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THE ORIENTATIONAL ORDER OF A RE-ENTRANT NEMATIC PHASE. AN ELECTRON RESONANCE INVESTIGATION

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ABSTRACT We have investigated the orientational order in a re-entrant nematic and its preceding phases using steroidal and alkyl nitroxide spin probes. The order parameter for the steroidal spin probe in the re-entrant nematic phase is found to be an extension of its value in the preceding smectic A phase. In contrast the gradient of the order parameter for the alkyl spin probe exhibits a marked discontinuity at the smectic A - re-entrant nematic transition.

At constant composition and pressure a system invariably undergoes phase transitions to states of higher order as the temperature is lowered. Such behaviour is well exemplified by the rich polymorphism of many mesogens;[1] thus terephthalylidene-bis-4-n-butylaniline exhibits the following sequence of phases on cooling - isotropic, nematic, smectic A, smectic C, smectic H and smectic G, each phase being more ordered than its predecessor. The discovery by Cladis[2] that a mesogen could possess a nematic, a smectic and then another nematic phase on cooling was therefore both fascinating and important. This third phase is called a re-entrant nematic and it is unexpected because it should be less ordered than the previous smectic A. The original discovery was made for a binary mixture of mesogens but it was soon shown that pure systems may also possess a re-entrant nematic phase, albeit at pressures above atmospheric.[3] However it was only a matter of time before re-entrant nematics existing at atmospheric pressure were obtained.[4]

To learn more about this important phase we have investigated the orientational order in mixtures of N-4-cyanobenzylidene-4'-n-octyloxyaniline (CBOOA) and 4-n-hexyloxybenzylidene-4'-aminobenzonitrile (HBAB) originally studied by Cladis.[2] CBOOA was synthesised without undue difficulty using a prescribed route;[5] the transition temperatures T_{CS_A} 74°C, T_{S_AN} 84.5°C and T_{NI} 108.5°C were in good agreement with the literature values.[6] However the synthesis of HBAB presented us with far greater difficulties; after trying several procedures we finally obtained this material by heating an equimolar mixture of 4-n-hexyloxy-benzaldehyde and 4-aminobenzonitrile under vacuum at 110°C for 24 hours. The product was recrystallized twice from n-hexane and its transition temperatures T_{CN} 57°C and T_{NI} 99°C were in good accord[7] with other studies. The re-entrant nematic phase is only observed for mixtures of CBOOA with small quantities of HBAB; these were prepared by heating the appropriate quantities in the isotropic phase at 120°C under vacuum for several hours.[2]

The orientational order was studied using electron resonance spectroscopy and so the mesogen had to be doped with a paramagnetic spin probe.[8] We have employed two nitroxide radicals for this purpose; they were the steroidal spin probe (3-spiro[2'-N-oxyl-3',3'-dimethyloxazolidene])-5α-cholestane and the alkyl probe 9-spiro[2'-N-oxyl-3',3'-dimethyloxazolidene]-n-heptadecane. These particular nitroxides were chosen because the steroidal probe tends to sample the order of the rigid core of the mesogen while the alkyl probe is ordered primarily via its interaction with the alkyl chains in the mesophase.[9] The electron resonance spectra of both spin probes in a monodomain sample consist of three nitrogen hyperfine lines. When the magnetic field is parallel to the director the hyperfine spacing, $\bar{a}$, is related to the orientational order by[8]

$$\bar{a} = a - (1/2)A'_{\parallel}\,\bar{P}_2$$

for the steroidal spin probe and

$$\bar{a} = a + A'_{\parallel}\,\bar{P}_2$$

for the alkyl probe. Here a is the isotropic nitrogen coupling constant and $A'_{\parallel}$ is the component of the anisotropic hyperfine tensor perpendicular to the oxazolidene ring. The ordering matrix[8] for the steroidal spin probe is essentially cylindrically symmetric about an axis in the plane of the oxazolidene ring and at an angle of about 108° to the N-O bond.[10] The order parameter for this effective symmetry axis is denoted by $\bar{P}_2$. For the alkyl spin probe, $\bar{P}_2$ corresponds to the order parameter for the axis perpendicular to the oxazolidene ring and so parallel to the long axis for the all-trans configuration. The value of $A_{\parallel}'$ is taken to be 48.6 MHz for both spin probes.[11]

We begin with the order parameter for the steroidal spin probe in pure CBOOA; the results for this are indicated by triangles in Fig.1 as a function of the relative temperature (T_{NI}-T). It is clear that the orientational order increases with decreasing temperature within the nematic range and that this behaviour persists in the smectic A phase. To within our experimental accuracy the order parameter $\overline{P}_2$ is continuous at the nematic-smectic A transition which we

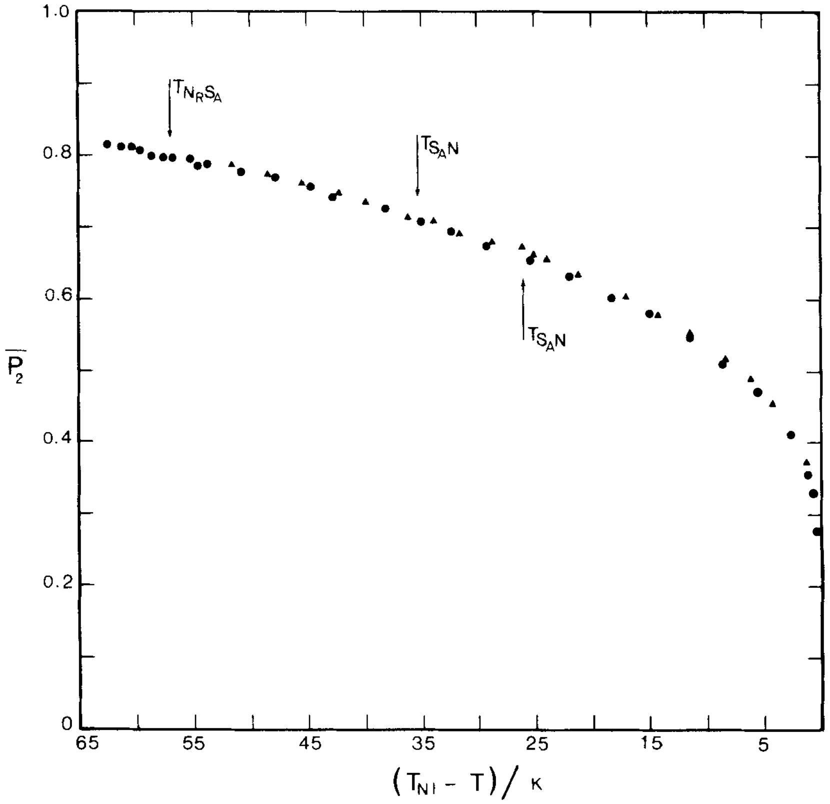

FIGURE 1. The dependence of the orientational order parameter for the steroidal spin probe on the relative temperature for CBOOA (▲) and the mixture containing 9% HBAB (●). The lower arrow indicates the transition temperature for CBOOA and the upper arrows are for the transitions exhibited by the mixture.

would class therefore as second order. This is in accord with some but not all previous studies of the transition;[12] however it is important to realise that different properties may well behave differently at the transition.

We have studied several mixtures of HBAB in CBOOA and for comparison we show the values of $\overline{P}_2$ obtained for the 9% HBAB mixture as circles in Fig.1. It is apparent that the order parameter for the steroidal spin probe in this mixture behaves in a virtually identical manner to that for pure CBOOA. More importantly the order parameter in the re-entrant nematic is simply a continuation of its behaviour in the preceding smectic A phase. We did confirm the presence of the re-entrant nematic by rotating the sample tube in the spectrometer and observing the magnetically induced realignment of the director via changes in the spectrum. Such realignment is not found for the smectic A phase.[8] It would appear therefore that the orientational order of the steroidal spin probe and hence that for the cores of the mesogenic molecules is insensitive to the spatial order or disorder of the various liquid crystal phases exhibited by the mixture. This conclusion is in accord with measurements of the magnetic anisotropy for the pure mesogen 4-n-octyloxybenzoyloxy-4'-cyanostilbene which exhibits a re-entrant nematic phase at atmospheric pressure.[13] Clearly any theory of the re-entrant nematic phase must be able to predict this independence for $\overline{P}_2$. Alternatively this behaviour may be used as justification for the neglect of the orientational order parameter in the Landau theory developed by Pershan and Prost.[14]

The results obtained for the alkyl spin probe are, in many ways, more intriguing than those found for the steroidal probe. The variation of the orientational order parameter with the relative temperature is shown in Fig.2 as triangles for CBOOA. We see that $\overline{P}_2$ increases with decreasing temperature within the nematic phase but then passes through a maximum near T_{S_AN} and falls slowly with decreasing temperature within the smectic A phase. This unusual behaviour may be understood in the following way. The spatial disorder characteristic of the nematic phase ensures that the spin probe is ordered by a molecular field generated by its interactions with both the alkyl chain and aromatic core of the mesogenic molecules. Since the orientational order and hence the molecular field of both increase with decreasing temperature the order for the spin probe will also increase. In contrast the layer structure of the smectic A phase provides an inhomogeneous environment with a region composed largely of alkyl chains and another of aromatic cores. For energetic and entropic reasons the alkyl spin probe prefers to associate more and more with the alkyl regions as the temperature is lowered. The spin probe moves therefore from a region of high order (the cores) to one of low order (the chains). Of course the orientational order of the chains increases with decreasing temperature but on balance the decreased association with the core region leads to a small reduction of $\overline{P}_2$ for the alkyl spin probe with decreasing temperature in the smectic A phase.

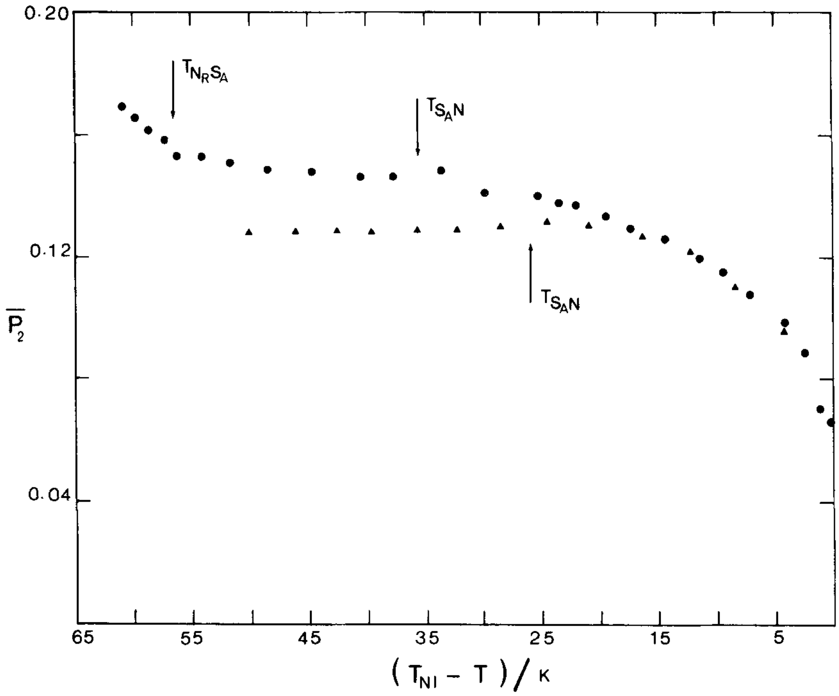

FIGURE 2. The temperature dependence of $\overline{P}_2$ for the alkyl spin probe dissolved in CBOOA (▲) and the mixture containing 9% HBAB (●). The lower arrow indicates the transition temperature for CBOOA and the upper arrows are for the transitions exhibited by the mixture.

We now turn to the behaviour of $\overline{P}_2$ for the alkyl spin probe in the 9% mixture of HBAB in CBOOA which possesses a re-entrant nematic phase. The results for this mixture are shown as circles in Fig.2. The most interesting and apparent feature of these results is the rapid rise of $\overline{P}_2$ with decreasing temperature in the re-entrant nematic which contrasts with the essential temperature independence of $\overline{P}_2$ in the preceding smectic A. In addition we can see that the order parameter in the smectic A phase of the mixture is significantly larger than in the same phase of pure CBOOA. Of course the increase in $\overline{P}_2$ for the smectic A phase of the mixture simply implies an increase in the strength of the molecular field experienced by the spin probe. This increase can be understood in terms of McMillan's theory of the smectic A phase.[15] The theory predicts that the increase in the length of the nematic range for the mixture produces an increase in the orientational order of the smectic A phase in comparison with pure CBOOA. Further the spatial order in the resultant smectic A should be less than that for CBOOA with its shorter nematic range;[15] as a result the inhomogeniety of the smectic phase is less pronounced. These two changes in the nature of the smectic A phase on the addition of HBAB to CBOOA predicted by McMillan's theory should produce the requisite increase in the strength of the molecular field experienced by the alkyl spin probe in the mixture. When the layer structure of the smectic A phase is destroyed at the transition to the re-entrant nematic we expect the order parameter of the alkyl spin probe to increase because its environment has a greater contribution from the cores. The observation that $\overline{P}_2$ is continuous at the transition suggests that the spatial order parameter also changes continuously. However the relatively rapid increase in the orientational order for the alkyl spin probe in the re-entrant nematic does imply that the environment of the spin probe changes dramatically. This contrasts with the small change found for the nematic phase preceding the smectic A. It would appear therefore that the pretransitional effects at the transition to the smectic A phase are less pronounced for the nematic than for the re-entrant nematic phase. However it remains to be seen whether the same behaviour is exhibited by other mesogens with re-entrant nematic phases.

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REFERENCES

1. See, for example, G.W. Gray, The Molecular Physics of Liquid Crystals, edited by G.R. Luckhurst and G.W. Gray (Academic Press 1979) chapter 12
2. P.E. Cladis, Phys. Rev. Lett., 35, 48 (1975)
3. P.E. Cladis, R.K. Bogardus, W.B. Daniels and G.N. Taylor, Phys. Rev. Lett., 39, 720 (1979)
4. F. Hardouin, G. Sigaud, M.F. Achard and H. Gasparoux, Phys. Lett., 71A, 347 (1979)
5. P. Keller and L. Liebert, Liquid Crystals, edited by L. Liebert (Solid State Physics, Supplement 14, Academic Press, 1978) chapter 2
6. P.E. Cladis, R.K. Bogardus and D. Aadsen, Phys. Rev., A18, 2292 (1978)
7. M. Schadt, J. Chem. Phys., 56, 1494 (1972)
8. See, for example, G.R. Luckhurst, Liquid Crystals and Plastic Crystals, Volume 2, edited by G.W. Gray and P.A. Winsor (Ellis Horwood, 1974) chapter 7
9. D. Sy and M. Ptak, Mol. Cryst. Liq. Cryst., 39, 53 (1977)
10. S.G. Carr, S.K. Khoo, G.R. Luckhurst and C. Zannoni, Mol. Cryst. Liq. Cryst., 35, 7 (1976)
11. R.J. Gaffney and H.M. McConnell, J. Magn. Resonance, 16, 1 (1974)
12. See, for example, D.E. Martire, The Molecular Physics of Liquid Crystals, edited by G.R. Luckhurst and G.W. Gray (Academic Press, 1979) chapter 10
13. F. Hardouin, G. Sigaud, M.F. Achard and H. Gasparoux, Sol. Stat. Comm., 30, 265 (1979)
14. P.S. Pershan and J. Prost, J. de Phys. Lett. (Paris) 40, L-27 (1979)
15. W.L. McMillan, Phys. Rev., A4, 1238 (1971)