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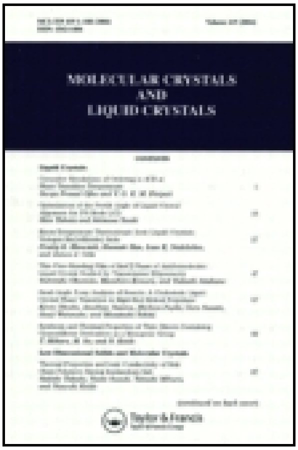

# Molecular Crystals and Liquid Crystals

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# Role of Molecular Dipoles in Liquid Crystals

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# ROLE OF MOLECULAR DIPOLES IN LIQUID CRYSTALS

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*A vast majority of compounds exhibiting liquid crystalline phases have polar molecules. The nematic director is apolar, even when the molecules have cyano or nitro end-groups, as neighbouring molecules tend to have an antiparallel short-range order. This leads to a partial bilayer structure in the smectic A phase of rod-like molecules as also many interesting phase transitions. The latter can be understood on the basis of a change over to a polar short-range order as the density of the medium is increased. If the molecules have bent-cores and cyano end-groups, a partial bilayer biaxial smectic A phase is also found, implying the formation of quartets with an apolar structure.*

*Lateral dipolar components lead to a tilting of molecules in smectic phases. This can be understood on the basis of the off-axis locations of such dipoles. A mean field theory of smectic C liquid crystals based on this mechanism gives results which reflect experimental trends. In appropriate cases, the possibility of occurrence of a cone-phase consisting of double-tilt cylinders is also pointed out.*

*Keywords*: antiparallel short-range order; biaxial smectic A phase; cone phase; polar molecules; polar short-range order; smectic C liquid crystals

## INTRODUCTION

An overwhelming majority of mesogenic compounds have anisotropic molecules with net permanent dipole moments. Indeed the first molecular theory of nematic liquid crystals proposed by Max Born [1] in 1916 assumed that dipolar interactions produce the orientational order resulting in a medium which is ferroelectric. (It is interesting that ferroelectricity in crystals was discovered only in 1920 [2]). Subsequent work by Onsager [3] showed that hard rod features alone can stabilise the nematic and Maier and Saupe [4] argued that the most important attractive intermolecular interactions

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arise from the London dispersion forces. It is indeed quite remarkable that the director is apolar even when the molecules are highly polar, with cyano or nitro or other end groups. The invention of the TN displays in 1971 gave a big impetus to the synthesis of such compounds to reduce the operating voltage. Schadt [5], who made the first careful measurements on the low frequency dielectric properties of such a nematic noticed an unusual feature, that the average dielectric constant $\bar{\varepsilon}$ had a *positive* jump across the nematic-isotropic transition. One would have normally expected a negative jump corresponding to that in the density of the medium. We [6] argued that the observed reverse trend implies that the neighbouring highly polar molecules have an antiparallel correlation. This can be easily understood as the dipolar interaction energy ($\propto -\mu^2/r^3$, $r$ being the relevant intermolecular separation) is much stronger for 'side-on' molecules with $r \cong 5$ Å,compared ,compared to that for the end-on molecules with $r \cong 25$ Å in typical cases. We treated the problem by assuming that the nearest neighbour interaction energy in a Bethe-type cluster of (z + 1) molecules to be of the form

$$U_{ij} = AP_1(\cos\theta_{ij}) - BP_2(\cos\theta_{ij}) \tag{1}$$

in which the second term arises from anisotropic dispersion interaction. Each outer molecule of the cluster is also subjected to a mean field

$$V_j = -B^* P_2(\cos\theta_j). \tag{2}$$

The problem can be solved using different types of approximations, used in equivalent problems in magnetism. The antiferroelectric short-range order reduces the contribution from the orientational polarization to the dielectric constant $\varepsilon_{\|}$ for the electric field parallel to the director $\hat{n}$. The short range order jumps to a lower value across the nematic-isotropic transition, thus relatively enhancing the average dielectric constant of the medium. Subsequent X-ray studies showed that the antiparallel short-range order in such materials leads to a smectic A like local structure with a layer spacing $\cong 1.4\,l$ where $l$ is the molecular length [7]. This can be understood as arising from the biphilic nature of these molecules, and the very large dispersion interaction between the aromatic moieties reflected in the second term of Eq. (1) (See Fig. 1). It is also quite obvious that the antiparallel short range order gives a natural explanation of the *apolar* nature of the director in such materials.

## POLAR END GROUPS AND LIQUID CRYSTALLINE ORDER

### (a) Rod-like Molecules

The higher homologues of compounds with the cyano or nitro end groups give rise to the smectic A phase with a layer spacing $d$ lying between $l$ and

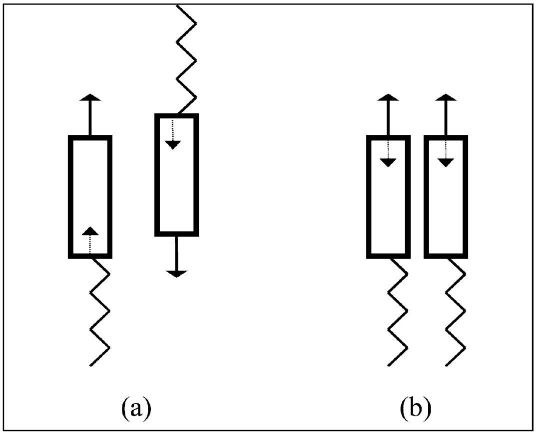

**FIGURE 1** Schematic diagram showing the molecular pairs with (a) antiparallel short range order. The dipole induced by the neighbour adds to the total dipole moment of the molecule. The pair has a length incommensurate with the molecular length. (b) When the molecules have a small separation, the parallel configuration is favoured. Now the induced dipole reduces the net dipole moment of the molecule.

$2l$, and called the 'partial bilayer' or $\mathrm{SmA_d}$ phase. Cladis [8] discovered that such compounds exhibit the reentrant nematic ($\mathrm{N_{re}}$) phase, which occurs at temperatures *lower* than those corresponding to the range of occurrence of the $\mathrm{SmA_d}$ phase. Subsequently a large number of highly polar compounds were synthesized, especially in Bordeaux and several other unusual phase sequences were discovered [9]. Some examples are: 1) double reentrance in which the phase sequence on cooling is Iso-N-$\mathrm{SmA_d}$-$\mathrm{N_{re}}$-$\mathrm{SmA_1}$ 2) quadruple reentrance, with the phase sequence: Iso-N-$\mathrm{SmA_d}$-$\mathrm{N_{re1}}$-$\mathrm{SmA_d}$-$\mathrm{N_{re2}}$-$\mathrm{SmA_1}$-SmC 3) first order transition between two smectic A phases with a jump in layer spacing and also (4) a first order transition between two nematic phases, with a jump in the orientational order parameter.

Prost developed a phenomenological Landau theory to account for these various phenomena by recognizing that there is a competition between two lengths in the medium [9]. As we noted earlier, the partial bilayer structure produces a length between $l$ and $2l$. Prost assumed that the other length is the 'natural' molecular length $l$. Smectic orders corresponding to both these lengths can condense in the medium, resulting in frustration, and the different phase sequences.

There have been several attempts to develop molecular theories of the phenomena. As Prost's theory is highly successful in explaining all the phenomena, the basic problem is to account for the two lengths assumed in the theory. Going back to the antiferrolectric short-range order generating the partial bilayer length $l_d$, it is quite feasible for antiparallel *pairs* to be stabilized, since the polar interaction of any third molecule with the pair is frustrated. One might think that as the temperature is raised, the pairs break up and the separated individual molecules give rise to the monomolecular length '$l$' involved in the phenomenological model. However, in doubly reentrant compounds the *lower* temperature smectic phase is the one with a layer spacing $d \cong l$ and denoted by $SmA_1$ and the higher temperature phase is the $SmA_d$ phase.

Berker and co-workers [10] have developed a model called the 'frustrated spin-gas' model which is similar to the one used to describe magnetic systems. The configurations of triplets of molecules which are assumed to be aligned perpendicular to a layer are considered. The molecules have translational freedom along the layer-normal, and the intermolecular potential is assumed to have notches arising from the details of molecular structure, including the zig-zag conformation of the chain. The triplet configurations are sensitive to the frustration effects mentioned earlier and if any configuration has a long range correlation in the layer, it is assumed to represent a smectic layer. Otherwise the molecules can slip out of the layer and the medium is assumed to be in the nematic phase. Though the topologies of the different calculated phase diagrams involving reentrant sequences are similar to the experimental ones, the model is 2-dimensional in nature and the predicted transition temperatures are rather too low. Further, it cannot predict the SmA-SmA or N-N transitions.

We [11] developed a simple molecular theory of polar compounds in which these deficiencies are removed. In all the compounds exhibiting the unusual phase sequences described earlier the strongly polar cyano or nitro end-group is attached to an aromatic core which is highly polarizable. This has two consequences: (i) The effective dipole moment of each molecule increases compared to that due to the end-group moment (ii) As the intermolecular separation is $\sim 5\,\text{Å}$, the dipole of a given molecule also induces a sizable dipole which is oriented in the opposite direction in its neighbour (Fig. 1). When the neighbours have an antiparallel configuration, the molecular dipole is enhanced further due to this intermolecular induction effect and the dipolar intermolecular energy is further lowered. However, in the resulting partial bilayer pair the aliphatic chains of the two molecules are on opposite sides of the structure and hardly interact.

If the two molecules are parallel, however (Fig. 1), the chains are in close proximity and there is a net gain in the intermolecular energy due to the dispersion interaction between the chains. In this configuration the parallel dipoles give rise to a repulsive intermolecular interaction. However, the dipole which is induced by the neigbouring molecule of the pair is now oriented opposite to the permanent dipole of the given molecule.

This reduces the net dipole moment on each molecule and hence the repulsive dipolar interaction as well.

Since the permanent dipole-permanent dipole interaction is $\propto 1/r^3$ while both the dispersion interaction between the chains and the dipole-induced dipole interaction are $\propto 1/r^6$, it is clear that the parallel configuration can become favourable if $r$ is small enough. The 'configurational' parts of the intermolecular energy are:

$$\begin{aligned} E_A &= E_{\uparrow\downarrow} = -\mu_{net}^2/r^3 \\ E_P &= E_{\uparrow\uparrow} = -\mu_{net}^2/r^3 - C/r^6 \end{aligned} \tag{3}$$

where $\mu_{net} = \mu_{perm} + \mu_{induced}$ and $C$ the coefficient of the dispersion interaction between the chains. $\mu_{net} = \mu_{perm}/(i \mp x/r^3)$ where $\chi$ is the longitudinal component of the polarizability of the aromatic core and the negative and positive signs correspond to antiparallel and parallel configurations respectively. Calculations [11] with very reasonable values of the parameters show that the parallel configuration is favoured for $r \leq 5$ Å. As the temperature is lowered the density of the medium increases and we can expect that below some temperature the parallel configuration is favoured over the antiparallel one. Assuming a linear relationship between density and temperature, it is convenient to write the difference in the configurational energy as

$$\Delta E = E_A - E_p = R_1 K_B T_{NI}(R_2/T_r - 1) \tag{4}$$

where $R_1 K_B T_{NI}$ is an interaction parameter expressed in terms of the Boltzmann constant $K_B$ and the NI transition temperature $T_{NI}$. The reduced temperature $T_r = T/T_{NI}$ and $R_2$ is the value of $T_r$ at which the density is such that $\Delta E = O$. A simple mean field theory of the medium can be written by assuming it to be a mixture of parallel and antiparallel pairs. As we mentioned earlier, pairs can be stabilized in the antiparallel configuration by frustration in the alignment of a third polar molecule. On the other hand, there is no such problem with parallel molecules and the short-range ferroelectric order can extend over several molecules. It is very convenient to treat the parallel configuration also to consist of effective pairs for the sake of simplicity. The McMillan theory of SmA can then be extended for the mixture of the two types of pairs. The McMillan parameter which is a measure of the smectic interaction strength is given by:

$$\alpha_A = 2\exp\{-[\pi r_o/(r_o + 2c)]^2\} \tag{5}$$

for the antiparallel (A) type pairs where $r_o$ is the length of the aromatic core and $c$ that of the end-chain, and $r_o + 2c = l_d$ that of the A-type pair. This has a considerably larger value than the McMillan parameter for the parallel pairs $\alpha_P$:

$$\alpha_P = 2\exp\{-[\pi r_o/(r_o + c)]^2\}. \tag{6}$$

It is now easy to understand the double reentrant sequence: The higher value of $\alpha_A$ of the antiparallel pairs whose concentration is large at higher temperatures (lower densities) stabilizes the $\mathrm{SmA_d}$ phase. As the temperature is lowered, and the P-type configurations prevail, the relevant McMillan parameter is too low to sustain the smectic order and the medium reenters the nematic ($\mathrm{N_{re}}$) phase. As the temperature is lowered further, the SmA phase with a layer spacing corresponding to the length of the 'P' type pairs which is just the molecular length is stabilized i.e., the medium goes over to the $\mathrm{SmA_1}$ phase. The double reentrant sequence occurs for a narrow range of values of $\alpha_A$.(Fig. 2). For larger values $\alpha_A$, the smectic is never destabilized: the layer spacing continuously evolves from the monolayer to the partial bilayer value as the temperature is raised. This phase diagram reflects the experimental trends extremely well.

The presence of other polar groups in addition to the cyano or nitro end group produces some variations in the phase behaviour. In particular, if there are one or more ester linkage groups in the aromatic core, and the

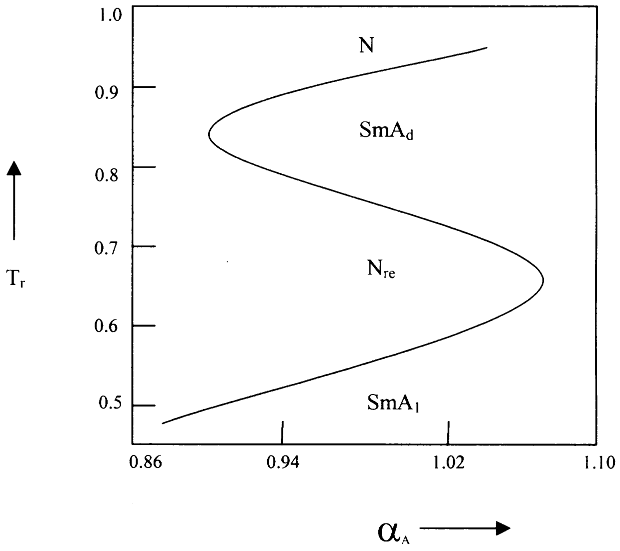

**FIGURE 2** The calculated phase diagram exhibiting the double re-entrant sequence over a narrow range of the McMillan parameter $\alpha_A$ corresponding to the antiparallel pairs (adapted from Ref. 11).

longitudinal components of their net dipole moments add to that of the end group, the double reentrant sequence occurs as discussed above. The X-ray scattering in the lower temperature phase clearly shows a monolayer spacing, implying that the polar order in successive layers is aligned. However it does not mean that $\mathrm{SmA_1}$ is a ferroelectric medium. The X-ray scattering [12] also shows diffuse spots corresponding to a lateral domain size $\sim 70\,\text{Å}$, implying that the polar order reverses sign in the smectic layers with that spacing.

If the central dipoles in the molecules are opposed to the end dipole, the net dipole moment is reduced considerably and in the lower temperature smectic phase the aromatic parts of adjacent layers can be in close proximity which is favoured by the dispersion interaction, and the repulsive interaction due to the ferroelectric short range order is not very large. Thus the medium exhibits a bilayer $\mathrm{SmA_2}$ phase, with an antiparallel order in successive layers.

Coming back to materials with additive dipolar groups, the model developed above *requires* the medium to have a polar short range order. In order to test if this is the case, we conducted experiments on the effect of high electric fields (upto $\sim 600\,\mathrm{esu}$) on such compounds [13]. In p-cyanophenyl p-n-heptyl benozate (CP7B) which is a nematogen with an ester group with its dipole moment adding to that of the cyano end-group, we conducted the experiment close to the critical point in the nematic-field induced paranematic transition. An electrical impedence analysis of the cell is used to measure the conductivity $\sigma_{\|}$, the dielectric constant $\varepsilon_{\|}$ as well as higher harmonics of the current flowing though the medium for an applied AC voltage at a frequency (f) of 11 KHz. The 3rd harmonic (3f) signal is proportional to the order parameter susceptibility $(\partial S/\partial \mathrm{E}^2)$ and exhibits a peak at the critical temperature $Tc$ (Fig. 3). The conductivity at f also shows a peak but at a temperature which is lower than $Tc$. The observation can be understood by assuming that the relaxation of polar short range ordered groups contribute to the dielectric loss and hence to the effective conductivity. The corresponding polarization will have a collective response as the critical point is approached. The Landau–Khalatnikov relaxation rate for the collective response satisfies

$$\frac{1}{\tau} \propto \frac{T_{c-}T}{T_c}. \tag{7}$$

The corresponding contribution to the conductivity is given by

$$\sigma_{\|}(\omega) = \varepsilon_o \frac{(\delta\varepsilon)}{1+\omega^2\tau^2}\tau\omega^2 \tag{8}$$

where $\varepsilon_o$ is the vacuum dielectric constant, and $\delta\varepsilon$ the difference between the low frequency and high frequency limits of the dielectric constant.

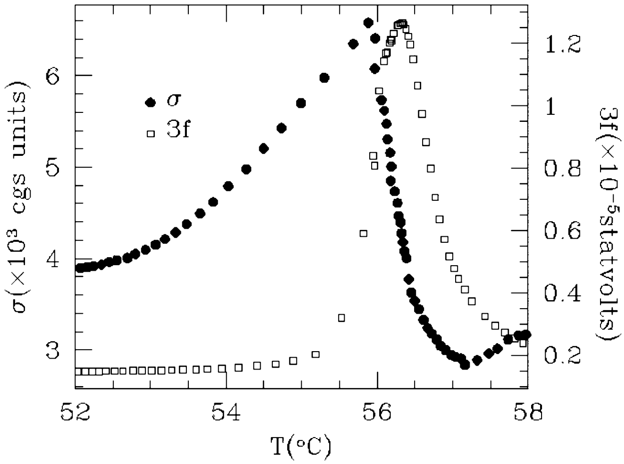

**FIGURE 3** Temperature variations of the electrical conductivity ($\sigma$) and the third harmonic signal of CP7B under an applied field of 472 esu at 11 KHz (after Ref. 13).

The peak of conductivity occurs at $\omega\tau = 1$ where $\omega = 2\pi f$. The experimental data could be fitted to the equation with $\delta\varepsilon \cong 3$. This shows that there is a fraction with the polar short range order contributing to the relaxation process. Indeed a weak second harmonic peak is also seen at a high field, again indicating that there are polarized domains which are unable to reorient with the field.

The theoretical model can be extended to get other phase diagrams by noting the following two points: (i) $\Delta E$, the difference in energy between the parallel and antiparallel configurations can be expected to increase with the chain length which contributes to the intermolecular energy in the parallel configuration. Calculations [14] show that $\Delta E \propto {\alpha_A}^4$ when $\alpha_A \cong 1$. (ii) The mutual interaction energy between the antiparallel and parallel pairs is assumed to have a negative deviation from the geometric mean rule. Experimentally it is known that in binary mixtures in which one component exhibits the SmA$_1$ phase while the other the SmA$_d$ phase, the SmA-N transition line plotted as a function of concentration has a concave shape. Thus it is assumed that the McMillan parameter for the mutual interaction

$$\alpha_{AP} = \alpha_{PA} = Q\sqrt{\alpha_A\alpha_p} \text{ with } Q < 1. \tag{9}$$

With these assumptions, the calculated phase diagram shows a nematic lake surrounded by the smectic phase on all sides as seen in many binary mixture phase diagrams [14]. Further, a first order SmA$_1$ to SmA$_d$ transition line is also obtained across which the layer spacing jumps. The line ends in a critical point beyond which there is a continuous evolution between the two smectics.

Indeed the $\mathrm{SmA_d}$–$\mathrm{SmA_1}$ line can extend to the reentrant nematic range as a weak first order transition between two nematic phases at which the orientational order parameter jumps and the specific heat exhibits a large peak [15]. This would correspond to a jump in the relative concentration of the A-and P-types of pairs across the transition point and requires a negative deviation in the mutual orientational potential between the two types of pairs i.e., $U_{AP} = P\sqrt{U_A U_P}$ with $P < 1$. Indeed there are examples in which the nematic-nematic transition occurs in purely nematogenic compounds i.e, not necessarily in the reentrant nematic range [16].

Another experimental observation which can be understood on the basis of the molecular model is the fact that the $\mathrm{SmA_d}$ phase is bounded in the pressure-temperature phase diagram [17]. Higher pressures bring the molecules closer thus destabilising the A-type of pairs. At sufficiently high pressures, the $\mathrm{SmA_d}$ phase is no longer stable. The theory has been extended [18] to include excluded volume effects in the medium by extending a model developed by Koda and Kimura [19] for smectic phases in mixtures. The A and P types of pairs are assumed to have the shape of right circular cylinders with the same volume but different aspect ratios $L/D$, where $L$ is the length and $D$ the diameter of the cylinders. Assuming a perfect orientational order, transitions between smectic and nematic phases have a second order character. Restricting the free energy expansion to the second virial term, the experimental trends in pressure-temperature phase diagrams are reproduced. The quadruple reentrant sequence is also obtained in a narrow parameter range. The $\mathrm{SmA_1}$–$\mathrm{SmA_d}$ and $\mathrm{N_1}$–$\mathrm{N_d}$ transitions are now reproduced without assuming the negative deviation from the geometric mean rule in the mutual interaction potential. Indeed it can be shown from the free energy expression that the excluded volume effects arising from the hard rod features of the pairs are equivalent to such a deviation in the attractive potential.

Experimentally, it has been shown that the $\mathrm{SmA_d}$ phase trends to get bounded as a function of electric field also [20]. The above model has been extended to include the effect of the field. The orientational order parameter increases substantially in the presence of the field ($\mathrm{E}^2$ is conjugate to $S$ as the latter is a second rank tensor). This is turn increases the density and hence the concentration of the P-type of pairs, destabilising the $\mathrm{SmA_d}$ phase.

Thus all the unusual phenomena seen in highly polar compounds can be accounted for by a change of configuration in the mutual orientation of molecular pairs, forming a parallel alignment at lower temperatures and an antiparallel one at higher temperatures. The experimental evidence so far is that the parallel configuration leads to a polar short-range order.

The obvious question is: can a polar *long* range order be stabilized in such a system, leading to a ferroelectric nematic as originally envisaged by Max Born? Indeed several theoretical studies and numerical simulations on polar molecules appear to indicate the possibility of occurrence of a ferroelectric nematic at low temperatures [21], though no experimental evidence has been found so far.

### (b) Bent-core Molecules with Cyano End-groups

Mesophases exhibited by bent-core molecules (the Bn phases) are now being studied extensively. If one end of the core has a cyano group and the other end a long enough alkyl chain, the compound is found to exhibit a *biaxial* smectic A phase which has a transverse *apolar* director in addition to the one associated with the long axes of molecules [22]. It is clear that the antiparallel *pair* in this case has fairly large transverse components of dipole moments contributed by the cyano end-groups of both molecules in the pair. The pair itself is bow-shaped and the transverse dipoles of two such pairs would tend to be antiparallel to lower the energy. Thus one can think of the medium to a consist of *quartets* of the bent-core molecules which are apolar in both longitudinal and transverse directions (Fig. 4). They are also highly biaxial and thus give rise to the biaxial SmA phase. However the chain-rich regions are sparsely populated as each quartet contributes only two chains to either side of a given layer and as the temperature is raised, the medium undergoes a transition to the uniaxial smectic A phase.

## ROD-LIKE MOLECULES WITH TRANSVERSE DIPOLES: TILTED SMECTIC PHASES

In smectic C liquid crystals the director makes a tilt angle $\omega$ with respect to the layer-normal. McMillan [23] proposed that the tilting mechanism has to do with a rotational freezing due to the dipolar intermolecular interaction between two outboard transverse components located on the axis of each molecule. Experimentally it is found that the hindrance to free rotation is extremely small and hence the mechanism does not work. There have been many other attempts, which are generally unsatisfactory to develop a molecular theory of smectic C liquid crystals, as discussed in detail by Goossens [24]. SmC* liquid crystals with chiral molecules exhibit a transverse polarization of the layers, and have interesting electrooptic effects which are now exploited commercially. Further, a large number of compounds have been synthesised which exhibit the antiferroelectric $\mathrm{SmC}^*_A$ phase

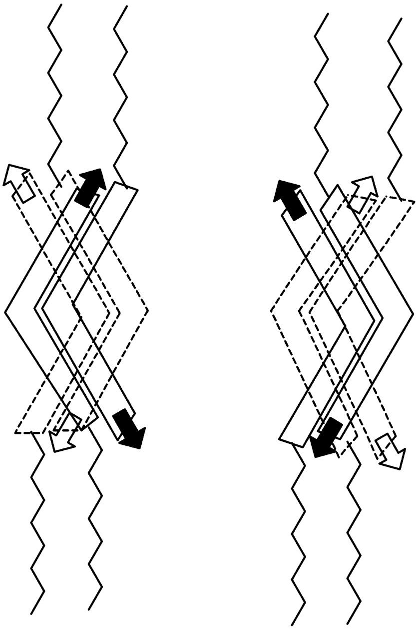

**FIGURE 4** Proposed quartet-structure in biaxial smectic layers of bent-core molecules with cyano end-groups. The structure which is highly biaxial is apolar in both longitudinal and transverse directions.

as well as hexatic phases with tilted molecules. It is obviously important to understand the molecular origin of tilt in all these liquid crystals.

We [25] recently proposed a model by noting that (a) transverse dipolar groups do indeed play an essential role in generating tilt [26] and (b) the molecular structure is generally such that the dipoles are *off-axis*, i.e, not located on the long axis of the molecule as assumed by McMillan. The $1/r^3$-dipolar interaction energy then leads to a strong repulsion when the dipoles of neighbours are opposed, which is not compensated by the weak attraction when they are parallel (Fig. 5), even when the molecules are freely rotating about their long axes in a smectic layer. The net repulsion energy can be lowered by a relative displacement of the molecules along the long axes. Taking into account the attractive dispersion energy which depends on the overlap length of the aromatic cores, and the up-down symmetry implied by the apolar nature of the director and averaging over all the near neighbour configurations in a smectic C layer in which the average tilting is confined to one plane, it can be shown that the intermolecular potential is minimised for a nonzero value of the tilt angle. The tilt angle naturally depends on the strengths and locations of all the transverse

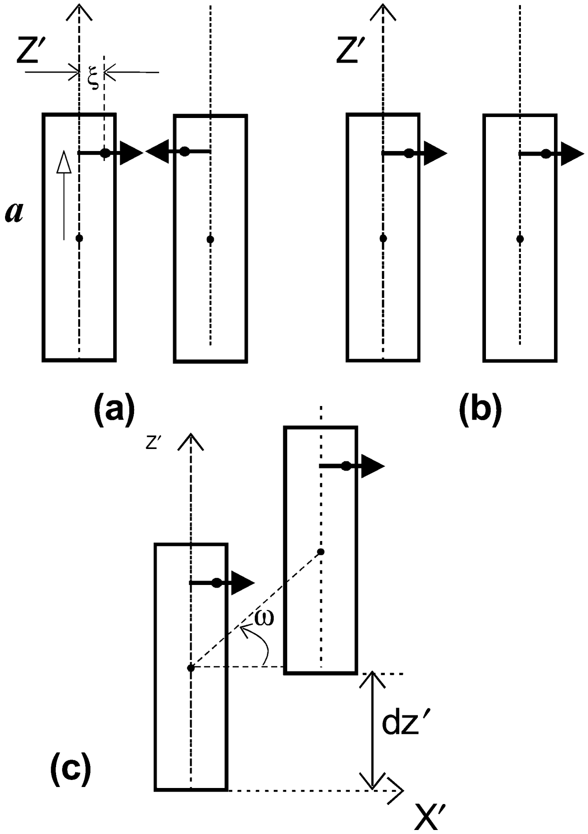

**FIGURE 5** The off-axis dipolar mechanism of tilt in smectic C layers. The repulsive energy of antiparallel configuration of dipoles (a) is much larger than the attractive energy of parallel configuration (b) resulting in a relative shift of the molecules (c) (after Ref. 25).

dipoles. A molecular mean field theory is then developed by using the single particle tilting potential

$$u_C(\theta_i, \phi_i) = -\beta\eta\tau^2 \sin 2\theta_i \cos\phi_i \tag{10}$$

where $\theta_{\mathrm{i}}$ and $\phi_{\mathrm{i}}$ are the polar and azimuthul angles of the $i$th molecule with respect to the Cartesian co-ordinate system with its z-axis along the layer normal and $u_c$ takes into account the biaxial symmetry of the smectic phase. $\eta = \langle \sin 2\theta \cos\phi \rangle$ is the tilt-order parameter, and $\tau = \langle \cos 2\pi z/d \rangle$ the transnational order parameter of the smectic liquid crystal. Adding this to the McMillan potential of the layering order, the molar internal energy is given by:

$$U = -(N/2)u_o\{(1+\alpha\tau^2)S^2 + \alpha\beta\tau^2\eta^2\} \tag{11}$$

in which N is the Avogadro number, $u_o$ is the strength of orienting potential, $u_o\alpha$ the strength of the layering potential of the orientationaly ordered molecules, and $u_o\alpha\beta$ the strength of tilting potential of the molecules having the layering order. $S = \langle 3cos^2\psi - 1/2\rangle$ is the orientational order parameter where $\psi$ is the angle made by the molecular long axis with the director $\hat{n}$. The molar entropy is given by

$$\mathscr{S} = Nk_B\left[\frac{1}{2\pi d}\int\limits_{-1}^{+1} d\cos\theta \int\limits_{o}^{\pi} d\phi \int\limits_{-d/2}^{d/2} dz \quad f\ln f + \gamma\tau^2\sin^2\omega\right] \tag{12}$$

where $k_B$ is the Boltzmann constant, $d$ the layer spacing, the first term arises from the single particle distribution function $f(\theta,\phi,z)$ and the second term is the hard-rod contribution to entropy which favours the smectic A phase with $\omega = O$ and $\gamma$ depends on the length to width ratio of the molecule. The molar free energy $F = U - T\mathscr{S}$ is now minimised with respect to the distribution function by a variational procedure. The order parameters $S$,$\tau$ and $\eta$ satisfy the usual consistency conditions, which also ensure that the free energy is minimised. The calculated phase diagrams as functions of $\alpha$ and $\beta$ are shown in Figure 6. They reflect the experimental trends. On increasing the chain length (and hence $\alpha$), the smectic A range shrinks to zero, giving rise to a first order SmC-N transition at which the tilt angle jumps from a finite value to zero. It is also known that the addition of an extra dipole to the molecular structure (and hence increase the tilting potential $\beta$) changes the N-SmA-SmC sequence to N-SmC sequence. Other experimentally observed phase diagrams like tricritical points in both SmC-SmA and SmA-N transition lines and the second-order SmC-SmA and SmA-N lines meeting the first order SmC-N line can be obtained by using appropriate parameters of the potentials [25] (see Fig. 7).

## POSSIBILITY OF A CONE-PHASE NEAR THE SMC-N TRANSITION POINT

It is clear from the mechanism for tilting illustrated in Figure 5, that the tilting need not be confined to a plane as in SmC liquid crystals. In the latter, in a direction orthogonal to the tilting plane, the intermolecular energy is not minimised. The energy can be lowered if all the molecules around a given one have displacements parallel to the long axes. This can be continued such that we can get a double-tilt cylinder which has an obvious

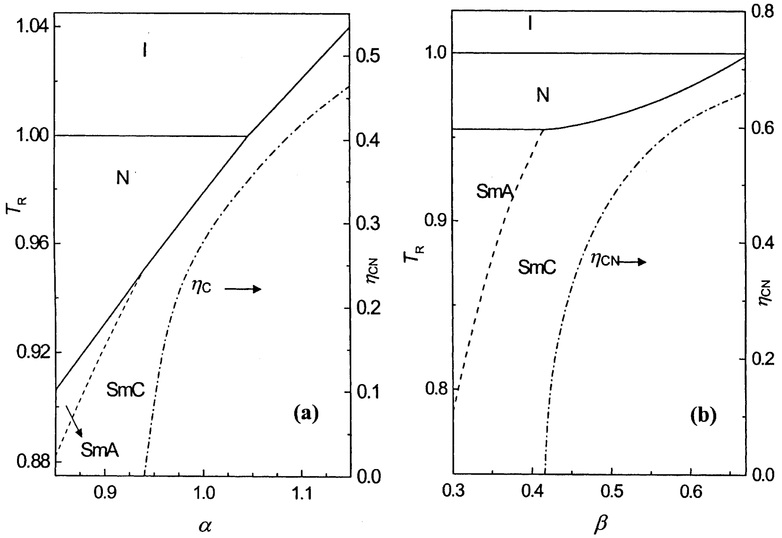

**FIGURE 6** Calculated phase diagrams for $\gamma = 3$, (a) as a function of $\alpha$, with $\beta = 0.42$ and (b) as a function of $\beta$ with $\alpha = 0.95$. The dashed line indicates a second order transition and solid line a first order transition. The jump in $\eta_{CN}$ at the first order SmC-N transition decreased to zero as the N-SmA-SmC point is reached.

analogy with the double twist cylinder responsible for the occurrence of blue phases near the cholesteric-isotropic transition point in highly chiral materials [9]. The double-tilt cylinder will have a stacking of conically distorted layers rather than flat layers as in the SmC liquid crystal. The cylinders can form a close packed triangular lattice, which will have interstices which can be filled by the higher temperature nematic phase. As the conical structure involves a disclination in the *c*-vector field and a Gaussian curvature of the bent layers at the apex, the relevant elastic energies have to included in the calculation and it can be shown that such a 'conical-phase' can be stabilized in a narrow range of temperatures for an appropriate set of parameters [27]. We are not aware of any experimental evidence for such a phase. However, it is known that several compounds [28,29] exhibit a wide nematic range with a well developed skew-cybotactic (i.e., with layers made of tilted molecules) *short-range* order but not undergoing a transition to the SmC or any other phase. In these cases, in addition to the strong scattering corresponding to the layers with a spacing $d < l$, meridional reflections upto 6 orders are also recorded, with $d \cong l$. This fiber-like pattern clearly points to a correlation of molecules *along* the director and can be understood easily if the fibers are made of the double-tilt conical structures. The nematic would then correspond to a 'melted line' phase.

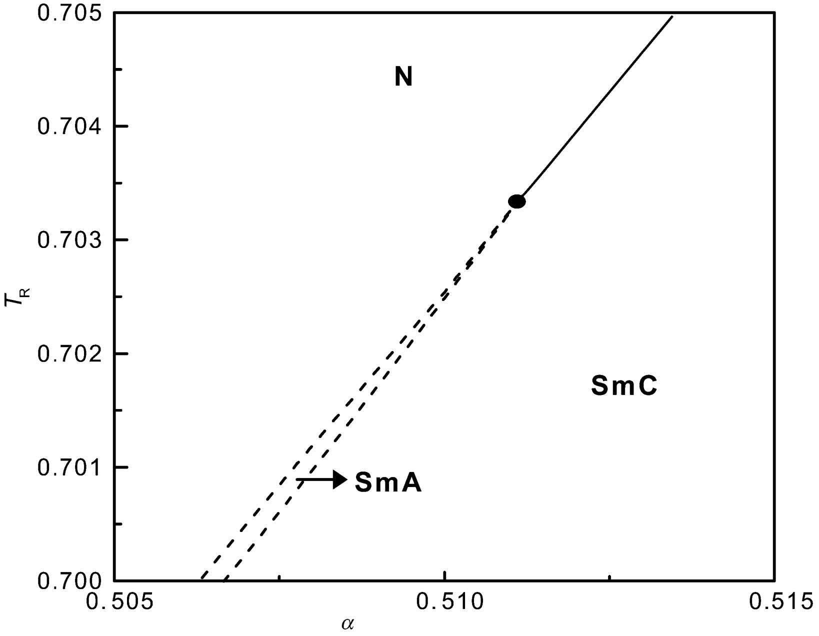

**FIGURE 7** Calculated phase diagram for $\gamma = 2$ and $\beta = 0.495$, showing the second order SmC-SmA and SmA-N transition lines meeting the first order Sm-C transition line at $\alpha = 0.5112$.

It would be interesting to look for the cone phase itself in related compounds.

## LIQUID CRYSTALS IN COMPOUNDS MADE OF BENT-CORE MOLECULES

Bent-core or bow shaped molecules with symmetrically (or nearly so) substituted end chains exhibit several different types of molecular organizations in liquid crystalline phases [30]. The dominating intermolecular interaction is steric, packing the molecules with their arrow axes along a common direction in layers. Thus the layers exhibit a large polarization (which can go up to a few $\mu C/cm^2$) as the molecules cannot freely rotate about the bow-axes. Unlike in the smectic C* phase, the molecules are not chiral but interestingly the molecules tilt in the layers about the arrow axes. Thus the layers spontaneously break achiral symmetry. The origin of the tilt can again be traced to dipolar intermolecular interactions, as in the case of SmC liquid crystals. The repulsive interaction between dipoles of neighbouring molecules which have components in the molecular plane can be reduced by the tilting about the arrow axes. If the dipole is as large as that of a cyano group attached to one end of the bent-core, the dipolar interaction energy is so large that quartet structures can form in the medium which organize themselves in an orthogonal smectic layer as we discussed earlier.

## CONCLUSIONS

Liquid crystals are soft materials exhibiting various electrooptic effects which have been exploited in flat panel displays. Molecular dipoles are very often useful in lowering the operating voltage, and there has been a large effort to synthesise compounds with dipolar groups. In both rod-like and bent-core molecules with cyano end-groups, the dipoles of neighbouring molecules interact so strongly that multi-molecular structures form and in turn produce new types of liquid crystalline phases and phase sequences. Again in both types of molecules transverse dipole moments can generate layered structures with tilted molecules and there is the possibility of a cone phase near the SmC-N transition point. If the rod-like molecules are chiral, the transverse dipoles also generate polarization in the tilted layers. In bent-core molecules which have an inherent layer polarization, the tilt generates chirality. In both cases, long range antiferroelectric interlayer interactions arise due to splay fluctuations of the layer polarization [31]. The second neighbour antiferroelectric interaction is always frustrated and can in turn generate intermediate ferrielectric phases in compounds with rod-like chiral molecules [32]. B2 phases exhibiting both antiferroelectric and ferroelectric order are now known, and the samples can often exhibit several different interlayer organizations. Some of them may presumably correspond to ferrielectric phases. Very recently the B5 phase which has an in-plane order in the layer structure has been shown to go over from a high temperature antiferroelectric to a low temperature ferroelectric state through a few intermediate structures which may be ferriphases [33]. The B7 phase is exhibited by compounds with the strongly polar cyano or nitro group attached in a direction opposite to the arrow axis on the central phenyl ring. The medium exhibits a 2-D lattice structure the details of which are not yet understood. However, the samples also exhibit some of the most beautiful liquid crystalline textures [30], whose origin ultimately may depend in the dipolar intermolecular interaction. Lastly, in binary mixtures of rod-like molecules one component having molecules with cyano or nitro-end groups and the other without such groups, charge complex formation between the two species leads to an induced-smectc phase [34]. Thus dipoles, which are not needed for the stability of the nematic phase, give rise to many other interesting mesophases.

# REFERENCES

[1] Born, M. (1916). *Sitz.d. Phys. Math., 25*, 614.
[2] Valasek, J. (1920). *Phys. Rev.*, *15*, 537.
[3] Onsager, L. (1949). *Ann. NYAcad. Sci.*, *51*, 627.
[4] Maier, W. & Saupe, A (1959). *Z. Naturforschg.*, *14a*, 882.
[5] Schadt, M. (1972). *J. Chem. Phys.*, *56*, 1494.
[6] Madhusudana, N. V. & Chandrasekhar, S. (1973). *Pramana Suppl.*, *1*, 57.
[7] Leadbettter, A. J., Richardson, R. M., & Colling, C. N. (1975). *J.de Physique*, *36*, C1-37.
[8] Cladis, P. E. (1975). *Phys. Rev. Lett.*, *35*, 48.
[9] deGennes, P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, Clarendon Press, Oxford. 2nd Ed.
[10] Indeku, J. O. & Berker, A. N. (1988). *J. de Physique*, *49*, 353.
[11] Madhusudana, N. V. & Rajan, J. (1990). *Liquid Crystals*, *7*, 31.
[12] Levelut, A. M., Hardouin, F., & Sigaud, G. (1980). *In: Liquid Crystals*, (Chandrasekhar, S. Eds.) Heyden, London, 143.
[13] Geetha, B. & Madhusudana, N. V. (1998). *Eur. Phys. J.*, *B1*, 179.
[14] Govind, A. S. & Madhusudana, N. V. (1997). *Liquid Crystals*, *23*, 327.
[15] Nounesis, G. Garland, C. W. & Shashidhar, R. (1991). *Phys. Rev.*, *A43*, 1849.
[16] Warrier, S. R., Vijayaraghavan, D. & Madhusudana, N. V. (1998). *Europhys. Letters*, *44*, 296.
[17] Cladis, P. E. (1981). *Mol. Cryst. Liquid Cryst.*, *67*, 177.
[18] Govind, A. S. & Madhusudana, N. V. (2000). *Liquid Crystals*, *27*, 1249.
[19] Koda, T. & Kimura, H. (1994). *J. Phys. Soc. Jap.*, *63*, 984.
[20] Geetha, B., Govind, A. S., & Madhusudana, N. V. (1997). *J. Physique II*, *7*, 1693.
[21] Zannoni, C. (2001). *J. Mater. Chem.*, *11*, 2637.
[22] Sadashiva, B. K., Amaranatha Reddy, R., Pratibha R., & Madhusudana, N. V. (2002). *J.Mater.Chem*, *12*, 943.
[23] McMillan, W. L. (1973). *Phys. Rev.*, *A8*, 1921.
[24] Goossens, W. J. A. (1985). *J. de Physique*, *46*, 1411.
[25] Govind, A. S. & Madhusudana, N. V. (2001). *Europhys. Letters*, *55*, 505 and to be published.
[26] Goodby, J. W. (1998). In: *Handbook of Liquid Crystals*, (D. Demus *et al.* Eds:), Wiley-VCH: New York, Chapter 5, Vol. *2A*.
[27] Hatwalne, Y. & Madhusudana, N. V. (to be published).
[28] Usha Deniz, K. Pepy, G. Keller, P. Farnoux. B., & Parette, G. (1985). *Mol. Cryst. Liq. Cryst.*, *127*, 81.
[29] Madhusudana, N. V., Moodithaya, K. P. L., & Suresh, K. A. *Mol. Cryst. Liq. Cryst.*, *99*, 239.
[30] Pelzl, G., Diele, S., & Weissflog, W. (1999). *Adv.Mater*, *11*, 707.
[31] Bruinsma, R. & Prost, J. (1994). *J. de Physique II.*, *4* 1209.
[32] Roy, A. & Madhusudana, N. V. (2000). *Eur. Phys. J.E.*, *1*, 319.
[33] Nadasi, H. *et al.*, *J. Mater. Chem*, (in press).
[34] de Jeu, W. H., Longa, L., & Demus, D. (1986). *J.Chem. Phys.*, *84*, 6410.