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Order parameter and the orientational distribution function for 4-cyanophenyl-4'-*n*-heptyl benzoate in the nematic phase

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X-ray diffraction studies on oriented samples of 4-cyanophenyl-4'-*n*-heptylbenzoate in the nematic phase are reported at different temperatures. The orientational distribution function $f(\beta)$ has been calculated from the angular distribution of the X-ray intensities. The orientational order parameters \bar{P}_2 and \bar{P}_4 have been determined from $f(\beta)$. \bar{P}_2 is found to be slightly greater than the value predicted by the Maier-Saupe molecular field theory, whereas the \bar{P}_4 values are much smaller than those given by theory. An approximate expression for the potential of the molecular field is obtained from the temperature variation of the distribution function. The value of l and the intermolecular distance D have been determined from X-ray photograph. l , which is often close to the molecular length is found to be 28 Å. The length as measured from a model in a completely extended form is found to be 21 Å. If we assume antiparallel associations of molecules as in most cyano compounds this difference can be explained.

1. INTRODUCTION

In this paper we report the results of X-ray studies on oriented and non-oriented samples of 4-cyanophenyl-4'-*n*-heptylbenzoate (CPHB). We have determined $f(\beta)$, the singlet orientational distribution function and hence derived the order parameters \bar{P}_2 and \bar{P}_4 from our diffraction photographs of the oriented sample.

A number of experiments have been performed to determine the order parameters for aligned nematic samples. Shen Jen *et al.* [1] have used the Raman scattering technique to measure both \bar{P}_2 and \bar{P}_4 for several nematics. Falgueirettes and de Lord [2, 3] have measured order parameters from X-ray diffraction studies of aligned samples while the order parameter \bar{P}_2 was determined by Bhattacharjee *et al.* [4] from X-ray diffraction data. de Vries [5] has obtained the cylindrical distribution function and order parameters from X-ray diffraction measurements. Thus a number of experiments have been performed which give \bar{P}_2 and \bar{P}_4 but the distribution functions have not always been calculated. Leadbetter *et al.* [6] have extracted the singlet orientational distribution function of the molecular long axes from X-ray diffraction measurements.

In our laboratory we are determining the order parameters of oriented liquid crystals by different techniques. The study of CPHB was undertaken in this context. Zeminder *et al.* [7] have obtained the order parameters of CPHB from optical birefringence but no X-ray diffraction studies on CPHB have been

reported so far. This compound was supplied to us by Messrs. F. Hoffmann-La-Roche and Co., Basel, Switzerland. According to their literature CPHB has the transition temperatures T_{CN} 43.5°C and T_{NI} 56°C. The temperatures as determined by us from X-ray diffraction and texture studies are identical to these although the nematic phase can be supercooled to ~33°C.

2. EXPERIMENTAL METHODS

CPHB was purified by recrystallization from acetone and was then dried in a vacuum desiccator. X-ray diffraction photographs were taken at different temperatures in the presence of a magnetic field using nickel filtered copper K_α radiation of wavelength 1.542 Å. A high temperature X-ray camera designed in our laboratory was used to obtain the photographs in the presence of a magnetic field [8].

The temperature was measured and regulated with an accuracy of $\pm 0.5^\circ\text{C}$ by using thermocouples inserted in the block containing the sample. The sample, in the form of a bead, was kept in the central hole of a stainless steel disc. Flat plate photographs were taken at different temperatures with an exposure time of 2–3 hours; the film to specimen distance was accurately determined by calibration with aluminium photographs. The characteristic photographs were scanned by an optical densitometer (ECIL Model DM 803). The optical densities obtained from the densitometer readings were converted to X-ray intensities with the help of a calibration curve [9].

Photographs of an oriented sample in the nematic phase were taken by heating the sample to the desired temperature in the presence of magnetic field of 0.58 T using an electromagnet. The field which was found to be sufficiently strong to produce monodomain samples was applied throughout the exposure. A photograph of an oriented sample at 34°C is shown in figure 1.

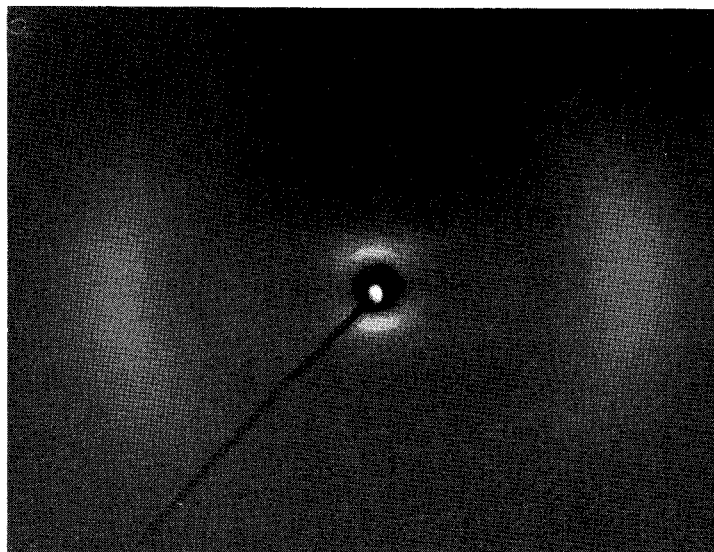


Figure 1. X-ray photograph of an oriented nematic at 34°C.

3. THEORETICAL BACKGROUND

In the nematic mesophase, the elongated molecules are relatively free to assume any orientation about their long axis and so may form statistically cylindrically symmetric rigid rods. For X-ray diffraction purposes of course, the molecules do not need to be physically rotating in order to liken them to cylindrically symmetric rods. The X-ray technique can only record intensities averaged over a relatively long time and over the irradiated macroscopic volume. The assumption of effective or average cylindrical symmetry is therefore justified [9 (a)]. The order parameters \bar{P}_2 and \bar{P}_4 for such rods in a uniaxial phase are defined by

$$\bar{P}_L = \int_0^{\pi/2} P_L(\cos \beta) f(\beta) \sin \beta \, d\beta \bigg/ \int_0^{\pi/2} f(\beta) \sin \beta \, d\beta.$$

with $L=2$ and 4 . $P_L(\cos \beta)$ is the Legendre polynomial of degree L and $f(\beta)$ is the singlet orientational distribution function. It gives the probability of finding a molecule at an angle β to the director, and describes the long range orientational ordering of the molecules. No measurements of $f(\beta)$ were reported until the work by Leadbetter and Norris [10] who gave a relationship between $I(\psi)$ and $f(\beta)$. According to them the intensity $I(\psi)$ around the diffuse equatorial arc is related to the distribution function by

$$I(\psi) = C \int_{\beta=\psi}^{\pi/2} f_a(\beta) \sec^2 \psi [\tan^2 \beta - \tan^2 \psi]^{-1/2} \sin \beta \, d\beta,$$

where $f_a(\beta)$ describes the distribution function for the orientation β of a local cluster of molecules with respect to the director. In deriving this expression they have assumed that the molecules are rigid, rod-like and are perfectly aligned in the cluster; they have shown that $f_a(\beta)$ may be expected to be close to the singlet distribution function $f(\beta)$.

A computer programme was written to calculate $f(\beta)$ using the experimental values of $I(\psi)$. $I(\psi)$ and $f(\beta)$ are expanded in series with even powers of $\cos \psi$ and $\cos \beta$ respectively. The coefficients of different terms in the expansion for $I(\psi)$ are determined from experiment and these were used to calculate the coefficients of different terms retained in the truncated series for $f(\beta)$. In all our calculations we have found that the series converge rapidly. We retained eight terms in the expansion and found that the agreement between observed and calculated intensities was nearly perfect.

Vainshtein [11] obtained a fairly good approximation for the order parameters by replacing $f(\beta)$ with $I(\beta)$, the X-ray intensity along the arc of the main equatorial reflection, keeping the Bragg angle constant ($\beta=0$, at the maximum). In our previous work on 4-methoxybenzylidene-4'-*n*-butylaniline [4] we calculated the order parameters using the Vainshtein approximation. In this paper the order parameters calculated from this approximation are denoted by \bar{P}_{2v} and \bar{P}_{4v} ; order parameters obtained from $f(\beta)$ are referred to as \bar{P}_{2d} and \bar{P}_{4d} .

4. RESULTS AND DISCUSSIONS

X-ray diffraction photographs of the sample were taken at different temperatures starting from the solid phase at room temperature to the isotropic phase. The photographs of the oriented sample have two diffuse outer maxima and two

inner maxima perpendicular to the outer ones as shown in figure 1. The diffraction patterns have been analysed to calculate l and D as given by de Vries [12]. D , the average distance between the neighbouring molecules, is calculated from the diameter of the outer ring with $2D \sin \theta = 1.117 \lambda$. l , which is often close to the molecular length is calculated from the Bragg formula from the diameter of the inner ring. The temperature dependence of these parameters has been discussed by de Vries [13, 14]. In our case it was found that D increases with temperature and remains fairly constant in the supercooled region. The dependence of l on temperature is not very clear, it varies between 27 Å to 29 Å. With the help of stereomodel units (Prentice Hall, Inc., West Nyack, New York 10984) we have constructed a possible conformation for CPHB and measured the molecular length in its completely extended form; this gives 21 Å. This value is seen to be much smaller than the experimental l result which is attributed to the antiparallel association of molecules in the nematic phase. It has been found that cyano compounds with alkyl end groups have very large dipole moment along their major axis. The anti-parallel ordering of the molecules may be due to dipole-dipole interactions. Similar results have been observed from X-ray diffraction studies by Leadbetter [15] and Lydon [16].

Variations of the normalized distribution function $f(\beta)$ with β as obtained from $I(\psi)$ at different temperatures are shown in figure 2. As expected the distribution function broadens at high temperatures. The temperature dependence of the order parameters \bar{P}_2 and \bar{P}_4 is shown in figures 3 together with the Maier-Saupe molecular field predictions [17]. The order parameters are estimated to be accurate to within ± 0.02 . The \bar{P}_{2d} and \bar{P}_{4d} values are always greater than the \bar{P}_{2v} and \bar{P}_{4v} values as predicted by Vainshtein [11]. Although the Maier-Saupe predictions show the same qualitative behaviour as the measured

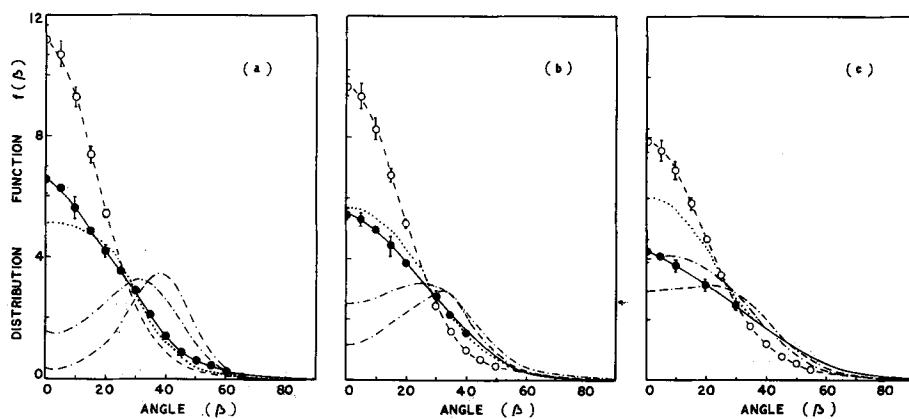


Figure 2. Normalized orientational distribution function $f(\beta)$ against β , (a) at 39°C, (b) at 49°C, (c) at 55.5°C. —●—●—●— Calculated $f(\beta)$ from X-ray intensity data. —○—○—○— Calculated $f(\beta)$ from the Maier-Saupe molecular field potential $U(\beta)k^{-1} = -(2137 \pm 83)\bar{P}_2P_2(\cos \beta)$. Calculated $f(\beta)$ from a pseudo-potential containing the $P_4(\cos \beta)$ term for $U(\beta)k^{-1} = -(2137)\bar{P}_2P_2(\cos \beta) + (3925 + 2139)\bar{P}_4P_4(\cos \beta)$, —·—·—·—·— $U(\beta)k^{-1} = -(2137)\bar{P}_2P_2(\cos \beta) + (3925)\bar{P}_4P_4(\cos \beta)$, - - - - $U(\beta)k^{-1} = -(2137)\bar{P}_2P_2(\cos \beta) + (3925 - 2139)\bar{P}_4P_4(\cos \beta)$.

quantities there are significant quantitative discrepancies. \bar{P}_2 is found to be larger than that predicted by the Maier-Saupe theory. Such differences were found by Leadbetter and Norris [10] for 4,4-di-*n*-heptyloxyazoxybenzene and 4,4'-di-*n*-octyloxyazoxybenzene. Short range dipole-dipole interactions may increase the value of \bar{P}_2 . \bar{P}_4 is significantly lower than the Maier-Saupe predictions. Such behaviour of \bar{P}_4 has already been observed in some liquid crystals [1, 18]. In certain cases, values of \bar{P}_4 are even found to be negative.

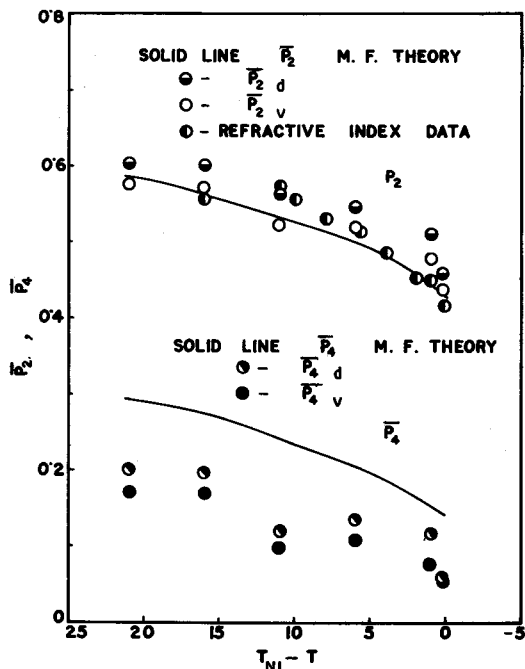


Figure 3. Variation of the order parameters with temperature.

The normalized singlet orientational distribution function $f(\beta)$ is related to the pseudo-potential $U(\beta)$ by

$$f(\beta) = \exp[-U(\beta)/kT] / \int_0^{\pi/2} \exp[-U(\beta)/kT] \sin \beta d\beta. \quad (1)$$

We have fitted our $f(\beta)$ values to

$$f(\beta) = Z^{-1} \exp \left[\sum_L a_L P_L(\cos \beta) \right], \quad (2)$$

where Z is the orientational partition function, which at a particular temperature is treated as a constant. Terms with L up to 10 (L even) were retained in the series and so a good idea of the form of the pseudopotential was obtained. This was achieved by a least square fitting of the $\ln f(\beta)$ values. The values of a_L obtained for different temperatures are given in the table ($a_0 \equiv -\ln Z$). Since the error analysis is time consuming on a desk top computer which we use, we estimated the errors for only two temperatures (34°C and 54°C). The percentage errors for the different coefficients are a_0 (≈ 2 per cent), a_2 (≈ 1 per cent),

a_4 (≈ 4 per cent), a_6 (≈ 5 per cent), a_8 (≈ 20 per cent) and a_{10} (≈ 25 per cent). We find that the first few coefficients are quite well defined within an acceptable range of values. The observation that the series is not dominated by the first term i.e. $a_2 P_2(\cos \beta)$ confirms our previous conclusion, in a more direct way, that the Maier-Saupe theory cannot be applied to this nematogen.

 a_L and b_L values

Temperature/ $^{\circ}\text{C}$	a_0	a_2	a_4	a_6	a_8	a_{10}	b_2/k	b_4/k
34	-1.328	4.001	-1.338	0.915	-0.743	0.460	2043	-2085
39	-1.306	3.909	-1.100	0.467	-0.449	0.337	2035	-1823
44	-1.197	3.808	-1.567	1.355	-1.367	0.861	2141	-2955
49	-1.170	3.803	-1.645	1.129	-0.808	0.486	2238	-3966
54	-0.926	3.309	-1.579	1.277	-0.693	0.333	2198	-5292
55.5	-0.826	3.088	-1.456	0.953	-0.712	0.432	2174	-7427

The appearance of higher rank terms in the pseudo-potential is consistent with developments [19, 20] of the Maier-Saupe theory to allow for a more general anisotropic pair potential. These predict [17]

$$U(\beta) = \sum_{L(\text{even})} b_L \bar{P}_L P_L(\cos \beta). \quad (3)$$

The coefficients b_L can now be determined simply using the relation $b_L = -ka_L T / \bar{P}_L$ and we have done so for b_2 and b_4 (cf. the last two columns of the table). It is expected that b_L should be a function of the average intermolecular separation, which in turn depends upon temperature. Hence, since we are confined to a narrow range of temperature ($\sim 20^{\circ}\text{C}$) and the cubic expansivity is expected to be small (except, perhaps near the transition) we can treat the b_L as constants. Indeed the b_2 values are observed to be almost constant and show no systematic variation with temperature. On the other hand the b_4 values do exhibit a systematic variation with temperature which is especially prominent near the transition temperature. We do not know why b_4 should show so large a temperature variation while b_2 is almost constant. This may be related to the pair potential between the CPHB molecules. These have large permanent dipole moments and so the pair potential has a large contribution from permanent dipole-permanent dipole interaction. It would be interesting to find out if other liquid crystal molecules having no permanent dipole moment show the same type of temperature variation of b_4 . Some work is progressing in our laboratory which may throw light on this point. This anomaly in the temperature dependence of b_2 and b_4 is quite unexpected, since according to theory [21] both of these coefficients should vary directly with the density, which in the narrow temperature range concerned is almost constant.

The temperature variation of b_4 shows quite clearly that the extension of the Maier-Saupe does not account for the behaviour of CPHB. This conclusion may be demonstrated in another way. If we neglect the temperature variation of b_4 , and take the average over six temperatures, we can write the angular part

of the pseudopotential up to the $P_4(\cos \beta)$ term as

$$U(\beta)k^{-1} = -(2137 \pm 83)\bar{P}_2P_2(\cos \beta) + (3925 \pm 2139)\bar{P}_4P_4(\cos \beta) \quad (4)$$

The large standard deviation of b_4 is caused by its temperature variation. Since, the temperature variation of density is greater near the transition temperature we also tried to calculate the pseudo-potential by taking an average over four temperatures (neglecting the values at 54°C and 55.5°C). This gives

$$U(\beta)k^{-1} = -(2114 \pm 95)\bar{P}_2P_2(\cos \beta) + (2707 \pm 968)\bar{P}_4P_4(\cos \beta).$$

The standard deviation of b_4 though reduced from the previous expression, is unreasonably large.

We have calculated the normalized $f(\beta)$ values using the pseudo-potentials in (4) as well as from the same potential but neglecting the $P_4(\cos \beta)$ term. Our results from three different temperatures are shown in figure 2 (*a*, *b*, *c*). We find that by retaining only the $P_2(\cos \beta)$ term in the pseudo-potential (Maier-Saupe theory) the value of $f(\beta)$ calculated are in poor agreement with the values determined from the X-ray data. Including $P_4(\cos \beta)$ terms in the potential [19] improves the agreement, however nothing definite can be said due to large uncertainty in b_4 . The need to include the $P_4(\cos \beta)$ term may however not stem from their presence in the pair potential but from the failure of the molecular field approximation as applied in the Maier-Saupe theory [22].

In conclusion, the orientational distribution functions obtained by us from the X-ray diffraction data do not agree well with the distribution function generated from the commonly accepted molecular field potential even after including the $P_4(\cos \beta)$ term. The discrepancy may have various causes. Firstly, it may be due to the particular pseudo-potential used, for example it has been shown by Humphries, James and Luckhurst [19] that under true cylindrical symmetry of the mesophase the pseudo-potential will contain terms of the type $P_L \langle \bar{P}_M \rangle$ ($L \neq M$) which are not generally included in the potential. Secondly, the permanent dipole-permanent dipole interaction may modify the pseudo-potential in our case. Chandrasekhar *et al.* [23] have included the dipole-dipole interaction in the potential and it is clear that the form of the orientational distribution function will depend upon this potential. Thirdly, the rigid cylindrical shape of the molecule assumed is obviously an over simplification. However, although an attempt has been made [24] to allow for the molecular flexibility the theory has not been used to evaluate the distribution function available from X-ray scattering experiments. In our opinion, further analysis of accurate experimental data on various liquid crystals is needed before the cause of the discrepancy can be accounted for with certainty.

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