On the polymorphism of the smectic A phases of highly polar compounds

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Abstract. The smectic A phase is characterized by a layered arrangement of rod-like molecules, with the average orientation of the molecules normal to the layers and a liquid-like organization within the layers. When the molecules have a strongly polar end group (like $-C\equiv N$, $-NO_2$ etc.,), neighbouring molecules prefer an antiparallel orientation. This results in a bilayer structure, with a layer spacing much larger than the molecular length. In many compounds, the structure of the bilayer is sensitive to temperature (or pressure). This results in some interesting phenomena: (a) reentrant phases, as for example, the appearance of a nematic phase below the temperature range of existence of the A phase; (b) a number of polymorphic forms of smectic A; and (c) an 'induced smectic A' phase when the compounds with the highly polar terminal groups are mixed with weakly polar compounds even when neither compound by itself exhibits the A phase. This article gives a brief summary of recent results on all these aspects.

Keywords. smectic A; polymorphism; reentrant phases; bilayer smectics; induced smectic phases.

1. Introduction

The smectic phases of liquid crystals are characterized by a layered arrangement of rod-like molecules (for a general introduction to liquid crystals, see Chandrasekhar, 1977; de Gennes 1975). Smectic A is the simplest kind of smectic phase with a liquid-like organisation within the layers, and the average orientation of the long axes of the molecules (indicated by a unit vector **n** called the director) normal to the layers. A drawing of the structure is shown in figure 1. However this figure is purely schematic. In reality, the periodicity along the z-axis is very well described as a sinusoidal density wave (McMillan, 1971; de Gennes 1972) given by

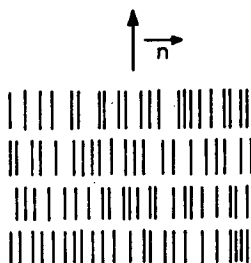$$\rho = \rho_0[1 + \mathrm{Re}\{|\psi|e^{i(q_0 z + \phi)}\}] \tag{1}$$

Figure 1. An idealised schematic drawing of the arrangement of molecules in the smectic A phase.

where $q_0 = 2\pi/d$, d being the layer spacing and ϕ a phase factor which fixes the position of the layers and $|\psi|$ the amplitude of the density wave (figure 2). Indeed even the second order maximum is hardly seen in the x-ray diffraction pattern from most of the compounds in the A phase (Schaetzing and Litster 1979). The first order reflection is also not a true Bragg spot but has a power law decay of the intensity as one moves away from q_0. This is a consequence of the well-known Landau-Peierls instability of an one-dimensional periodic order (Landau and Lifshitz 1959; Peierls 1934).

The chemical structure of a typical mesogenic compound with rod-like molecules has a central aromatic core which is quite rigid and a relatively flexible alkyl chain at one or both ends (figure 3). Experimentally it is well known that the lower homologues (*i.e.*, compounds with shorter alkyl chains) exhibit only the nematic (N) phase which is characterised by a purely orientational long range order. The smectic phase makes its appearance when the alkyl chain is relatively long. The first member exhibiting the A phase shows a relatively weak A–N transition, but as the chain length is increased, the strength of the transition increases and beyond a certain chain length, the A phase goes over directly to the isotropic phase. These observations can be understood by assuming that the strongest intermolecular attractive interactions are confined to the aromatic cores of the molecules. This would naturally lead to the formation of a layered arrangement of molecules with relatively long alkyl chains at both ends. This is the physical idea behind the molecular theory of the A phase proposed by McMillan (1971). Assuming that the translational and orientational orders are coupled, he showed that the A–N transition can be of second order character if the orientational order at the transition point is sufficiently high.

As we saw earlier, the order parameter characterising the A phase has two components *viz* the amplitude and the phase of the density wave (equation (1)). This is rather analogous to the order parameter of a superconductor. Further, because of the layered arrangement, the A phase does not allow a **curl n** distortion which requires a change of layer spacing. This is analogous to the expulsion of a magnetic field by a
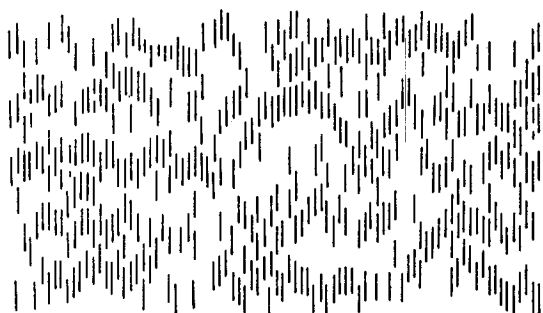

Figure 2. A realistic distribution of molecules in the A phase (from Schaetzing and Litster 1979).
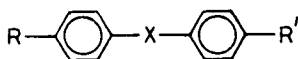

Figure 3. Chemical structure of a typical mesogenic compound.

superconductor. The close analogy between the (second-order) A–N transition and superconductor-normal metal transition was recognised by de Gennes (1972) who wrote the relevant Landau-Ginzburg free energy functional. Using this analogy, he predicted the divergence of twist and bend elastic constants as T_{AN} (the A–N transition point) is approached from the nematic side. [For a review of the experimental situation up to 1978 see Chandrasekhar and Madhusudana 1978. For recent results see Als-Nielsen 1981]. He also predicted a reduction in T_{AN} due to a **curl n** type of distortion (which was only recently confirmed experimentally; Madhusudana and Srikanta 1982). However the analogy is not exact. For example, it has been found that $\xi_{\parallel}$ and $\xi_{\perp}$, the correlation lengths parallel and perpendicular to the director diverge with different critical indices as T_{AN} is approached. The theory of AN transition still continues to be a very active area of investigation (see for example, Als-Nielsen 1981).

In this article we shall confine our attention to some interesting features exhibited by the smectic A phase when the compound has a highly polar end group. Many compounds have been synthesised in recent years which have either a cyano ($-C\equiv N$) or nitro ($-NO_2$) end group, both of which have a longitudinal dipole moment of ~ 4 Debyes. Till about a decade ago the longitudinal dipoles were thought to play only a minor role in stabilising the nematic and smectic A phases, especially after it was recognized that Born's theory of the nematic phase (Born 1916) which is based entirely on interactions between permanent dipoles is inadequate (Maier and Saupe 1959). We proposed that for minimising the mutual interaction energy, neighbouring molecules with strong longitudinal dipoles should favour an antiparallel arrangement (Madhusudana and Chandrasekhar 1973; Madhusudana *et al* 1977). This was amply confirmed by x-ray and neutron scattering studies (Leadbetter *et al* 1975, 1979; Lyden and Coakley 1975) which showed that in alkyl (or alkoxy) cyanobiphenyls the smectic A phase is characterized by a layer spacing which is ~ 1.4 times the molecular length (figure 4). As we pointed out earlier, the attractive interaction between neighbouring molecules would favour aromatic regions to overlap, and the antiparallel correlation
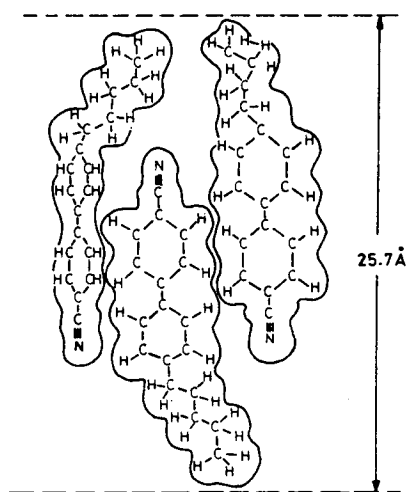

Figure 4. Schematic diagram of antiparallel local structure in pentyl-cyanobiphenyl (Leadbetter *et al* 1975).

brought about by the strong dipole moments would then lead to a structure as shown in figure 4. Another way of describing such a structure would be to say that two such molecules would form an antiparallel 'pair', which should be a relatively stable unit because of frustration effects which any additional molecule would be subjected to in the neighbourhood of such a pair. An interesting consequence of the formation of such pairs is that they are much more symmetric than the individual molecules which are highly asymmetric because of the presence of the alkyl chain only at one end of the aromatic core. The pairs have chains at both ends and the McMillan argument regarding the conditions of formation of the smectic A phase is now applicable for the pairs and thus many such compounds with cyano end groups exhibit the A phase (de Jeu 1982). The A phase thus formed is referred to as a bilayer A phase for obvious reasons. Even if the chain length is too short to form the A phase, such compounds exhibit a strong smectic-like short range order in the nematic phase, the short range order having bilayer characteristics. The structure of the bilayer should depend on the chemical structure of the aromatic core. Further, in any given case the bilayer structure is an extra degree of freedom, which can be influenced by variations in temperature, pressure or, in the case of mixtures, the composition. This in turn leads to several interesting phenomena which will be discussed in the following sections.

2. Reentrant phases

Cladis (1975) discovered that some binary mixtures of compounds with cyano end groups exhibit the following sequence of transitions as the mixture is cooled from the isotropic phase:
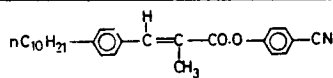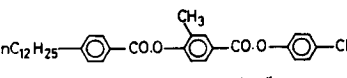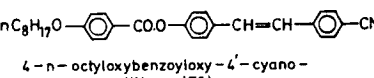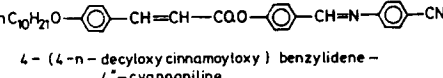
$$\text{isotropic} \rightarrow \text{nematic} \rightarrow \text{smectic A} \rightarrow \text{nematic}.$$

The translational order of the A phase is lost both when it is heated and cooled. The nematic phase occurring at temperatures lower than the range of stability of the smectic A phase is called the 'reentrant' nematic ((N_R) phase, in analogy with similar reentrant phases in certain superconductors doped with magnetic impurities (Riblet and Winzer 1971) and the solid-liquid ^{3}He transition (Anderson *et al* 1963).

Subsequently Cladis *et al* (1978) found that some pure compounds exhibited the reentrant nematic phase at elevated pressures and a little later pure compounds were found which exhibited the reentrant phase even at atmospheric pressure (Madhusudana *et al* 1979; Hardouin *et al* 1979; Subramanya Raj Urs and Sadashiva 1982). During the past 3 years a large number of compounds have been synthesized which exhibit reentrant phases. (For a recent review on the chemistry of these compounds, see Tinh 1983). Table 1 gives a representative list of compounds which exhibit reentrant phases. It is seen that some compounds not only exhibit a reentrant nematic phase, but also a reentrant smectic A (A_R) phase which is obtained on cooling the N_R phase.

Though one might expect that changes in the bilayer structure should be responsible for the occurrence of the N_R phase, x-ray investigations do not reveal any universal trend in the thermal variation of the bilayer *spacing* close to the AN_R transition point. In some cases which exhibit only the N_R phase below the A phase, the bilayer expands as the sample is cooled to T_{AN_R} (Chandrasekhar *et al* 1979). This expansion is also reflected in the low frequency dielectric dispersion which arises due to the flipping of the molecules about their short axes, the corresponding activation energy changing

Table 1.

STRUCTURAL FORMULA AND NAME	SEQUENCE OF TRANSITIONS AS THE COMPOUND IS COOLED
$nC_{10}H_{21}$—⬡—C=C—CO.O—⬡—CN (with H above and CH_3 below the C=C) trans — p — n — decyloxy — α — methyl — p'— cyanophenyl cinnamate (10 OMCPC)	I 73.5 N 56.8 A_d 32.5 N_R
$nC_{12}H_{25}$—⬡—CO.O—⬡—CO.O—⬡—CN (with CH_3 above) 4 — cyanophenyl — 3 — methyl — 4'(4'' — n — dodecyl benzoyloxy) benzoate (12 CPMBB)	I 148 N 138.5 A_d 59.8 N_R
$nC_8H_{17}O$—⬡—CO.O—⬡—CH=CH—⬡—CN 4 — n — octyloxybenzoyloxy — 4' — cyano — stilbene (T8)	I 283 N 248 A_d 138 N_R 94.5 A_1
$nC_{10}H_{21}O$—⬡—CH=CH—CO.O—⬡—CH=N—⬡—CN 4 — (4 — n — decyloxy cinnamoyloxy) benzylidene — 4'' — cyanoaniline	I 267 N 257 A_d 87 C 70 N_R

distinctly (Ratna *et al* 1979). The activation energy of the N_R phase itself is much larger than in the normal N phase. But in compounds exhibiting the A_R phase also, the trend is quite different. The bilayer spacing decreases rapidly from $\sim 1.25\,l$ to $1.1\,l$ as the temperature of the A phase is lowered to T_{AN_R}. In the reentrant smectic A phase there is a temperature independent layer spacing which is $\simeq l$, i.e., the A_R phase is a monolayer smectic (Hardouin and Levelut 1980). Moreover, the A_R phase gives rise to a diffuse scattering of x-rays indicative of a two-dimensional superlattice type of modulation of the layers with periodicities of $\sim 70\,\text{Å}$ in the plane of the layer and a periodicity of ~ 4 layers along the z-direction (figure 5). The activation energy of the low frequency
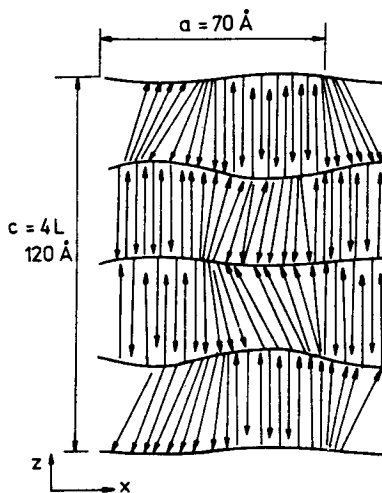

Figure 5. Schematic diagram of the structure of the reentrant smectic phase. The arrows represent the cyano-end groups of the molecules.

dielectric dispersion in the A_R phase is nearly twice that of the bilayer A phase (Benguigui and Hardouin 1981). Further, the N_R phase has fluctuations of both A_d and A_R phases, as revealed by x-ray and dielectric studies.

Most of the compounds exhibiting the reentrant phases have three benzene rings with some bridging groups in between in the aromatic core excepting two compounds which have only two benzene rings (see table 1). The length of the core appears to play an important role and Tinh (1983) has concluded that the core has to have a length lying between 16 Å and 22 Å for the compounds to exhibit the reentrant phase.

There have been some attempts to develop a theory for the occurrence of the N_R phase on the basis of the antiparallel orientations of neighbouring molecules. Assuming that associated pairs are formed in the medium, Cladis (1979) argued that as the temperature decreases (or equivalently the pressure increases) the stability as well as the number of such pairs should increase. The associated pairs are obviously much less polar than the individual molecules. If it is now assumed that the lateral interactions leading to the formation of layers are greater if the molecules are effectively *more* polar; it is clear that the smectic phase stability is *decreased* as the pairing is more efficient. Further, for the aromatic part of the molecular pairs, it will not be sterically advantageous to remain in the layers beyond a certain density. Equivalently, one can assume that there is an optimum density for the stability of the smectic A phase of the bilayer kind. Pershan and Prost (1979) have used this idea in developing a Landau theory of the reentrant nematic-bilayer smectic A transition. By adding a term of the form $g(\rho)|\psi|^2$ to the usual Landau theory of the A–N transition where $|\psi|$ is the smectic order parameter, and expanding $g(\rho)$ to the leading power in $(\rho - \rho_0)$ where ρ_0 is the optimum density, they can account for both A–N and A–N_R transitions. Further, using this model, they can account for the experimental observation that the bilayer A phase is bounded by the N phase in the PT plane (Cladis *et al* 1977; for a more detailed account of the high pressure studies, see the article by Shashidhar 1983). Indeed the A phase is also bounded in phase diagrams of binary mixtures of two cyano compounds, if only one of the components exhibits the N_R phase (figure 6). This can also be accounted for by using the Landau model if g is taken to be a function of both density and composition (Pershan and Prost 1979). Thermodynamic models to explain such non-linear phase diagrams have also been developed (Clark 1979; Klug and Whalley 1979; Heppke and Schneider 1979; Billard 1979).

Longa and de Jeu (1982) have given a detailed molecular theory of the AN_R transition. By treating the system as a mixture of monomers and dimers interacting through both attractive and hard-core repulsive interactions, they essentially work out the requirements for the occurrence of the optimum density that was referred to in the previous paragraph. They show, using the framework of the McMillan model of the A phase, that unfavourable packing of the dimers in planes leads to N_R phase for $d/l \simeq 1\cdot3$–$1\cdot4$. We might also mention here a paper by Hida (1981) who has developed a lattice theory of the AN_R transition by assuming that dimer pairs occupy an fcc lattice. Allowing for vacancies in such a lattice, he shows that reentrance is possible for certain model parameters.

Another model for the occurrence of the reentrant phases was proposed by Berker and Walker (1981). It is based on the competition between short-range positional order in the layers and long-range antiferroelectric order which arises due to interactions between the dipole moments. This is called the 'frustrated spin-gas' model, since, as we mentioned earlier, frustration is inherent in a triangular (or equivalently hexagonal)
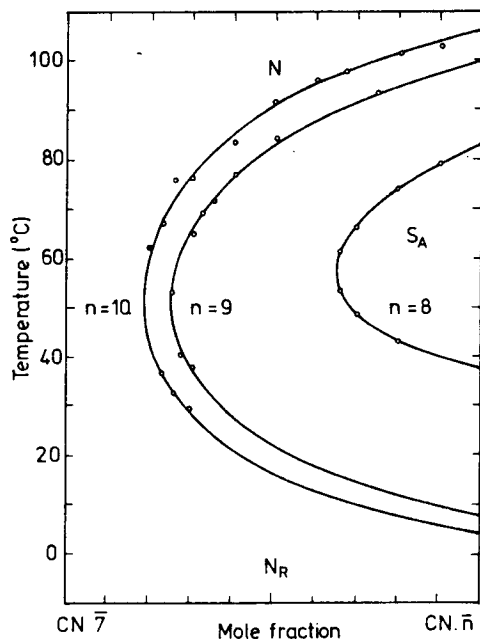
Figure 6. Phase diagram of the binary mixtures of 4-cyano-benzylidene-4'-alkoxyanilines. The lines are calculated on the basis of a thermodynamic theory (Heppke and Schneider 1979).
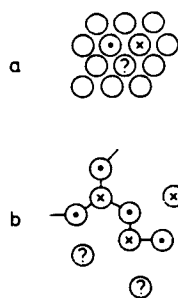

Figure 7. The frustrated spin model for the occurrence of N_R phase. A triangular lattice (b) in which two bonds are stronger than the third can form a network. As the density is increased, the molecules would like to be in a close packed triangular lattice (a), thus bringing in 'frustration' and hence a transition to the N_R phase.

close packing of the molecules in the layers: if two molecules have already formed an antiparallel pair, a third molecule which would try to sit on a triangular lattice with respect to the first two would be subjected to 'frustration' in respect of its orientation. The authors propose that this can be relieved by packing the molecules in a triangular lattice such that there are two strong bonds and a weak bond, thus leading to the formation of a network (figure 7), and this obviously favours the formation of a (bilayer) smectic A phase. As the density is increased, the molecules have to come closer, and pack in a regular triangular lattice. Frustration effects will destroy the network and

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the system goes over to the re-entrant nematic phase. By assuming attractive interactions between the alkyl chains, a reentrant monolayer smectic A phase is predicted to occur with a ferroelectric order in the layers. However, it may be pointed out that according to this model, the bilayer would have a long range antiferroelectric order in the networks, and this should have profoundly influenced both the static and dynamic parts of dielectric anisotropy. The measurements mentioned earlier do not appear to support this model.

Prost (1980) points out that the reentrant nematic phase occurring between the bilayer and monolayer A phases has fluctuations of both types; and it is thus a result of the mutual exclusion of the two types of smectic phases which are competing for condensation. The reentrant phenomenon in this model comes out as one of the possibilities in a system in which two lengths are important, the other possibilities being different modifications of the smectic A phase which will be discussed in the next section.

On the experimental side, some of the more recent findings include a sequence $NACN_R$ (Tinh *et al* 1982b; The Halle group has found many mixtures with such a sequence, see Pelzl *et al* 1981), a (tilted) smectic C phase appearing between the A and N_R phases (see table 1) and a more exotic triple reentrant behaviour which will be referred to in the next section.

3. Polymorphism of smectic A

X-ray investigations of compounds with cyano end groups have shown various other remarkable phenomena in recent years. For example, in pentyl cyanoterphenyl, a compound which exhibits only a nematic phase, short-range correlations corresponding to two *incommensurate* wavelengths (at $\simeq l$ and $\simeq 1.5 \ l$) have been found (Brownsey and Leadbetter 1980), just as in the N_R phase separating A and A_R phases discussed in the previous section.

4-*n*-Pentylphenyl-4′-(4″-cyanobenzoyloxy)benzoate (hereafter called DB5, see table 2) has two ester linkage groups in the aromatic core which are arranged such that their dipole moments are essentially antiparallel to the dipole moment of the cyano end group. This compound has an NA transition which occurs at $\sim 110°$ below T_{NI}, and according to the McMillan criterion (McMillan 1971) should have had only a second order NA transition. Actually, however, it has a moderately large first order NA transition. Meyer and Lubensky (1976) accounted for this by developing a mean field theory of the A phase with a coupling between the first and second translational order parameters. Indeed as we shall see presently, DB5 and similar compounds have been found to possess a bilayer spacing which is close to twice the molecular length, which in turn give rise to a rich variety of smectic A polymorphism.

The first direct evidence for the coupling between the first and second fourier components of the density wave was obtained in a mixture of DB5 with a weakly polar compound, *viz* terephthal-*bis*-butylaniline (T_{BBA}) which exhibits a monolayer A phase (Sigaud *et al* 1979). Calorimetric and x-ray investigations clearly indicate a first order transition from a monolayer phase (A_1) to a bilayer phase whose layer spacing is $\simeq 2 \ l$ (A_2 phase). Figure 8 shows the proposed molecular arrangement in the two phases. Pure DB7, a higher homologue DB5 (see table 2) exhibits at higher temperatures of its A phase a layer spacing of $\sim 1.6 \ l$ with a coexisting diffuse spot corresponding to $\sim l$.

Table 2.

COMPOUND or MIXTURE		SEQUENCE OF TRANSITIONS
nC_5H_{11} —◯—O.OC—◯—O.OC—◯—CN 4-n-pentylphenyl-4-(4-cyanobenzoyloxy)benzoate (DB5) + C_4H_9—◯—N=CH—◯—CH=N—◯—C_4H_9 terephthal-bis(-p-butylaniline)(TBBA)	83.4% $\Big\}$ 16.6%	N 134 A_1 117 A_2
nC_7H_{15}—◯—O.OC—◯—O.OC—◯—CN (DB7)		I 233 N 172 A_d 168 A_2
nC_5H_{11}—◯—CH=CH—◯—O.OC—◯—CN 4'-(4-n-pentylstyryl)phenyl-4"-cyanobenzoate (C5 stilbene) + DB5	46% $\Big\}$ 54%	N 145 A_1 125 $\tilde{A}$ 116 A_2
nC_7H_{15}—◯—O.OC—◯—O.OC—◯—NO_2 4-n-heptylphenyl-4-nitrobenzoyloxy benzoate (DB7NO2)		N 95 A_1 90$\tilde{A}$
$nC_{10}H_{21}$—◯—O.OC—◯^{CH_3}—O.OC—◯—CN 4-n-decylphenyl-3'-methyl-4'-(4"-cyanobenzoyloxy) benzoate (10 PMCBB)		N 139.5 A_d 124.5 A_2
$nC_9H_{19}O$—◯—O.OC—◯—O.OC—◯—NO_2 (DB90NO2)		I 224 N 195 A_d 156 N_R 138 A_d- 127 N_R 124 A_1 118 $S_?$ 96 C_2
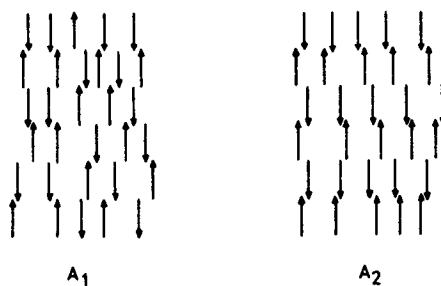
Figure 8.   The molecular arrangement in (a) the A_1 phase, and (b) the A_2 phase.

This phase with $l \lesssim d \lesssim 2l$ is called the A_d phase. (All the bilayer A phases of compounds exhibiting reentrant nematic phases belong to this class.) As the temperature is lowered, a phase transition occurs such that in the lower temperature phase, there are two Bragg spots corresponding to $d \simeq l$ and $d \simeq 2l$, i.e. there is a commensurate lock-in of the two wavelengths in the lower temperature A_2 phase.

Yet another type of smectic A (known as smectic antiphase, $\tilde{A}$) is found in some pure compounds and mixtures. For example, some mixtures of DB5 and C5 stilbene (table 2) show a high temperature A_1 phase (with $d = 2\pi/q_2 \simeq l$) with a diffuse scattering at wave vector q_1 which is split such that $q_2/q_{1z} \simeq 2$. On cooling this compound, a phase transition occurs such that q_2 is not altered but diffuse maxima corresponding to q_1 get condensed. As a result, a superlattice long range order with

$2\pi/q_{1x} \simeq 130$ A develops in the *lateral* direction (figure 9). Cooling the sample further, yet another transition takes place such that a collinear commensurate locking of the two wavelengths occurs along the z-direction. In other words, the lateral superlattice collapses in favour of an A_2 phase. Thus the sequence of transitions on cooling this mixture from the nematic phase is $N-A_1-\tilde{A}-A_2$. Some pure compounds are also now known to exhibit the $\tilde{A}$ phase (table 2).

We have recently studied many compounds with the basic chemical structure similar to that of the DBn series, except for the presence of a lateral methyl or methoxy substituent. Indeed the resulting 4-cyanophenyl-3'-methyl-4'(4"-n-alkyl-benzoyloxy)benzoates (called nPMCBB) are obtained by interchanging the two end groups of nCPMBB compounds, some of which exhibit the N_R phase (tables 1 and 2). 10 PMCBB exhibits a large increase of its bilayer spacing as the temperature is lowered, with a jump of ~ 0.4 A at $T_{AN} - T \simeq 15°$ (figure 10) (Madhusudana *et al* 1982b). The second order reflection is hardly seen in the high temperature phase but shows up strongly in the lower temperature A phase and the transition corresponds to an A_d-A_2 transition. The physical interpretation (Madhusudana *et al* 1982c) of this phenomenon can be understood from figure 11. In 12 CPMBB, which exhibits the N_R phase, the two ester group dipole moments are parallel to the dipole moment of the cyano group, and neighbouring molecules are arranged as in figure 11a, to minimise the mutual interaction energy arising from dispersion as well as dipolar forces. On the other hand in 12 PMCBB, such an arrangement (figure 11b) is not likely to lead to a minimum in the interaction energy. Though mutual dispersion interactions should favour this configuration, it is clear that the dipolar energy between the cyano group and one of the ester groups of the neighbouring molecule would be repulsive. The molecules would then prefer the arrangement shown in figure 11c so as to make the dipolar interaction energy highly negative. Indeed this energy $(\sim \mu^2/r^3)$ is a few times the thermal energy k_BT. However, this interaction is confined to one *end* of the molecule and the structure is
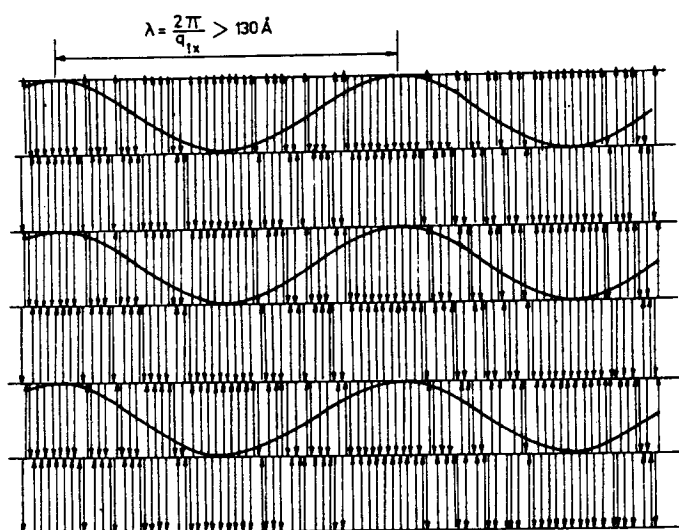
Figure 9. Schematic diagram of the arrangement of molecules in a smectic antiphase ($\tilde{A}$).
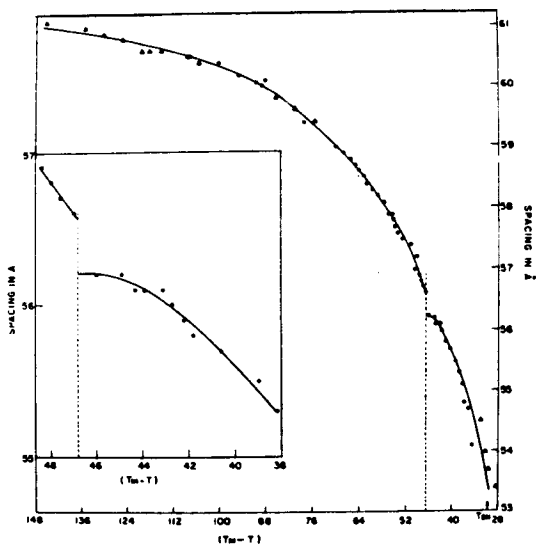
Figure 10. Temperature variation of the layer spacing of 10 PMCBB. The A_d-A_2 transition occurs with a jump in the layer spacing at the temperature corresponding to the dashed line. The region around this transition point is shown on a magnified scale in the inset.
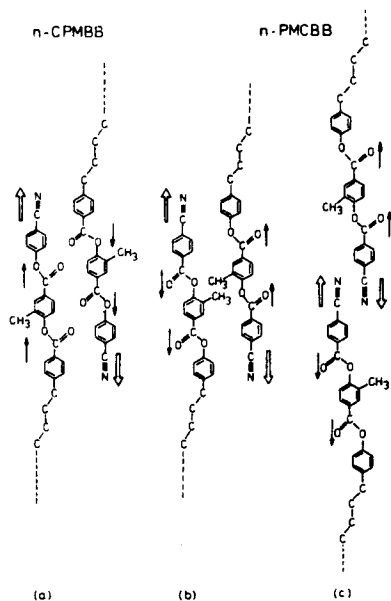
Figure 11. Schematic diagrams showing the disposition of various dipolar groups of a pair of (a) n-CPMBB, (b) n-PMCBB molecules with an overlap of the aromatic cores and (c) a pair of n-PMCBB molecules with an overlap of the polar end groups.

hence rather fragile, especially since the molecules have a relatively long alkyl chain and the lateral methyl group. As the temperature is raised, the structure easily breaks up and more molecules form associations as in figure 11b which should still have a negative interaction energy. As a consequence the layer spacing rapidly decreases with increase of temperature. If the energy difference between the arrangements of figures 11b and 11c is w, the number of molecules having configuration c is $\propto \exp(-w/kT]$ and one can calculate the temperature variation of the layer spacing (Guillon and Skoulios 1983).

If we replace the cyano end group of 10 PMCBB with a nitro group, the trend of the thermal variation of the layer spacing becomes somewhat different (figure 12; Madhusudana *et al* 1982a). The sign of the curvature of the variation is opposite to that of 10 PMCBB (figure 10) and further, there is no phase transition in the smectic range. The longitudinal component of the dipole moment of the NO_2 group is practically the same as that of CN group. However the lateral components of NO bonds should make the mutual interactions in configuration c of figure 11 somewhat repulsive and hence lead to the difference in the trend of layer spacing variation.

The dielectric properties of such compounds also are in conformity with the model given above. For example, as shown in figure 13, the dielectric anisotropy changes sign, becoming negative at lower temperatures of the A phase of 10 PMNBB, as more and more molecules take the configuration of figure 11c, and hence the contribution of the strong end group dipole moment to the dielectric constant parallel to the director is reduced.

Figure 14 gives a schematic diagram of the expected x-ray diffraction pattern for different modifications of the A phase. A comprehensive theory to describe the various polymorphic forms of the A phase and transitions between them has been developed by Prost (1980, 1981). He has written down a general Landau free energy expression with two coupled order parameters which describe the tendency of the molecules to condense at two (generally incommensurate) wavelengths. The variety of A phases observed is a consequence of the competition between the two wavelengths. According to this model, each of these A phases is in effect a 'frustrated' smectic, in which the competition between the two wavelengths is sorted out in a specific manner. Thus, for instance, the A phase (figure 9) is essentially an escape from incommensurability when
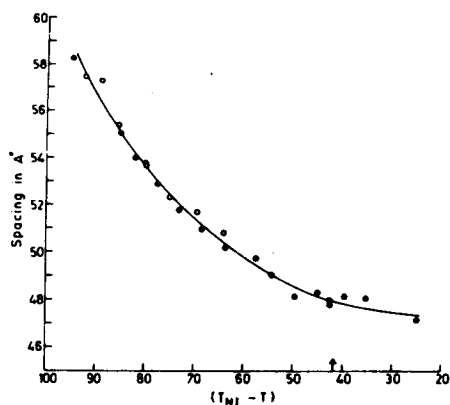

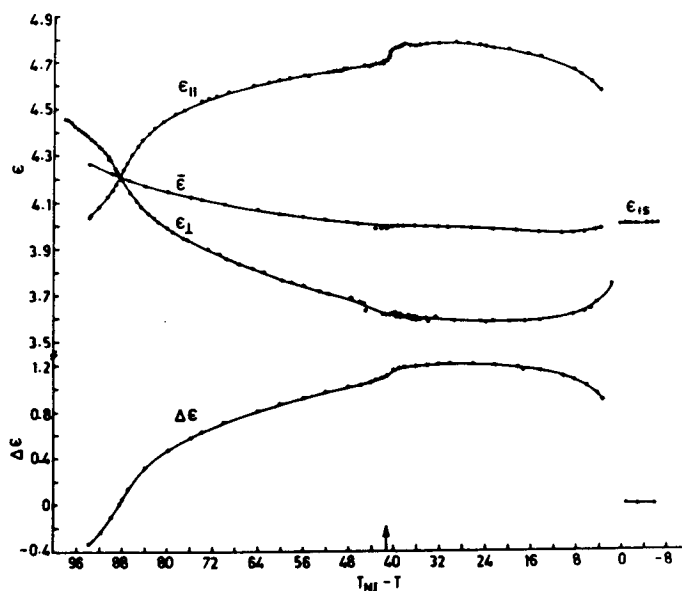**Figure 12.** Temperature variation of the layer spacing of 10 PMNBB.

Figure 13. Temperature variations of the dielectric constants and anisotropy of 10 PMNBB.
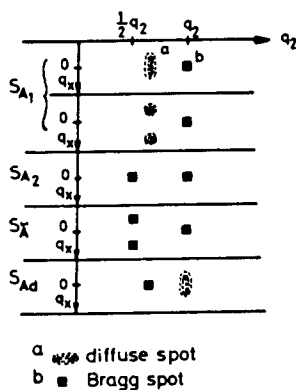
Figure 14. Schematic diagram of the expected x-ray diffraction spots from different modifications of smectic A phase (Levelut *et al* 1981).

it is too large, *i.e.* l' is much different from $2l$. Then the dipolar heads switch from one layer to another periodically, thus developing a transverse two-dimensional order. As we saw at the end of the previous section, Prost has also described the reentrant phenomenon $(NA_d N_R A_1)$ in the same framework, but including the effect of fluctuations. We end this section by pointing out a remarkable result recently found by Tinh *et al* (1982a) in a compound similar to the DBn series, except that the end cyano group is replaced by a nitro group. 4-nonyloxyphenyl-4'-nitro-benzoyloxy benzoate (table 2) exhibits the following sequence on cooling:

$$INA_d N_R A_{dR} N_R A_1 S(?)C_2.$$

Though many other compounds with similar structure exhibit only A_2 and $\tilde{A}$ phases, this particular compound with a nonyloxy end chain rather unexpectedly shows two reentrant nematic phases.

4. Induced smectic phases

When two nematogenic compounds are mixed, one would expect that the mixtures also exhibit only the nematic mesophase. However, when one of the components has the strongly polar cyano or nitro group and the other component has no such end group, in certain composition ranges the mixture actually exhibits an 'induced' smectic phase which is usually of the A type (Dave *et al* 1966; Pelzl *et al* 1968; Park *et al* 1975). Such a phase diagram is displayed in figure 15 (Moodithaya and Madhusudana 1979). Thus permanent dipole-induced dipole interactions appear to be important for the occurrence of the induced phase. Further, there is experimental evidence that a charge transfer complex formation takes place between the molecules of the two kinds (Sharma *et al* 1980), the highly polar component acting as an acceptor while the other component acts like a donor. Such an interaction appears to lead to the formation of a layered arrangement characteristic of smectic phases. (In some cases even the smectic E phase which has orthorhombic symmetry is induced, see for example, Schneider and Sharma 1981).

If the highly polar compound itself exhibits a bilayer A_d phase, then the mixtures of such a compound with some weakly polar compounds exhibit a maximum as well as a minimum in the A–N transition boundary (Srikanta and Madhusudana 1982). Figure 16 illustrates such a phase diagram. The maximum which occurs at ~ 50 mole % of the two components, corresponds to the induced A phase. It is obvious from the occurrence
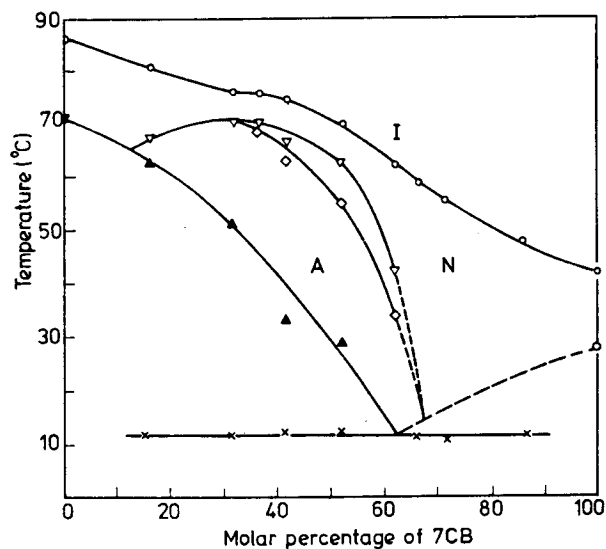

Figure 15. Phase diagram of mixtures of (2-hydroxy)-*p*-ethoxy-benzylidene-*p'*-butylaniline (OHEBBA) with 7CB.
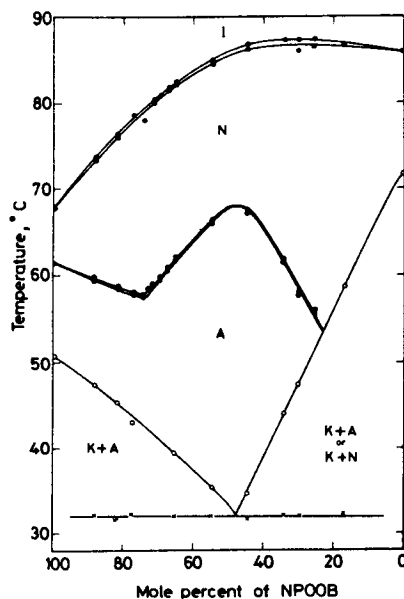
Figure 16. Phase diagram of mixtures of *p'*-nitrophenyl-*p-n*-octyloxybenzoate (NPOOB) and OH-EBBA.

of the minimum in the AN transition boundary that the induced A phase is essentially incompatible with the bilayer A_d phase of the highly polar component. Indeed x-ray studies show that for compositions rich in the weakly polar component, the layer spacing corresponds to an appropriate average molecular length of the two components (Engelen *et al* 1979; Srikanta and Madhusudana 1982). In other words, it is an A_1 phase.

The layer spacing in the A_d phase of NPOOB is $\simeq 1 \cdot 2 \, l$. For compositions between the minimum and maximum, the medium has a mixture of monolayer and bilayer species. This coexistence appears to smear out any possible A_d–A_1 transition which could in principle occur near the minimum of the AN boundary. However, as the minimum is approached from either side, the thermal expansion coefficient of the layer spacing increases significantly (figure 17). We can understand this by assuming that the interaction energy between the strongly polar and weakly polar components (including contributions from both dipole-induced dipole interactions and charge transfer complex formation) is only slightly higher than the interaction energy which gives rise to antiparallel correlations between two neighbouring NPOOB molecules. Consequently, as the temperature is increased, the strongly polar-weakly polar pairs break up allowing NPOOB molecules to form more antiparallel pairs (We note that at the composition corresponding to the minimum in the AN boundary, there are 3 NPOOB molecules for every OH-EBBA molecule). This naturally leads to a considerable thermal expansion of the layers. The dielectric studies on the same system confirm this mechanism (Srikanta and Madhusudana 1982). Thus this system also manifests the effect of a competition between two characteristic lengths at the molecular level.

In conclusion, strong longitudinal dipole moments in rod-like molecules give rise to an antiparallel correlation between neighbouring molecules. Depending on the detailed
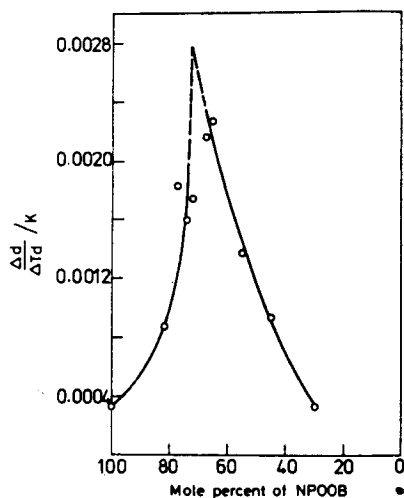
Figure 17. The thermal expansion coefficients of the layer spacings of various mixtures of NPOOB with OH-EBBA at $T_{AN} - T \simeq 2.5°$.

chemical structure of the molecules, this in turn gives rise to a 'bilayer' of a thickness which lies between 1 and 2 molecular lengths. The coupling between this length and the molecular length which would usually characterize a density wave in the medium gives rise to a variety of interesting phenomena in the smectic phases formed by such systems.

Acknowledgement

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