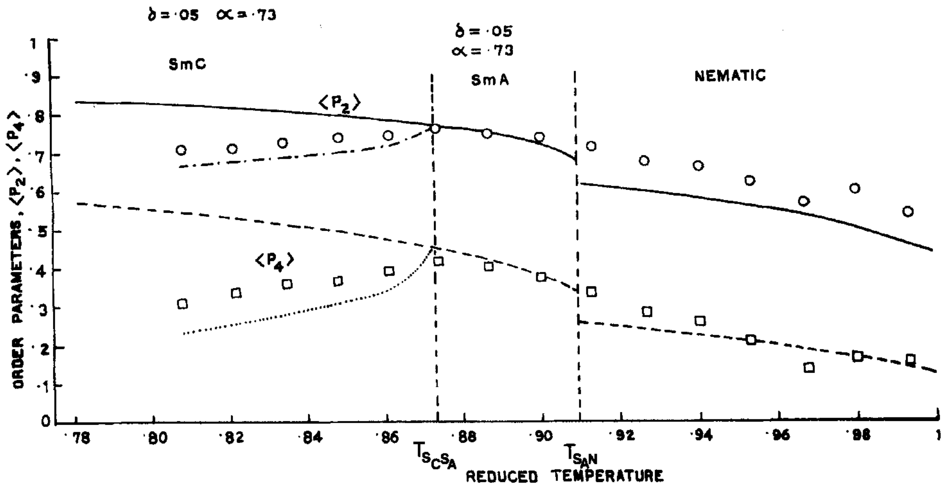


Figure 4. The orientational order parameters for 6040; ○, experimental $\langle P_2(\cos\theta)\rangle$; solid line is theoretical $\langle P_2(\cos\theta)\rangle$ from the McMillan potential; □, experimental $\langle P_4(\cos\theta)\rangle$; dashed line is theoretical $\langle P_4(\cos\theta)\rangle$ from the McMillan potential. In the smectic C phase the experimental points ○ and □ correspond to apparent values of the order parameters determined with respect to the layer normal. Theoretical apparent order parameters for the smectic C phase including allowance for the tilt angle are represented as follows: —·—, apparent $\langle P_2(\cos\theta)\rangle$; ··········, apparent $\langle P_4 \cos\theta)\rangle$ (see text).

Not surprisingly, the agreement between the experimental and calculated $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ in the smectic C phase is poor (see figure 4). We find that the experimental order parameters decrease with decreasing temperature. This is caused by the fact that the tilt angle increases at lower temperatures, and hence the molecular orientational distribution function with respect to the layer normal becomes broader as the temperature decreases. Since the layer normal is parallel to the applied magnetic field direction and normal to the X-ray beam, the diffraction pattern is caused by the apparent orientational distribution function about the layer normal and not by the real distribution function about the director. Figure 5 shows the relative orientations of the layer normal (z), the local director (**n**) and the long axis of a molecule (**l**) and it is clear from the figure that

$$\cos\theta = \cos\theta_t \cos\phi + \sin\theta_t \sin\phi \cos\omega. \tag{3}$$

Substituting this value of $\cos\theta$ in equation (2), we get for the orientational distribution function about the layer normal

$$f'(\cos\phi) = N \int \exp\left[-\varepsilon(\theta_t, \phi, \omega, z)/kT\right] dz\, d\omega, \tag{4}$$

where N is a normalising constant. It is clear that the distribution function $f'(\cos\phi)$ is obtained from the analysis of our X-ray data, and knowing the tilt angle θ_t, the expression for $f'(\cos\phi)$ can be integrated and apparent order parameters $\langle P_2(\cos\theta)\rangle_{\text{app}}$ and $\langle P_4(\cos\theta)\rangle_{\text{app}}$ calculated. Figure 4 also shows $\langle P_2(\cos\theta)\rangle_{\text{app}}$ and $\langle P_4(\cos\theta)\rangle_{\text{app}}$ in the smectic C phase calculated by the above method, assuming experimental tilt angles only, i.e. introducing no adjustable parameter. It can be seen that the agreement of the recalculated order parameter values with the experimental values is surprisingly good (see figure 4).

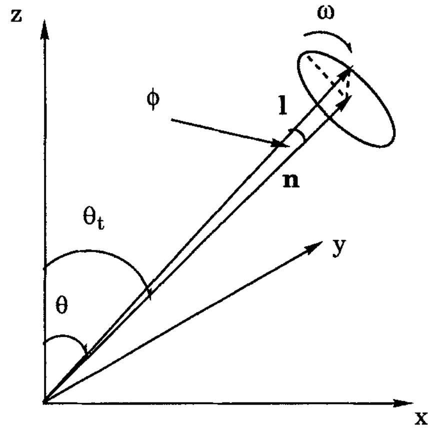


Figure 5. The definition of the parameters: θ_t = smectic C tilt angle, **l** is a unit vector along the molecular axis, **n** is the director and the z axis represents the smectic layer normal.

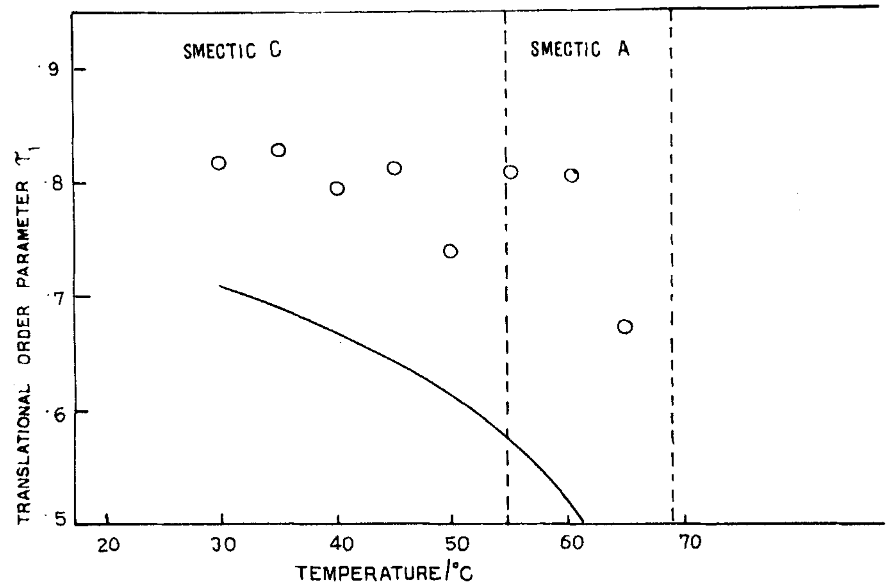


Figure 6. The translational order parameter τ for the smectic phases of 6040. ○, Experimental; ——, theoretical values.

We have also determined the translational order parameter τ from our experimental data using a simple procedure described by Leadbetter *et al.* [3], and these are compared with values obtained from McMillan's theory in figure 6. However agreement is poor, which may be due to the crudeness of the model used for calculating τ from the X-ray data. The values of the mixed order parameter σ have also been calculated from McMillan's theory, and σ varies from 0·64 at 20°C to 0·28 at the smectic A to nematic transition temperature; in the absence of any method of calculating the mixed order parameter from the experimental data, we are unable to make any comparison between theory and experiment. The method of analysis used here assumes that nearest neighbour molecules are parallel, and justification for this is provided by the results of computer simulations [9] which show that in a nematic phase of hard ellipsoids, the orientational pair correlation function $\langle P_2(\cos\theta(r)_{12})\rangle$ is $\sim 0{\cdot}9$ at the nearest neighbour separation. Thus both translational and orientational order parameters can be obtained from measurements of the scattered X-ray intensities from liquid crystals, and can be used to test theoretical models and to compare with the results of computer modelling. Systematic studies of materials with different molecular structures could provide a route to the interpretation of the parameters of mean field theories in terms of molecular properties, and so advance the capabilities of molecular design in the area of liquid crystals.

We are grateful to Merck Ltd (formerly BDH Ltd) for supplying the materials, and thanks are due to the University of Sheffield Research Fund for support. Drs R. Buckley (Department of Engineering Materials) and N. Cowlam (Department of Physics) are thanked for providing X-ray facilities and equipment, and Messrs A. Hall, C. Lumley and M. Manterfield for technical assistance.

References

[1] JHA, B., and PAUL, R., 1976, *Proc. Nucl. Phys. Solid St. Phys. Symp.* (*India*), **19C**, 481.
[2] KLUG, H. P., and ALEXANDER, L. E., 1974, *X-ray Diffraction Procedure* (Wiley), p. 477.
[3] LEADBETTER, A. J., and NORRIS, E. K., 1979, *Molec. Phys.*, **38**, 669.
[4] WISE, R. A., SMITH, D. H., and DOANE, J. W., 1973, 1973, *Phys. Rev.* A, **7**, 1366.
[5] BARTOLINO, R., DOUCET, J., and DURAND, G., 1978, *Ann. Phys., Paris*, **3**, 389.
[6] FLANDERS, P. J., 1976, *Appl. Phys. Lett.*, **28**, 571.
[7] BHATTACHARJEE, B., PAUL, S., and PAUL, R., 1981, *Molec. Phys.*, **44**, 1391.
[8] MCMILLAN, W. L., 1972, *Phys. Rev.* A, **6**, 936.
[9] FRENKEL, D., 1988, *J. phys. Chem.*, **92**, 3280.