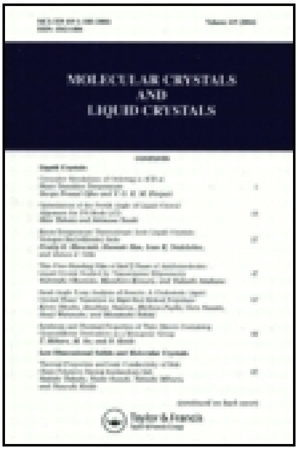

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Orientational Order Parameters of Binary Mixture 8OCB + 6OCB Showing Re-entrant Nematic Phase

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Orientational order parameters have been determined for the mixture of hexyloxy cyanobiphenyl (6OCB) and octyloxy cyanobiphenyl (8OCB) for three different compositions containing molar concentration 0.289, 0.337 and 0.401 of 6OCB over the complete mesomorphic ranges. Both x-ray diffraction and refractive index measurements on aligned samples have been used for order parameter calculations. The experimental order parameter values show a small enhancement with decreasing temperature in the smectic phase, but decrease on entering the re-entrant nematic phase. Smectic fluctuations were observed even in the nematic phase of the mixtures not having any smectic or re-entrant nematic phase. Previous order parameter values obtained from NMR studies are much smaller than ours. However, since this NMR measurement used a rather small molecule (*p*-xylene) as a probe, the ordering of these probe molecules may be less than that of the liquid crystalline mesophase studied.

Keywords: re-entrant nematic, smectic fluctuations, order parameters

INTRODUCTION

Since its discovery by Cladis[1] in 1975, the re-entrant nematic phase has been studied extensively. This phase has been observed in mixtures[1,2] as well as in single components at high[3] and atmospheric[4] pressures. However, orientational order parameter, $\langle P_2 \rangle$, measurements on systems showing re-entrant nematic phase seem to be scanty.[5,6,7] Moreover there is some anomaly in the values obtained from ESR[5] and NMR[6,7] depending upon the nature of the probe used. We are not aware of any $\langle P_2 \rangle$ determination in re-entrant nematic system from x-ray diffraction studies. Hence, we decided to study the variation of $\langle P_2 \rangle$ with temperature in the mixtures of hexyloxycyanobiphenyl (6OCB) and octyloxycyanobiphenyl (8OCB), one of the most common systems showing re-entrant nematic phase from both x-ray diffraction and refractive index measurements. This mixture shows normal nematic, smectic A and re-entrant nematic phases only if the molar concentration of 6OCB is less than 0.30. In the present paper, we have used mixtures of 6OCB and 8OCB having molar concentrations 0.289, 0.337 and 0.401 of 6OCB, i.e., only one (0.289) showing re-entrant phase. Due to the lack of cooling capability in our experimental set up, we could not work with other compositions which exhibit re-entrant phase below room temperature. The reason for the determination of order parameters in the mixtures showing only normal nematic phase was to check if $\langle P_2 \rangle$ values are enhanced due to smectic fluctuations. Such smectic fluctuations in the normal nematic phase of this mixture have been observed experimentally, among others, by Guillon *et al.*,[2] Jadzya *et al.*,[8] and Kortan *et al.*[9]

EXPERIMENTAL

The chemicals 60CB and 80CB were obtained from British Drug House, (at present M/S E. Merck), U.K. and were used without further purification. After mixing the weighed amount of components, each mixture was heated to a temperature slightly above its nematic-isotropic transition temperature and kept at that temperature for 24 hours to ensure the formation of a homogeneous mixture. Three mixtures having molar concentrations 0.289 (mixture A), 0.337 (mixture B) and 0.401 (mixture C) of 60CB were prepared. Transition temperatures of the pure compounds and these mixtures were determined using a Mettler FP 80/82 Thermosystem. The measured values agree well with those that can be read from the phase diagram for this system given by Kortan *et al.*[9] The experimental set up and the procedure for order parameter determination from x-ray diffraction[10] and refractive index[11] studies have been described in detail in earlier publications.

RESULTS AND DISCUSSIONS

The temperature variations of the orientational order parameters $\langle P_2 \rangle$, as obtained from x-ray diffraction and refractive index measurements, are shown in Figure 1 for mixture A. Also shown in the same figure are the $\langle P_4 \rangle$ values obtained from the x-ray study over the same temperature range. Figures 2 and 3 show the corresponding quantities for mixture B and mixture C, respectively. In all the cases we find that the $\langle P_2 \rangle$ values determined from the x-ray diffraction measurements are substantially lower than those obtained from the refractive index data, except near the nematic-isotropic transition temperature. This type of discrepancy between two sets of experimental $\langle P_2 \rangle$ values, one calculated from x-ray and the other from refractive index data, has been noted before and the possible reasons for this have been discussed in detail by Mitra *et al.*[12] In the present case the $\langle P_2 \rangle$ values obtained from the refractive index data are much larger than those obtained from x-ray diffraction data. This may be due to the fact that the Haller's procedure,[12a] used in calculating molecular polarizability anisotropy, is somewhat arbitrary and the resulting $\langle P_2 \rangle$ values are relative rather than absolute. Moreover, refractive index $\langle P_2 \rangle$ values show anomalous temperature variation in the smectic phase. It is well-known that in a smectic phase, which is precursor of a re-entrant nematic phase, a change in degree and form of molecular association takes place with the change in temperature. In calculating the order parameter $\langle P_2 \rangle$, from the refractive index data, we assume that the molecular polarizability anisotropy does not change with

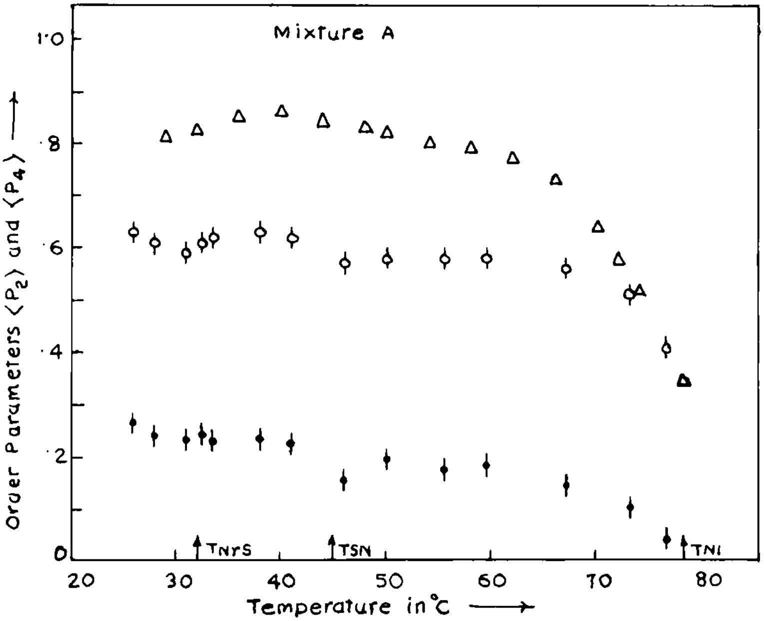

FIGURE 1 Temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for mixture A. Key to symbols: (△) Refractive index data for $\langle P_2 \rangle$. (○) x-ray data for $\langle P_2 \rangle$. (●) x-ray data for $\langle P_4 \rangle$. T_{NI} = nematic-isotropic transition temperature. T_{SN} = smectic-nematic transition temperature. T_{NrS} = re-entrant nematic-smectic transition temperature. Vertical bars show estimated errors.

temperature. However, in the present case it is certain that effective molecular polarizability anisotropy will change with temperature due to change in degree and form of molecular association. In fact we expect that with decreasing temperature the degree of molecular association will increase, thereby decreasing the effective molecular polarizability anisotropy, since a dimer of two cyanobiphenyl molecules will have smaller length to width ratio than a single cyanobiphenyl molecule. Thus, by a crude reasoning, we can understand why order parameters in the smectic phase calculated from the refractive index data behaves anomalously. The refractive index data in the re-entrant nematic phase is scanty, since the surface aligned sample solidify at a higher temperature than the sample aligned magnetically for x-ray studies. However, from Figure 1 it can be seen that experimental $\langle P_2 \rangle$ values, obtained from x-ray diffraction data, show an enhancement in their magnitudes within the smectic phase, they also show a definite decrease with decreasing temperature within the re-entrant nematic phase. This behaviour appears to be in agreement with the theoretical prediction of Luckhurst and Timmi.[14] However, we have not tried to implement a quantitative fit with this theory in view of the fact that no physical insight into the re-entrant phenomenon in mixtures seems likely from the temperature variation of the α parameter which is used in the theory. Regarding mixtures B and C, which show normal nematic phase only, there seems to be some enhancement of the $\langle P_2 \rangle$ values, as obtained from the x-ray data, within the temperature range in which mixture A shows a smectic phase (Figures 2 and 3). Both the sets of $\langle P_2 \rangle$ values for mixture B show a decrease with decreasing

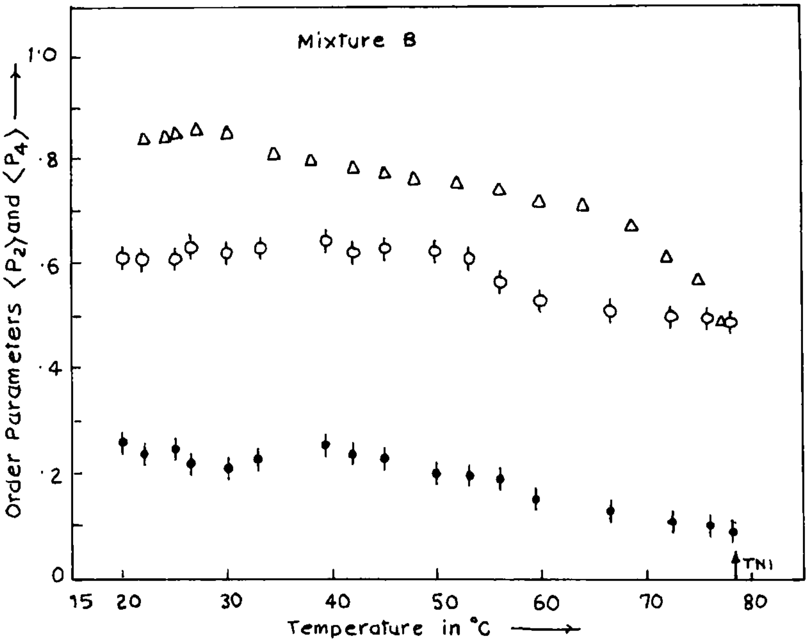

FIGURE 2 Temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for mixture B. Symbols have same meaning as in Figure 1.

temperature in the range 20°C to 30°C. It is interesting to note that mixture A shows re-entrant nematic phase exactly in this temperature range. For mixture C (Figure 3) while the temperature variation of $\langle P_2 \rangle$ values from refractive index data show normal trend, those calculated from x-ray data again show anomalous temperature dependence near 30°C. However, enhancement of $\langle P_2 \rangle$ values in the temperature range 35°C to 50°C is more pronounced in the mixture B than in mixture C where it is barely noticeable. This is expected, because the composition of mixture B ($x = 0.337$) is quite near to that of mixture A ($x = 0.289$), which shows smectic and re-entrant nematic phases. Mixture C ($x = 0.401$) is far off from the mixture A and hence the effect of smectic fluctuations on it is much less. Figure 4 shows the x-ray photograph of an aligned sample of mixture B at 40°C, where a pair of spots in the meridional direction can be seen. Such spots in an otherwise normal nematic phase x-ray pattern indicate the presence of cybotactic groups which can be considered as the result of smectic fluctuations. Such smectic fluctuations in the nematic phase of mixtures showing smectic and re-entrant nematic phases have been previously observed by Guillon *et al.*[2] from x-ray studies. However, our case differs from theirs in as much as mixtures B and C have *a nematic phase only*. Jadzyn *et al.*,[8] from dielectric measurements, inferred the presence of smectic fluctuations in the similar mixtures showing a nematic phase only. Kortan *et al.*[9] also observed smectic fluctuations in their x-ray diffraction studies of the same mixture. Hence, our results not only confirm the previous observations but also show that the orientational order parameter values increase in the temperature range where purely nematic mixtures show smectic fluctuations.

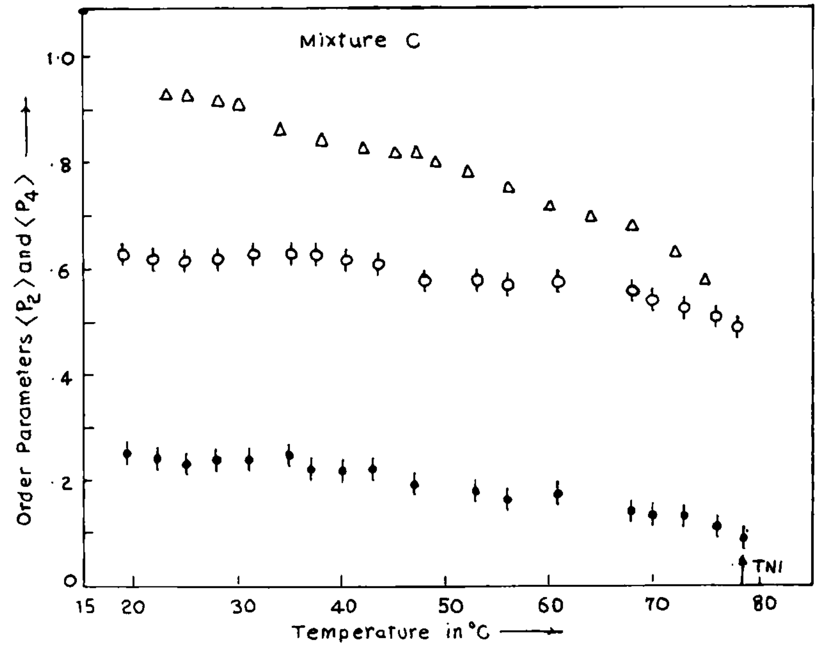

FIGURE 3 Temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for mixture C. Symbols have same meaning as in Figure 1.

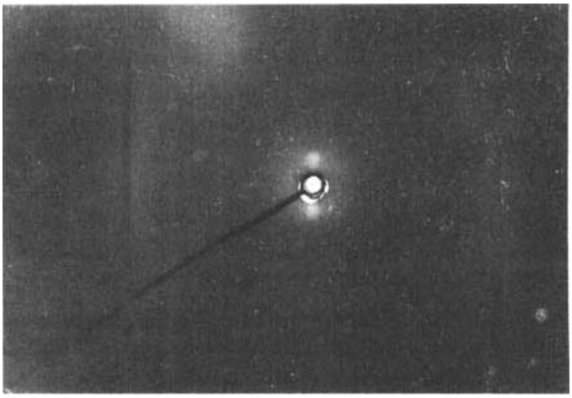

FIGURE 4 X-ray diffraction photograph from an aligned sample of mixture B recorded at 40°C.

We have also observed two sets of equatorial arcs in our x-ray diffraction photographs. We believe that the two sets correspond to diffraction from the nearest and the next nearest neighbours. The ratio of the distances between the nearest and the next nearest neighbours, calculated using the Bragg equations, is approximately 1.8. This value is somewhat greater than 1.732 which corresponds to hexagonal packing. This difference can be explained in that the nematic phase does not have translational order. We have also calculated $\langle P_2 \rangle$ from the inner pair of arcs (i.e. from the diffraction pattern corresponding to the next nearest neighbours).

We have obtained almost identical $\langle P_2 \rangle$ values as from the outer pair of arcs. This means that the orientational correlation between the molecules are very good at least up to the second nearest neighbour. This inference justifies the approximation made by Leadbetter[15] for the analysis of x-ray data, where he assumes that liquid crystal mesophase consists of many very small domains, each domain having order parameter equal to one, and an angular distribution of the directors of the domains which is identical to a singlet distribution function.

Our order parameter values for mixture A do not agree with those obtained by Vaz *et al.*[6,7] for a mixture with almost identical composition and obtained using NMR techniques. However, in their study Vaz *et al.*[6,7] used a probe molecule, namely, *p*-xylene. We believe that since *p*-xylene is a short molecule (molecular length 9 Å) when compared to 6OCB (length 17.5 Å) or 8OCB (length 20.5 Å), it does not orient well in the liquid crystalline matrix of the mixture, and hence gives an underestimate of the $\langle P_2 \rangle$ values. The shape of the probe can have a large effect as can be seen in the ESR study[5] in another re-entrant system. However, it should be noted that while NMR data can be analysed to obtain both orientational order parameter ($S_{zz} \equiv \langle P_2 \rangle$) and biaxial parameter ($S_{xx} - S_{yy}$), the x-ray diffraction intensity data, being space and time average of scattering from electron distribution of molecules assume molecules to have cylindrical symmetry, can only be utilized to calculate $\langle P_2 \rangle$ values. Hence, it may not be proper to compare the order parameter values obtained by using these two different techniques. Our results are in agreement with those of the birefringence measurements of Chen[13] at least over the limited temperature range over which they presented their data.

Acknowledgments

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