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## Molecular Crystals and Liquid Crystals

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S. Chandrasekhar<sup>a</sup>

<sup>a</sup> Raman Research Institute, Bangalore, India

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# Relation Between Molecular Structure and Liquid Crystalline Properties†

S. CHANDRASEKHAR

*Raman Research Institute, Bangalore 560080, India*

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The paper draws attention to a few selected problems that are of interest from the molecular point of view. In particular, the following topics are discussed briefly: (i) the activation energy for low frequency dielectric relaxation in the nematic and smectic *A* phases, (ii) near-neighbor correlation and some of its consequences, e.g., reentrant polymorphism, and (iii) the possibility of producing new kinds of thermotropic phases, e.g., biaxial nematics and discotic smectics, by bridging the gap between rod-like and disk-like mesogens.

## INTRODUCTION

Advances in liquid crystal research in the last 10 or 15 years have depended a great deal on the preparation of new and stable materials. Progress in the area of material development has been largely a matter of chemical intuition and experience, and not so much due to any theory relating liquid crystalline properties and molecular structure. The success of molecular theories of mesophases has not been all that spectacular primarily because the molecules themselves are so complex. For example, even a seemingly trivial question such as defining the long molecular axis does not have a straightforward answer: the geometrical long axis may not be the same as that derived from the optical polarizability or the diamagnetic susceptibility or the axis of molecular rotation. Not surprisingly, therefore, many simplifications

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have to be made in attempting to develop molecular models. The current theoretical situation has been summarized recently by Martha Cotter<sup>1</sup> and will not be repeated here. The aim of the present paper is to highlight a few selected problems which are of interest from the molecular point of view.

## LOW FREQUENCY DIELECTRIC RELAXATION

From the molecular arrangements in the nematic and smectic *A* phases, one would expect that a reorientation of the molecule about its short axis would be more difficult in the latter phase, or, more precisely, that the activation energy (*W*) for this reorientation would be greater in smectic *A*. Surprisingly, however, the converse is true in almost all the cases studied so far.

The available data are presented in Table I for three types of materials which show *N* and *A* phases. (i) Table I (a): negative dielectric anisotropy materials,  $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} < 0$ , the *A* phase is monolayer,  $d \sim l$ , where  $d$  is the layer spacing and  $l$  the molecular length; (ii) Table I (b): positive anisotropy materials  $\Delta\epsilon > 0$ ; the *A* phase is partially bilayer and designated  $A_d$  ( $l < d < 2l$ ); and (iii)

TABLE I  
Activation energies for low frequency dielectric relaxation  
in the nematic and smectic *A* phases

(a)  $\Delta\epsilon < 0$ , smectic *A*—monolayer

Chemical formula	Activation Energy (eV)		Ref.
	<i>N</i>	<i>A</i>	
$C_6H_{13}O-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-C_6H_{13}$	3.5	1.4	2
$C_{10}H_{21}O-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_5H_{11}$	2.1	1.56	3
$C_{10}H_{21}O-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_6H_{13}$	3.21	1.97	4
$C_{10}H_{21}O-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_7H_{15}$	3.18	2.16	5

(b)  $\Delta\epsilon > 0$ , smectic *A*—partially bilayer ( $A_u$ )

$C_8H_{17}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	0.67 0.69	0.46 0.50	6 7
$\text{CN}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{C}_8\text{H}_{17}\text{O}$	0.63	0.55	8
$\text{NO}_2-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{C}_8\text{H}_{17}\text{O}$	0.63	0.48	9
$C_{10}H_{21}\text{O}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_3(\text{Cl})-\text{OOC}-\text{C}_6\text{H}_4-\text{NO}_2$	0.81 (0.92)	0.52	10
$\text{CN}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{CH}_3\text{O})-\text{COO}-\text{C}_6\text{H}_4-\text{C}_{11}\text{H}_{23}$	1.27	0.78	11
$C_6H_{13}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$ (6OCB) +	0.82 (1.71)	0.72	12
$C_8H_{17}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$ (8OCB)			
$C_{10}H_{21}O-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3-\text{CN}$ +	1.0 (1.2)	0.6	10
$C_9H_{19}O-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{COO}-\text{C}_6\text{H}_3-\text{CN}$			
$C_7H_{15}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{CN}$ +	0.52	0.52	13
$C_8H_{17}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{CN}$			

(c)  $\Delta\epsilon > 0$ , smectic *A*—bilayer ( $A_2$ )

$\text{CN}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_5\text{H}_{11}$	0.70	0.63	14
$\text{CN}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_7\text{H}_{15}$	0.74	0.67	14

The activation energies given in brackets represent the values in the reentrant nematic phase.

Table I (c):  $\Delta\epsilon > 0$ ; the  $A$  phase is bilayer and designated  $A_2$  ( $d \sim 2l$ ). In all of them,  $W_A < W_N$ , except for the last case given in Table I(b), for which  $W_A = W_N$ . (It should be pointed out here that the definitions of  $A_d$  and  $A_2$  above and of  $A_1$  given later, though adequate for the present purpose, are somewhat crude. A more accurate description of these structures is based on the nature of the X-ray diffraction patterns obtained from these phases.)<sup>57</sup>

Even allowing for experimental inaccuracies, the overall evidence cannot be ignored. It may perhaps be argued that the packing in the  $A$  phase is such that there are more voids within the layers making it easier for the molecules to swing around. If this were the case, one would expect it to manifest itself in the lateral intermolecular spacing and in the in-plane correlation. However, X-ray evidence is definitely to the contrary. The early studies of de Vries<sup>15</sup> on 702, a negative anisotropy compound, indicate that the lateral intermolecular spacing as well as the lateral thermal expansion are, if anything, greater in the nematic than in the smectic, but the most convincing evidence is the recent *high resolution* X-ray work carried out by the MIT group<sup>16</sup> on the 8 OCB-6 OCB mixture. Figure 1 presents the scans (parallel and perpendicular to the director) of the liquid peak in the  $N$ ,  $A$  and

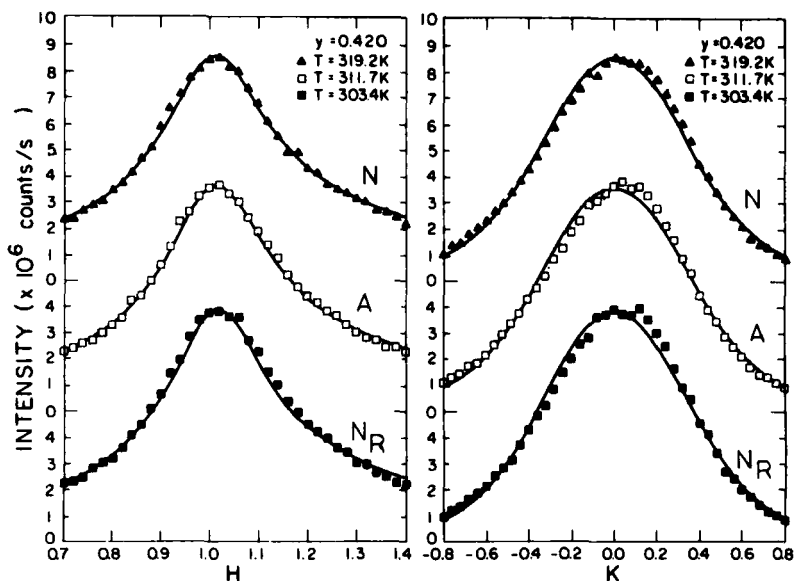


FIGURE 1 Parallel and perpendicular scans of the in-plane (liquid) peak in the nematic, smectic  $A$  and reentrant nematic phases of the 8 OCB-6 OCB mixture. (Molecular ratio of 8 OCB/6 OCB = 0.42.) The profiles are identical in the three phases except for a very small change in the overall intensity (Kortan *et al.*<sup>16</sup>).

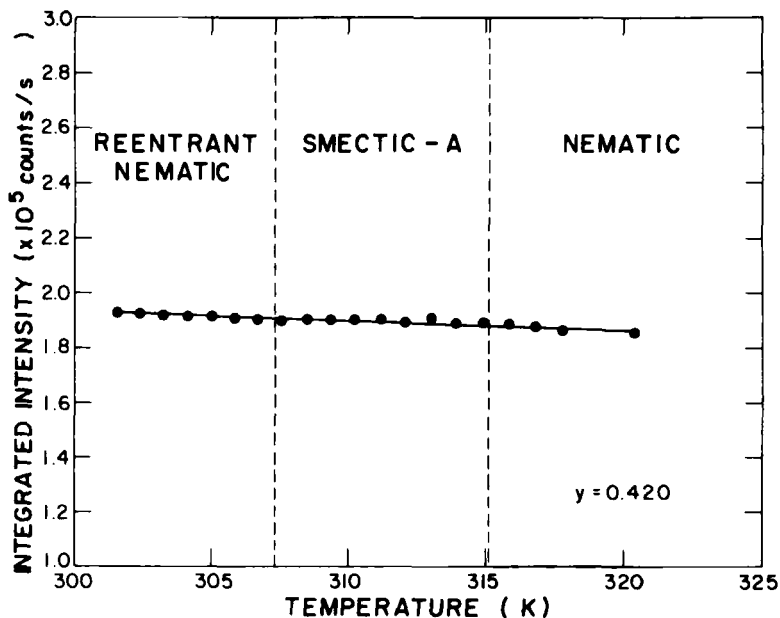


FIGURE 2 Transverse (liquid) structure factor as a function of temperature for the 8 OCB-6 OCB mixture. This again demonstrates the invariance of the in-plane order in the three phases. The slight increase in the integrated intensity on cooling may be attributed to the Debye-Waller factor (Kortan *et al.*<sup>16</sup>).

reentrant nematic ( $N_R$ ) phases and Figure 2 the liquid structure factor as a function of temperature. No detectable change was found in the lateral spacing or in the in-plane correlations in the three phases. Yet as we have seen in Table I(b), the activation energy in  $A_d$  phase of this mixture is lower than in the  $N$  phase, and much lower than in the  $N_R$  phase.






















Very recently, a model has been proposed which relates to the dielectric relaxation frequency with the square of the orientational order parameter ( $S$ ).<sup>17</sup> Very precise birefringence ( $\Delta n$ ) measurements have been made on the 8 OCB-6 OCB mixture by Chen *et al.*<sup>18</sup> Taking  $\Delta n$  as a measure of  $S$ , the data indicate that  $S$  varies with temperature at a slower rate in the  $A$  phase than in the  $N$  phase. (See also reference 19 for determinations of  $S$  for similar reentrant systems). Qualitatively, therefore, according to the model, one may expect that  $W_{A_d} < W_N$ , which is in conformity with experiment. On the other hand,  $S$  varies with temperature at an even slower rate in the  $N_R$  phase, whereas experimentally  $W_{N_R}$  is more than twice  $W_N$  for this mixture (see Table I(b)). Thus as things stand at present, the problem would appear to be unresolved.

Recent measurements suggest that there may be exceptions to the rule (that  $W_A < W_N$ ) when the smectic  $A$  phase is of the monolayer type composed of strongly polar molecules (designated as  $A_1$ ). In three out of the five cases studied,  $W_{A_1} > W_N$  (Table II). This result may be significant; why the  $A_1$  phase should behave differently from others is an interesting question in itself.

In summary, one really cannot claim to have understood the mechanism of low frequency dielectric relaxation in the nematic and smectic  $A$  phases. It remains one of the major unsolved problems in the molecular physics of liquid crystals.

TABLE II  
Activation energies for low frequency dielectric relaxation  
in the nematic and smectic  $A$  phases

$\Delta\epsilon > 0$ , smectic  $A$ —monolayer ( $A_1$ )

Chemical formula	Activation Energy (eV)		Ref.
	$N$	$A_1$	
$C_4H_9O$ —  —COO—  —N=N—  —CN	0.68	0.59	20
CN—  —COO—  —COO—  — $C_6H_{13}$ + $C_5H_{11}$ —  —COO—  —CH=CH—  —CN	0.75	0.75	21
$C_8H_{17}O$ —  —COO—  —N=N—  —CN	0.83	0.89	20
$C_8H_{17}$ —  —COO—  —OOC—  —CN	0.60 (0.85)	0.90	10
$C_8H_{17}O$ —  —COO—  —N=N—  —CN + $C_9H_{19}O$ —  —COO—  —N=N—  —CN	0.44 (0.88)	0.98	20

The activation energies given in brackets represent the values in the reentrant nematic phase.

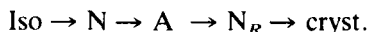
## NEAR NEIGHBOR CORRELATION

The first attempt at discussing near neighbor correlation and some of its consequences was made in 1973<sup>22-24</sup> using the well known Bethe-Peierls cluster approximation. Subsequently there have been other attempts based essentially on the same type of approximation.<sup>25-27</sup> It is well known that the mean field approach—whether it is the Maier-Saupe theory, the hard rod model, or the generalized Van der Waals theory—is quite inadequate when it comes to explaining the pretransition effects near the  $I-N$  transition. The cluster approximation gives a substantial improvement over the mean field prediction, but is still very much in error as compared with experiment. A satisfactory molecular treatment of near-neighbor correlations is a formidable problem and perhaps unlikely to be solved in the near future. However, one important idea that emerged from this exercise was the concept of antiferroelectric short range order in strongly polar systems. This was again discussed in terms of the Bethe-Peierls approximation.<sup>23,24</sup> A prediction of this model was that the mean dielectric constant in the nematic phase should be less than the isotropic value because of the increased antiparallel correlation in the ordered phase. Experimental studies on strongly polar materials have amply confirmed this prediction,<sup>28-39</sup> probably the most precise measurements being those of Bradshaw and Raynes,<sup>38,39</sup> whose data reveal even a pretransition anomaly in the antiparallel correlations. Direct evidence for antiparallel arrangement in such compounds was also obtained by Leadbetter *et al.*<sup>40</sup> from X-ray and neutron scattering studies.

Antiparallel correlations give rise to a variety of interesting effects, e.g., reentrant phases, smectic  $A$ —smectic  $A$  transitions etc.

### Reentrant polymorphism

This phenomenon was discovered by Cladis in 1975.<sup>41</sup> The simplest example of reentrance is one in which the sequence of transitions, on cooling, is as follows.



Examples of more complex behavior are now known, but we shall first consider this simple type of reentrance and for convenience, the specific case of the 8 OCB-6 OCB mixture (see Table I(b)) which has been very thoroughly investigated experimentally. Some relevant



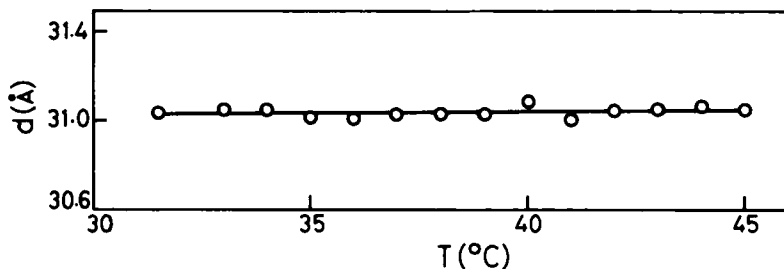


FIGURE 3 Smectic  $A$  layer spacing vs. temperature in the 8 OCB-6 OCB mixture (Raja and Shashidhar<sup>42</sup>).

experimental facts pertaining to this mixture are (i) the molecules are strongly polar and thus antiparallel correlations play a fundamental role, (ii) the smectic layer spacing is partially bilayer ( $A_d$ ) and practically independent of temperature,<sup>42</sup> (Figure 3) and (iii) the dielectric anisotropy  $\Delta\epsilon$  increases as one cools the sample from  $N$  through  $A_d$  into the  $N_R$  phase.<sup>12</sup> (Figure 4).

From the molecular point of view, only an approximate, qualitative explanation of reentrant behavior has been possible. The basic idea underlying the molecular model is that because of the antiparallel correlations the molecules form dimers, which are assumed to be somewhat bulgy in the middle (Figure 5(a)). Once the smectic phase is formed the bulgy parts are lined up in a plane, but the alkyl chains cannot fill the rest of the space. With increasing dimer formation (i.e. with decreasing temperature) and also possibly with the stiffening of the end chains, the packing becomes so unfavorable that the  $A_d$  phase is destabilized and the nematic reenters (Figure 5(b)). The elements of the model were proposed by Cladis<sup>43-45</sup> but a more complete theoretical discussion involving attractive forces and hard core repulsions has been presented by Longa and de Jeu,<sup>46</sup> who showed that there can indeed be a lower temperature nematic phase. Qualitatively this is very satisfactory. However, antiferroelectric short range order is a statistical effect, and to look upon the system as a sum of two extreme situations, the perfectly paired dimer with the dipoles compensated and the completely unpaired monomer with the full value of the dipole moment is a rather gross approximation. As emphasized by these authors themselves<sup>46</sup> the quantitative aspects of the model should be treated with caution. We shall now discuss this point in some detail. In their calculations, the variation of the dimer concentration with decreasing temperature is taken to be of form given in curve 1 of Figure 6, the dimer concentration increasing from about

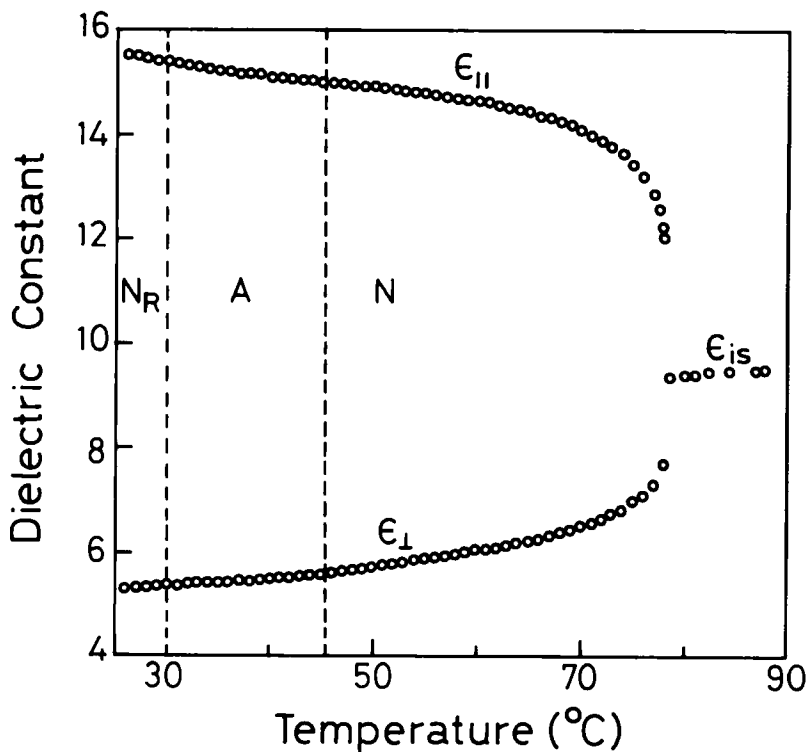


FIGURE 4 Principal dielectric constants of the 8 OCB-6 OCB mixture (Ratna *et al.*<sup>12</sup>).

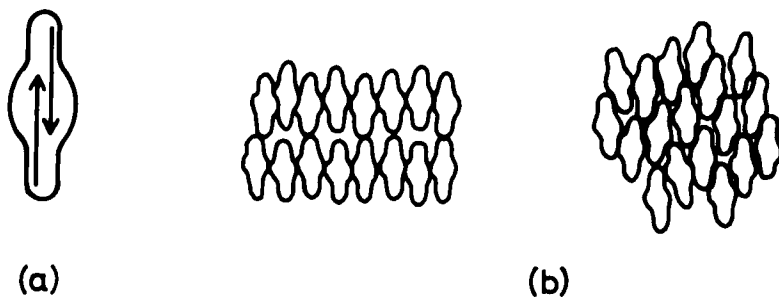


FIGURE 5 Schematic representation of (a) a dimer unit consisting of two antiparallel molecules, (b) the mechanism of destabilization of the smectic  $A$  phase (Cladis<sup>43</sup>).

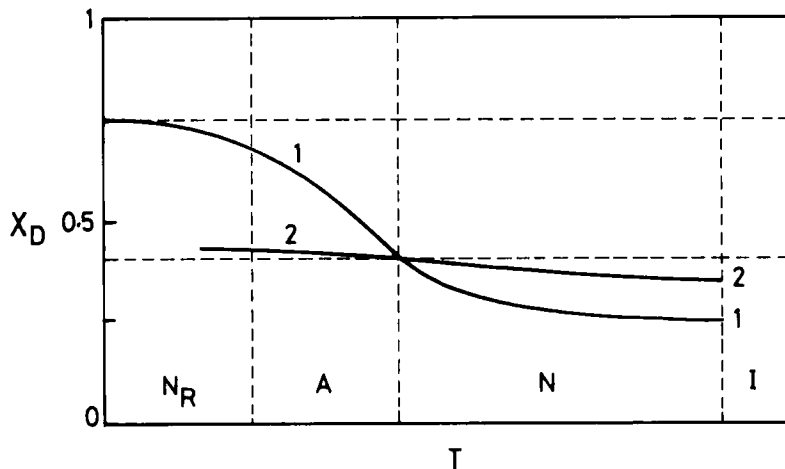


FIGURE 6 Curve 1: The variation of the dimer concentration through the  $N$ ,  $A$  and  $N_R$  phases assumed in the molecular model of Longa and de Jeu.<sup>46</sup> Curve 2: Variation of the dimer concentration derived from the experimental dielectric data for the 8 OCB-6 OCB mixture (see Figure 4).

40%–70% in the  $A$  phase. If this were so, the dielectric anisotropy should decrease with decrease of temperature. As an illustration, we have calculated this for the 8 OCB-6 OCB mixture; the calculated  $\Delta\epsilon$  drops rapidly with decreasing temperature in the  $A$  phase in contrast to what is observed experimentally (Figure 7). (In these calculations, we have used the density measurements of Bouchet and Cladis,<sup>47</sup> and the order parameter and polarizability data for pure 8 OCB reported by Karat and Madhusudana.<sup>48</sup>) In fact, the experimental dielectric data require only a very small variation of the dimer concentration with temperature, shown in curve 2 of Figure 6. There is another equally serious difficulty. As remarked earlier, experimentally the layer spacing in the  $A_d$  phase remains practically constant.<sup>42,49</sup> In order to account for this, the assumption has to be made in the theory that although there is an enormous variation in the dimer/monomer ratio, the monomers just float around in the  $S_A$  layers without affecting the layer spacing. This appears to be contrary to experience.<sup>44,50,51</sup> For example, Figure 8 gives the smectic  $A$  layer spacing vs. concentration in a binary mixture of CBOOA (which forms a bilayer smectic) and  $\bar{8}05$  (which forms a monolayer smectic).<sup>50</sup> There is in fact a striking variation of the layer spacing with concentration, in contrast to what is actually observed in reentrant systems (see Figure 3). We may conclude that the occurrence of the reentrant

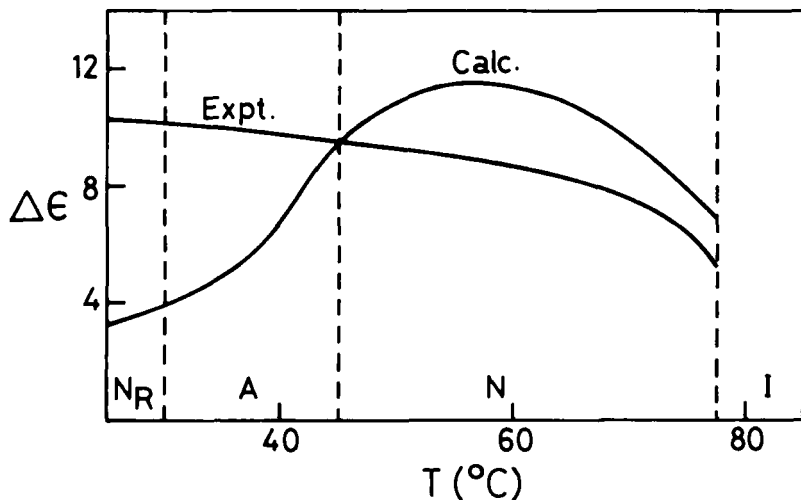


FIGURE 7 Expected form of the dielectric anisotropy ( $\Delta\epsilon$ ) of the 8 OCB-6 OCB mixture calculated from curve 1 of Figure 6. The calculated  $\Delta\epsilon$  decreases rapidly with decreasing temperature in the *A* phase, in contrast to what is found experimentally.

phase involves much more subtle structural changes than expected from the current molecular treatments of this phenomenon.<sup>52</sup> Essentially the same conclusions have been drawn by the MIT group<sup>16</sup> from high resolution X-ray studies (see Figures 1 and 2).

The pressure-temperature phase diagrams of compounds and mixtures showing the reentrant nematic phase have been extensively studied.<sup>43,53-56</sup> The nematic-smectic phase boundary is elliptical in shape, and there is a maximum pressure  $P_m$  above which the *A* phase ceases to exist. Shashidhar<sup>55</sup> has found a simple relationship between  $P_m$  and  $R$ , the temperature range of existence of the *A* phase at atmospheric pressure:

$$P_m = P_0 \exp(-mR)$$

where  $P_0$  and  $m$  are constants that depend only on the number of benzene rings in the molecular structure. Figure 9 presents the data for a large number of 2 and 3 benzene ring systems (pure compounds and mixtures) and as can be seen they obey this relationship very well. At present there is no theoretical understanding of this expression, but it may be expected to play a role in future molecular theories of reentrance.

We have so far discussed the simplest type of reentrant behavior,

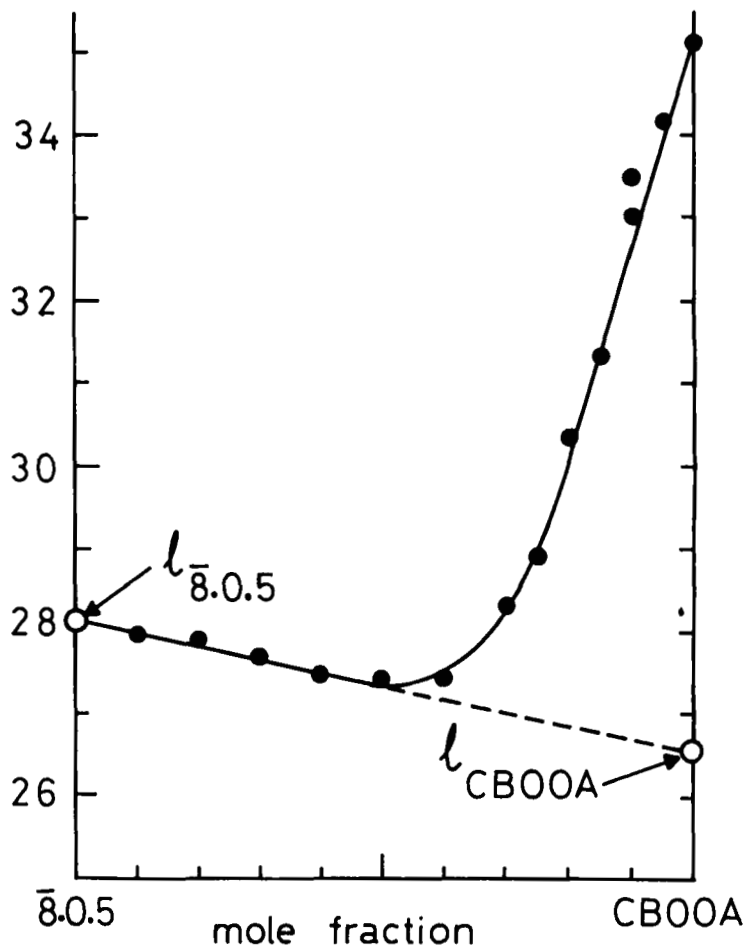


FIGURE 8 The smectic A layer spacing vs. concentration in a binary mixture of CBOOA and 805 (Engelen *et al.*<sup>50</sup>).

but much more complex cases have been found, notably by the Bordeaux Group.<sup>57,58</sup> It emerges that reentrant polymorphism is extremely sensitive to the molecular structure. We illustrate this by considering the properties of pure compounds composed of 3 benzene rings. The compounds, having the structural formula as shown below, fall into 4 distinct types, the arrows representing the directions of the longitudinal components of the dipole moments of the bridging groups X and Y.

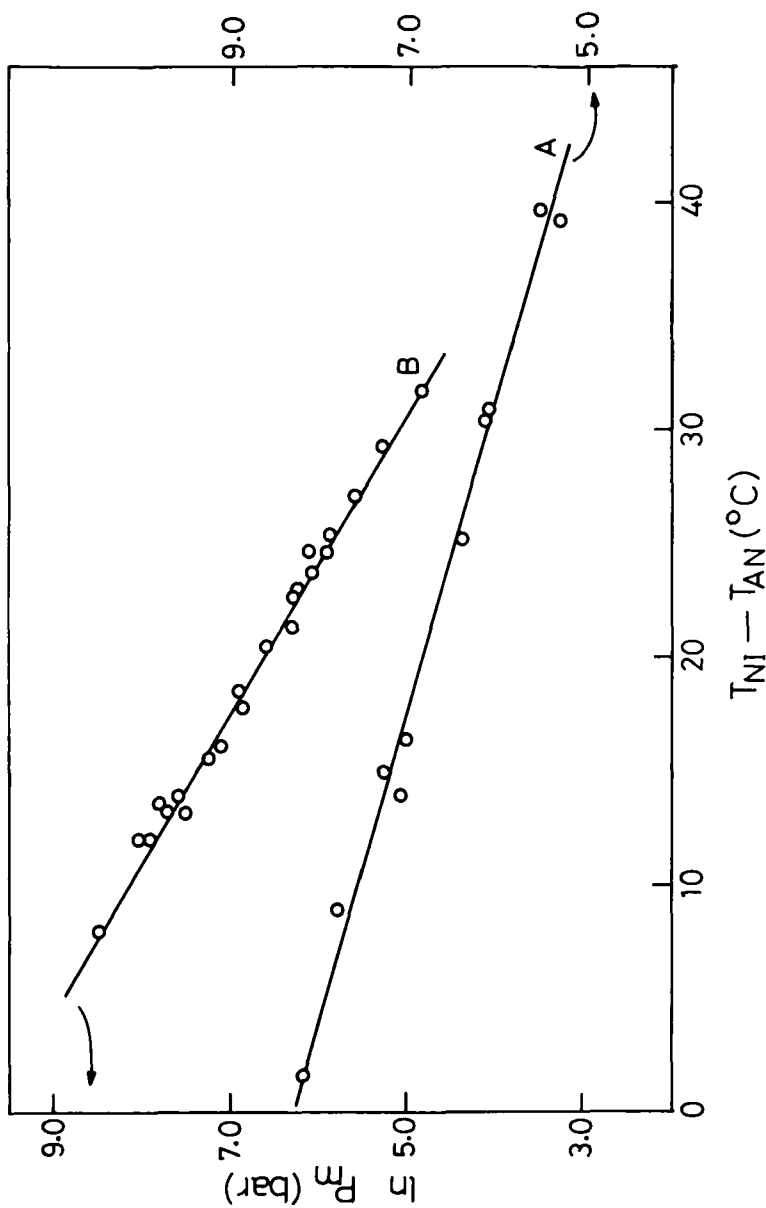


FIGURE 9  $\ln P_m$  vs.  $(T_{NI} - T_{AN})$ , where  $P_m$  is the maximum pressure of existence of the smectic A phase. All the available data fall on one or the other of two straight lines depending on whether the compounds have (A) three benzene rings or (B) two benzene rings. (From Kalkura *et al.*<sup>55</sup> Since the publication of reference 55, seven other two-benzene ring systems and one other three benzene ring system have been investigated. The data points for these eight cases have also been included in the diagram.)

	$X$ $Y$ $E$	
Type I	$\rightarrow$ $\rightarrow$ CN or $\leftarrow$ or non-polar	Reentrant Nematic
Type II	$\rightarrow$ $\rightarrow$ NO <sub>2</sub> or $\leftarrow$ or non-polar	No Reentrance No A-A Transition
Type III	$\leftarrow$ $\leftarrow$ CN	A-A Transitions No Reentrance
Type IV	$\leftarrow$ $\leftarrow$ NO <sub>2</sub>	Reentrance & A-A Transitions

Needless to say, we are nowhere near explaining these facts from a molecular theoretical point of view (though a beginning has been made by Longa and de Jeu<sup>59</sup> to try and develop a molecular model to account for the different types of *A* phases).

In principle, reentrant phases can occur in nonpolar systems as well.<sup>46,60</sup> Flonnie Dowell<sup>60</sup> has discussed this possibility in some detail by treating the molecules as hard rigid cores with semiflexible tails and interacting *via* segmental hard repulsions. In the *A* phase the molecules are segregated into layers. Her calculations show that as the tails become more rigid at lower temperatures, the lamellar packing may become disadvantageous and the *A* phase can be destabilized. Experimental evidence has been found by the Halle group of reentrant phases in non-polar systems.<sup>61,62</sup> X-ray studies indicate that the *A* phase is monolayer, lending some support to the mechanism proposed by Dowell.

### The induced smectic phase

This phase occurs most commonly in binary mixtures of a compound having a strongly polar terminal group and a compound having a non-polar terminal group.<sup>63-78</sup> Evidently, dipole-induced dipole interactions play a part in the phase induction. There is also evidence of

charge transfer complex formation, the polar molecule acting as the acceptor and the other as the donor.<sup>63,73,79</sup> Recently, however, phase induction has been observed in other types of mixtures.<sup>80-82</sup> For example, mixtures of two cyano-compounds have been found to give rise to an induced *C* phase.<sup>80,81</sup> Thus no generalizations are possible as yet and the precise role of near neighbor interactions and correlations in promoting phase induction is not clear.

## BRIDGING THE GAP BETWEEN ROD-LIKE AND DISK-LIKE MESOGENS

### Biaxial nematics

The biaxial nematic was discovered by Yu and Saupe<sup>83,84</sup> in amphiphilic systems. Over a range of concentration/temperature, potassium laurate + 1-decanol + D<sub>2</sub>O shows two uniaxial nematic phases, one composed of disk-shaped constituent (micellar) units and the other of rod-like units, and these two phases are separated by a biaxial nematic phase ( $N_{bx}$ ). One may presume that in the  $N_{bx}$  phase the constituent units are neither exactly rod-like nor exactly disk-like.

Attention has been focused recently on the thermotropic  $N_{bx}$  phase because of some theoretical work on the NAC multicritical point. Grinstein and Toner<sup>85</sup> have presented a dislocation loop theory of this point and found that  $N_{bx}$  should intervene between the *N* and *C* phases. The most detailed studies of the NAC point have been by Johnson *et al.*<sup>86,87</sup> on binary systems and by Shashidhar *et al.*<sup>88</sup> on a single component system. However, in neither of these studies was there any evidence of a fourth phase as predicted by Grinstein and Toner, a possible explanation being that the region of existence of the  $N_{bx}$  phase is unobservably small.

There are advantages in obtaining a thermotropic  $N_{bx}$  phase because the constituent units, which in this case are molecules and not micellar units, are stable and insensitive to temperature: thus it offers a more convenient system for carrying out detailed physical studies. Theoretically it has been shown that the material properties of  $N_{bx}$  are significantly different from those of the usual *N* phase.<sup>89-93</sup> For example, Saupe<sup>92</sup> and Kini<sup>93</sup> who used different theoretical approaches, have concluded that the orthorhombic  $N_{bx}$  has 15 curvature elastic and 15 viscous constants. It is evidently of considerable interest to verify these and other ideas. While there have been a number of statistical treatments<sup>94-97</sup> of the biaxial phase, a thermotropic  $N_{bx}$  phase has not so far been found.



I venture to suggest that the easiest way of producing a stable thermotropic  $N_{bx}$  may be to choose discotic systems. Liquid crystals of disk-like molecules are of two types, the columnar and the nematic.<sup>98</sup> Now if the disks were elliptical in shape rather than circular the chances are that the nematic would be optically biaxial (Figure 10). This may not be too far-fetched. For instance, rufigallol-hexan-octanoate<sup>99</sup> definitely has an elliptically shaped core though as it turns out this compound shows only rectangular columnar phases. With some chemical ingenuity, it may be possible to produce a biaxial nematic as well.

### Discotic smectics

The columnar-nematic transition<sup>100</sup> can be qualitatively explained by extending McMillan's theory of the  $A$ - $N$  transition so that the density wave is now periodic in two-dimensions.<sup>101,102</sup> Calculations show that when the lattice is hexagonal or departs from it only slightly, both components of the density wave 'melt' simultaneously and the columnar structure transforms to the nematic. However, when the lattice becomes highly asymmetric, i.e., the axial ratio departs significantly from the hexagonal value of  $\sqrt{3}$ , theory predicts that one component of the 2D density wave should melt before the other and give rise to a smectic  $A$ -like phase, which is biaxial.<sup>102</sup> A schematic representation of the structure of this new phase is shown in Figure 11. Such highly asymmetric lattices have not yet been found in any of the columnar structures studied so far, but again, as in the case of biaxial nematics, this can perhaps be realized only by making elliptically shaped disks.

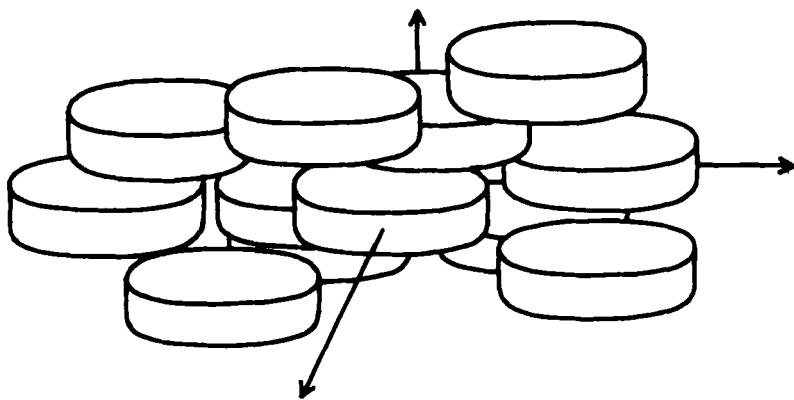


FIGURE 10 Possible biaxial nematic structure composed of elliptically shaped disks.

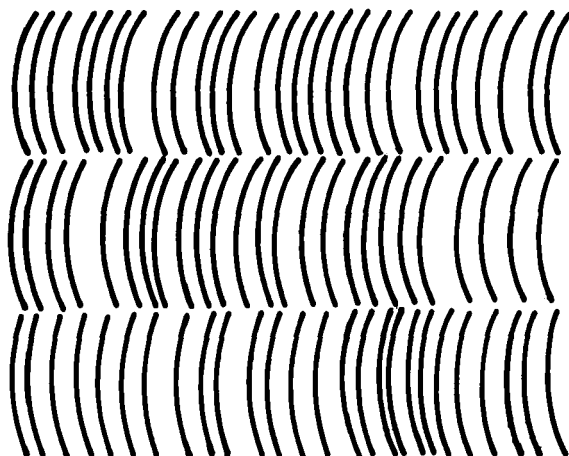


FIGURE 11 Schematic representation of the molecular arrangement in the theoretically predicted<sup>102</sup> smectic phase composed of disk-like molecules. Variants of this structure, e.g., a tilted form analogous to smectic C, are also possible.

Thus it would seem that some exciting possibilities may be opened up by bridging the gap between rod-like and disk-like mesogens.

*Note added in proof:* Evidence of a smectic-like phase in bis(p-n-decylbenzoyl)methanato copper (II), a disk-like mesogen, has been reported very recently by A. C. Ribeiro, A. F. Martins and A. M. Giroud-Godquin (presented at the Fourth National Physics Conference, Evora, Portugal, 16–20 April 1984—to be published in the Proceedings).

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