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Liquid Crystalline Materials: Physical Properties and Intermolecular Interactions [and Discussion]

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Liquid crystalline materials: physical properties and intermolecular interactions

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The physical properties and the phase behaviour of some nematic liquid crystals are discussed, with emphasis on the influence of short-range antiparallel dipole correlation that occurs in mesogenic compounds with a strong terminal dipole moment. Evidence for this effect, which stems especially from dielectric studies, is summarized. Variations of the dipole correlation with molecular structure can explain the sometimes unexpected phase behaviour and physical properties of these substances. A qualitative model is given in terms of a monomer–dimer equilibrium.

1. Introduction

During the last decade a growing interest has developed in the 'molecular engineering' of liquid crystalline materials to obtain specific properties. Here three aspects can be distinguished: chemical properties (discussed by others at this meeting); phase behaviour, like mesomorphic temperature range and nematic–smectic behaviour; physical properties, like birefringence, dielectric anisotropy and visco-elastic properties. The demands with respect to the first two points being largely satisfied, attention has shifted to methods of influencing the physical properties. Here we can distinguish two points: the properties of the molecules themselves, and the interactions through which a molecular property influences the macroscopic behaviour.

So far attention has been directed mainly towards the first of these two. However, it seems that the interactions mentioned above are far more variable than was commonly thought some years ago. This insight is mainly due to new results from the synthetic chemists, who have presented us with new mesogenic compounds that often show a behaviour that is rather unexpected from a more traditional point of view. In this paper I wish to show that many of these unexpected results can be rationalized in terms of differences in short-range correlation between the molecules.

The plan of the paper is as follows. In § 2 some of the more classical relations between molecular properties and macroscopic physical properties will be summarized. Next, in § 3, the evidence for short-range correlations will be discussed, emphasizing results from relatively recently synthesized compounds with strongly polar end-groups like CN, saturated ring systems, or both. Finally these results are used to understand at least qualitatively some of the features of the observed phase behaviour (§ 4) and of the macroscopic physical properties (§ 5).

2. Mesogenic molecules and anisotropic physical properties

The orientational statistics of the molecules giving a nematic phase is in principle well known. Usually it is assumed that in spite of possible internal motions a rigid body can be used to represent a molecule in its 'average' conformation. The simplest choice is then a body with cylindrical symmetry, which implies that any possible bias in the rotation of the molecules around their long axis is disregarded. A molecular property can be described by a second-rank tensor $\boldsymbol{\lambda}$ which now has a particularly simple form: only the elements λ_l (longitudinal) and λ_t (transverse) are different. The anisotropy observed macroscopically is related to $\lambda_l - \lambda_t$ and to the degree of orientational order. The latter is given by $S \equiv \langle P_2 \rangle = \langle \frac{3}{2}\cos^2\beta - \frac{1}{2} \rangle$, where the angular brackets indicate an average over all orientations, and β is the angle between the long molecular axis and the director $\boldsymbol{n}$ (preferred direction). I shall now discuss the type of relations given so far for various physical properties (de Jeu 1980, 1981).

(*a*) *Birefringence*

The birefringence of a nematic is given by the difference between the extraordinary and ordinary refractive index: $\Delta n = n_e - n_o = n_\parallel - n_\perp$, where the subscripts $_\parallel$ and $_\perp$ refer to the directions parallel and perpendicular to $\boldsymbol{n}$, respectively. In practice Δn is positive and varies from values close to zero to about 0.4. The refractive index is related to the response of matter to an electric field. On application of a field $\boldsymbol{E}$, an electric polarization $\boldsymbol{P}$ is induced, given by

$$\boldsymbol{P} = \epsilon_0(\boldsymbol{\epsilon} - \boldsymbol{I})\,\boldsymbol{E}, \tag{1}$$

where ϵ_0 is the permittivity of free space, $\boldsymbol{\epsilon}$ the relative permittivity tensor, and $\boldsymbol{I}$ the unit tensor. Taking $\boldsymbol{n}$ parallel to the z axis of a laboratory frame, $\boldsymbol{\epsilon}$ will be diagonal. In the optical frequency range

$$\epsilon_{ii} = n_i^2, \quad i = x, y, z, \tag{2}$$

with $n_\parallel = n_z$ and $n_\perp = [\frac{1}{2}(n_x^2 + n_y^2)]^{\frac{1}{2}}$. For a microscopic interpretation of the refractive index one considers the polarizability tensor $\boldsymbol{\alpha}$ associated with a molecule. Then one arrives at a macroscopic polarization

$$\boldsymbol{P} = N\langle \boldsymbol{\alpha} \cdot \boldsymbol{E}_i \rangle, \tag{3}$$

which can be equated to (1). Here N is the number of molecules and $\boldsymbol{E}_i$ the internal field, the sum of the macroscopic field and the average field of the dipoles of the surrounding molecules.

There are two reasons why attempts to predict the birefringence quantitatively are not very successful. In principle reasonable estimates of the electronic polarizabilities of a molecule can be obtained from the addition of tabulated bond polarizabilities. However, there is often an extra contribution, due to the conjugation of various groups, that is difficult to estimate. For mesogenic molecules this may be the most important contribution to the optical anisotropy. Secondly, there seems to be no satisfactory procedure to calculate the internal field and its possible anisotropy. In this situation the best one can do is inspect the molecule for the presence of unsaturated bonds and estimate where conjugation is possible. Comparison with results obtained from molecules with similar groups provides a fair idea of the possible birefringence.

(*b*) *Dielectric permittivity*

For non-polar compounds one finds for the static dielectric anisotropy similar values to those for $n_\parallel^2 - n_\perp^2$, as expected. By substitution of polar groups much larger anisotropies can be obtained. For *p*-cyano-substituted compounds anisotropies between 6 and 12 are found. When several polar groups are present, all having a dipole component in the same direction among the long molecular axis, $\Delta\epsilon$ values of more than 30 can be obtained. Substituting cyano groups at two *ortho* positions at a benzene ring, $\Delta\epsilon < -20$ has been observed.

In polar molecules the orientation polarization must be added to (3). Combination with (1) then gives

$$(\boldsymbol{\epsilon} - \boldsymbol{I})\,\boldsymbol{E} = (N/\epsilon_0)\,(\langle \boldsymbol{\alpha} \cdot \boldsymbol{E}_i \rangle + \langle \bar{\boldsymbol{\mu}} \rangle), \tag{4}$$

where $\bar{\mu}$ is the average value of the permanent dipole in the presence of the electric field. For the problems related to the description of the internal field E_l and of the directing field involved in the calculation of $\langle\bar{\mu}\rangle$ we refer to the literature (Böttcher & Bordewijk 1978; de Jeu 1978). For strongly polar molecules the dipole contribution to ϵ dominates. Independently of the details of the theoretical treatment one finds

$$\bar{\epsilon} \approx \mu^2/T, \quad \Delta\epsilon \approx \mu^2 S/T. \tag{5}$$

As we shall see in the next section, in several cases deviations from these functional relations are observed that must be interpreted as being due to short-range correlation between the dipole moments. Consequently attempts to calculate $\Delta\epsilon$ from group moments (which are in principle well known) can easily be in error by a factor of two.

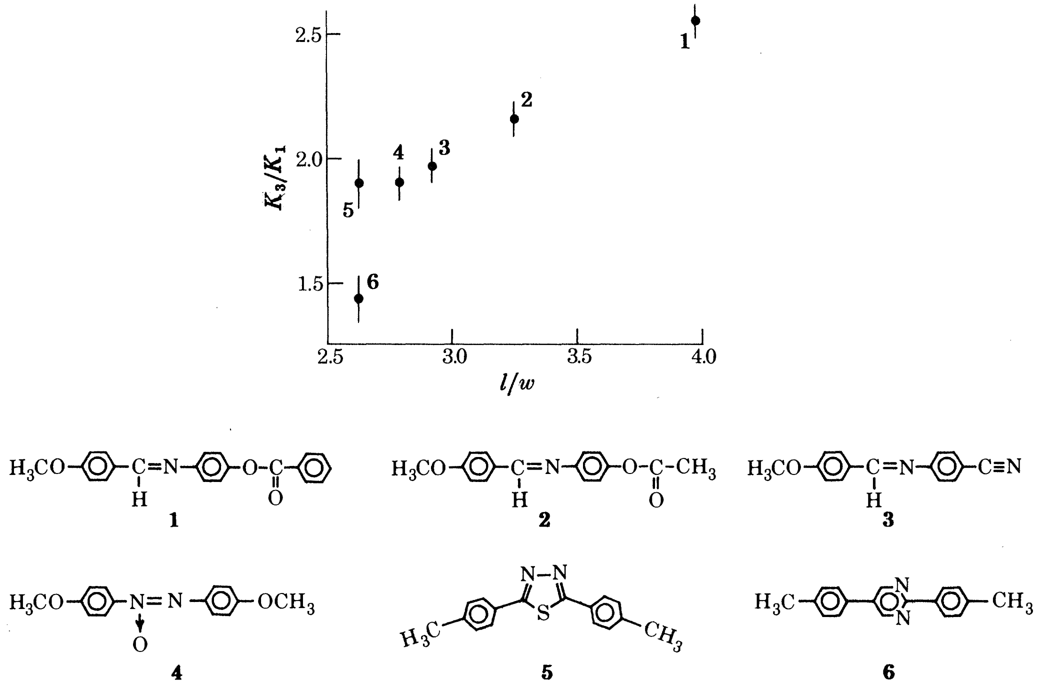


Figure 1. K_3/K_1 and the length/width ratio of some nematics without flexible alkyl chains (after Leenhouts & Dekker 1981).

(c) *Elastic constants*

The bulk elastic properties associated with the curvature of the director of a nematic liquid crystal are described by three elastic constants. These are associated with the restoring torques opposing splay (K_1), twist (K_2), or bend (K_3) of the director pattern. The ratio K_3/K_1 has been found to vary considerably, in contrast to K_2/K_1. For various compounds one finds approximately:

$$0.5 < K_3/K_1 < 4.0,$$

$$0.5 < K_2/K_1 < 1.2.$$

In fact in most cases $K_2/K_1 \lesssim 0.7$.

Leenhouts & Dekker (1981) established experimentally a relation between K_3/K_1 and the length/width ratio of the molecules. This is illustrated in figure 1, where also a new result for a banana-shaped molecule (**5**) has been included. In that case there is a possibility of adjusting to the bend field, which could lead to a lowering of K_3. As we see, this effect, if any, must be small, as **5** fits rather well into the general trend for K_3/K_1. This relation with length/width ratio is roughly in agreement with theoretical calculations of various types. However, it holds experimentally only for relatively rigid molecules. Homologous series show a very different trend. Here, K_3/K_1 is found to *decrease* with increasing length of the alkyl chain. This is a quite dramatic effect. If for compound **1** the terminal benzene ring is replaced by a butyl chain (which does not differ much in length), K_3/K_1 decreases from 2.4 to 1.3. A model that accounts for these differences has recently been given by Van der Meer *et al.* (1982). It incorporates increasing smectic-like short-range order with increasing alkyl chain length. Within the framework of various approximations this can reproduce the trend observed experimentally. Because the elastic constants are related to the gradients of the molecular interactions they can indeed be expected to be rather sensitive to short-range correlations.

(*d*) *Viscosity coefficients*

There seems to be a renewed interest in the viscous behaviour of liquid crystals these days. From the point of view of applications one may wish to compare the viscosities of various classes of compound. Then a simple flow experiment in which the orientation of $\boldsymbol{n}$ is not controlled may suffice (Constant & Raynes 1980). As discussed by F. M. Leslie at this meeting, from a more fundamental point of view the situation is rather complicated. If in a simple shear experiment the orientation of $\boldsymbol{n}$ is fixed, three different viscosities are immediately evident (figure 2). In addition to these shears, which are antisymmetric in the coordinates, a symmetric contribution also exists (figure 2*d*). If the orientation of $\boldsymbol{n}$ is not fixed, the motion of the director comes also into play. In the cases of figure 2*a*, *b* the shear will exert a torque on $\boldsymbol{n}$. The corresponding shear-torque coefficients (with the dimensions of a viscosity) are denoted by κ_1 and κ_2, respectively. Note that the associated rotation of $\boldsymbol{n}$ does not necessarily involve fluid motion. In the shear-plane in principle a situation of vanishing shear-torque can exist. Then $\boldsymbol{n}$ makes an angle θ_0 with the flow direction, given by

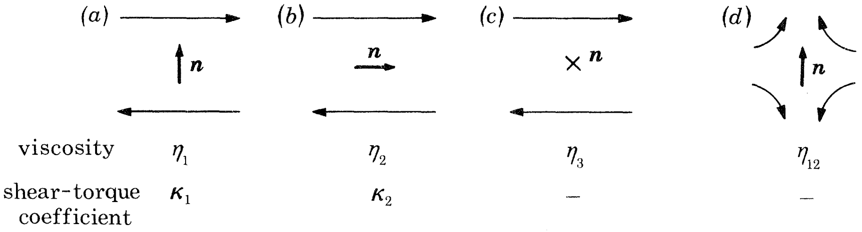


FIGURE 2. Definition of the various viscosity and shear-torque coefficients.

$$\tan^2\theta_0 = -\kappa_2/\kappa_1. \tag{6}$$

Sorting out the precise temperature dependence of the nematic viscosities proves to be rather difficult, let alone the molecular influences. The viscosity of an isotropic liquid varies approximately as

$$\eta_{\text{is}} = \eta_0 \exp(E/k_B T), \tag{7}$$

where $E > 0$ is an activation energy for diffusion. In the nematic phase the additional dependence on the order parameter will modify this activated process. As the temperature dependence of S is very weak compared with that in (7), this is difficult to determine. Kneppe *et al.* (1981) found that for several substances the reduced viscosities $\eta_i/\bar{\eta}$ $(i = 1, 2, 3)$ where $\bar{\eta} = \frac{1}{3}(\eta_1+\eta_2+\eta_3)$, behave in a very similar way (see figure 3).

As far as the shear-torque coefficients are concerned, many results are available for $\gamma_1 = \kappa_1+\kappa_2$, but there is no agreement yet on the actual dependence on S (Prost *et al.* 1976; Diogo & Martins 1981). The coefficient κ_2 is often rather small, leading to values of θ_0 close to zero. Interestingly, in several cases κ_2 changes sign as a function of temperature, in which case there is no longer a real solution to (6).

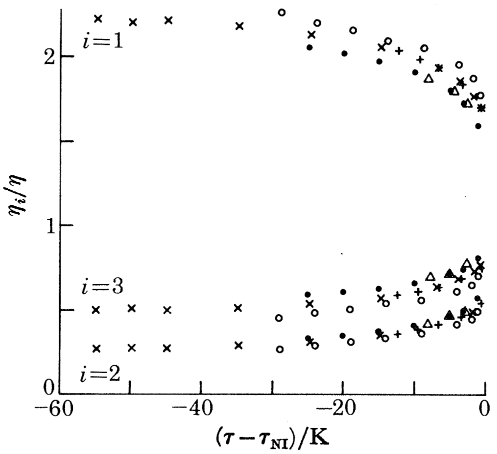


FIGURE 3. Reduced viscosities $\eta_i/\bar{\eta}$ for various compounds (after Kneppe *et al.* 1981).

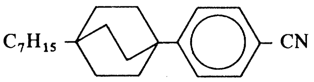
3. SHORT-RANGE CORRELATIONS

During the last few years synthetic organic chemists have presented us with several series of new mesomorphic compounds. Two aspects are here of special interest:

extensive use of strongly polar end groups (especially CN) to obtain a large positive $\Delta\epsilon$ – the best known examples are the *p*,*p*′-alkylcyanobiphenyls (*n*CB series; see **7** in table 1);

replacement of the traditional aromatic rings (benzene) by saturated ring systems such as cyclohexane and bicyclo(2,2,2)octane.

Very often both aspects are found in combination, which is probably not accidental. Some examples of compounds with cyclohexane rings are given in table 1. We can compare with

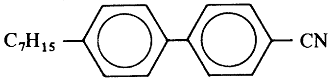
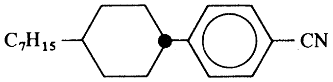
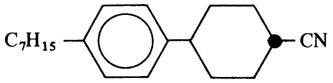
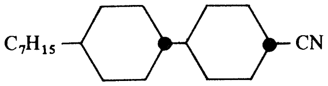


$$\mathrm{Cr} \xrightarrow{61\ ^\circ\mathrm{C}} \mathrm{N} \xrightarrow{95\ ^\circ\mathrm{C}} \mathrm{I}$$

In the absence of a terminal CN-group, compounds with saturated ring systems show often pronounced smectic tendencies.

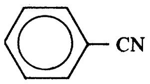
From table 1 we see that T_{NI} increases in the order **7**, **8**, **10**, and that T_{NI} of **9** is very low. *A priori* this order is somewhat unexpected: from the steric point of view these molecules are very similar, while one also does not expect the attractive dispersion forces to change in this order. Looking at some physical properties we note that n_{is} and also Δn decrease in the same order as T_{NI} increases. This decrease is evidently due to the replacement of the anisotropic and polarizable benzene rings by cyclohexane. More unexpectedly there are also important differences in ϵ_{is} at T_{NI}. This has often been too easily attributed to differences in conjugation. Conjugation of the CN dipole with an aromatic ring in fact can lead to two effects: an increase of the effective dipole moment, and delocalization of the dipole over the entire conjugated part of the molecule. The first effect is relatively small, as indicated in table 2, and is not sufficient to explain the large differences in ϵ_{is}. Furthermore ϵ_{is} is anyway smaller than expected for molecules with such a large dipole moment. This is all evidence for antiparallel dipole correlation. This idea is confirmed by the results given in figure 4, where we see that the temperature dependence of both ϵ_{is} and $\bar{\epsilon}$ in the nematic phase does not follow (5). In fact both are rather constant. This behaviour is typical for associated compounds, the association becoming stronger at lower temperatures. Then μ^2 must be replaced by $g\mu^2$, g being the dipole correlation factor. In our cases we find for **7**, **8** and **10** g of the order of 0.5.

TABLE 1. CLEARING POINTS AND SOME PHYSICAL PROPERTIES OF FOUR MESOGENS

	compound	m.p./°C	T_{NI}/°C	Δn†	$n_{is}(T_{NI})$	$\epsilon_{is}(T_{NI})$
7		29	42	0.16	1.56	9.7
8		30	57	0.09	1.50	8.5
9		18	−20†	—	—	—
10		71	83	0.05	1.47	5.6

† At $T_{NI} - T$ = 10 °C and 589 nm.
‡ Approximate value extrapolated from binary mixtures.

TABLE 2. DIPOLE MOMENTS OF THE CYANO GROUP (MINKIN *et al.* 1970)

compound	$\mu_{gas}/10^{-30}$ C m	$\mu_{solution}/10^{-30}$ C m†
C_4H_9CN	13.6	11.9
	14.6	13.1

† In benzene at 25 °C.

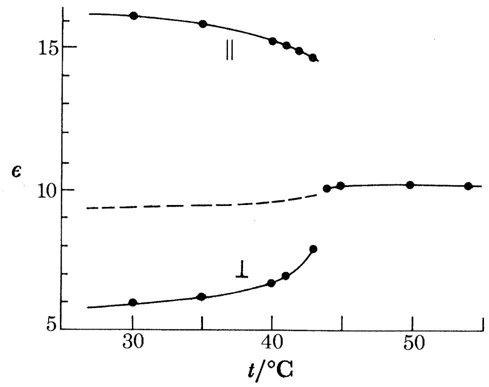


FIGURE 4. Static dielectric permittivities of 7CB (**7**).

Antiparallel dipole correlations in liquids can be described in a model as a monomer–dimer equilibrium:

$$\mathrm{D} \leftrightarrows 2\mathrm{M}. \tag{8}$$

The associated pairs need not necessarily exist on a human time scale, and a dynamic equilibrium will be involved. From the permittivity data of the CB series one can calculate values of the order of 0.4 for the dimer concentration x_D. Higher order n-mers will occur only with a low probability. This is mainly due to the effect of frustration (Toulouse 1977): if three parallel molecules are put on, for example, a triangular lattice, two can orient their dipole moments antiparallel, but the direction of the third is undetermined (figure 5). Only very specific choices of the lattice can avoid this frustration effect, for example four dipoles on a square lattice. The important conclusion is that with spatial disorder, as in a liquid, frustration of n-mers cannot be avoided. Only the dimers are free of it, and the formation of these is the most efficient way to lower the electrostatic part of the free energy. Summarizing, we can say that the formation of dimers is a consequence of the antiferroelectric interactions between dipole moments and probably also induced dipoles, in combination with the liquid structure.

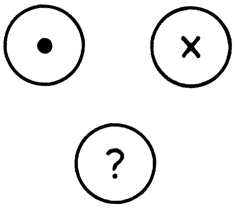


FIGURE 5. Frustration effect for three parallel dipoles on a triangular lattice.

The idea of molecular association of nitriles in both the nematic and the isotropic phase is supported by X-ray measurements (Leadbetter *et al.* 1975) and nuclear magnetic resonance studies (Saito *et al.* 1973). Additional information can sometimes be obtained from the layer spacing of a smectic A phase, when this phase occurs at lower temperatures. The spacing is usually not commensurate with the molecular length l, but varies for different compounds from $1.1\,l$ up to $1.6\,l$. This has been interpreted as variations in the degree of overlap of the molecules forming the dimer.

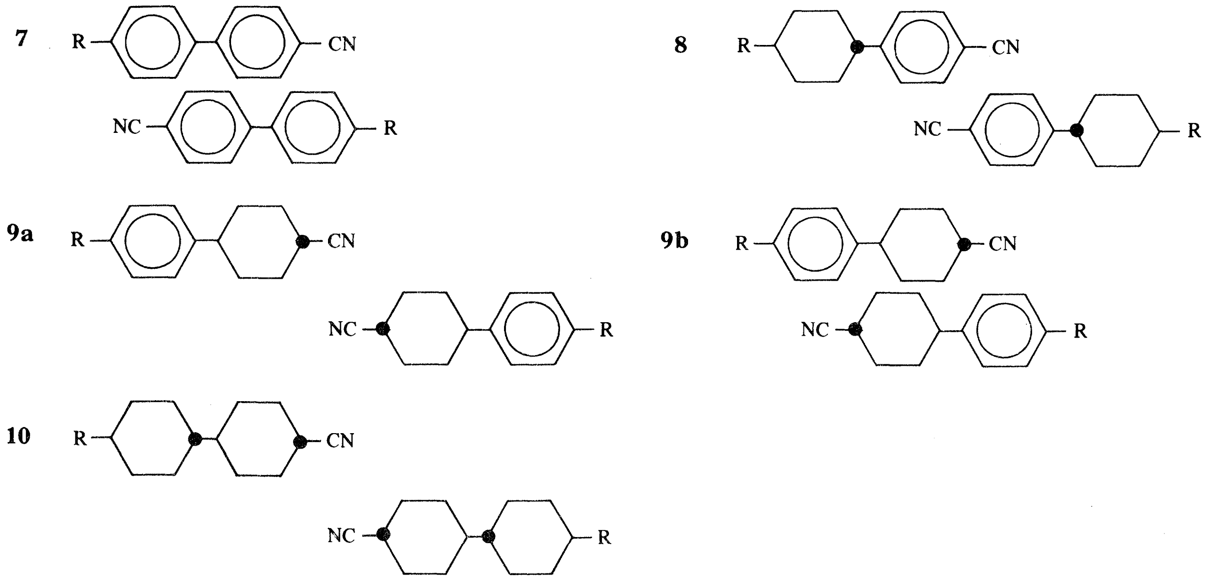
4. APPLICATIONS TO PHASE BEHAVIOUR

(*a*) *Nematic–isotropic phase transition*

According to the van der Waals theory of nematics, discussed by M.A. Cotter at this meeting, the isotropic–nematic phase transition is due to the combination of attractive dispersion forces and an anisotropic excluded volume. The new insight from it is that the dispersion forces themselves need not be anisotropic. An orienting effect is obtained anyway when combined with an anisotropic excluded volume. Applied to mesogenic molecules in a very qualitative way, one could say that T_{NI} increases with: (i) increasing molecular polarizability, and (ii) an increasingly anisotropic excluded volume. This seems to fit in with observations on many molecules, and the better that one condition is fufilled, the less the other is needed.

Combination of these ideas with the monomer–dimer equilibrium could provide the explanation for some of the unexpectedly high T_{NI} values, as already noted by Gray (1981). The degree of overlap of two monomers when forming a dimer depends on the extension of the permanent dipole moment (related to the amount of conjugation), and on the possibilities of creating induced dipole moments in the most polarizable parts of the molecule. Often, but not necessarily, these two effects combine. In table 3 I have drawn the structures of the dimers for the compounds of table 1, as they follow from this point of view. In the order **7**, **8**, **10** there is a decrease in polarizability (both for monomer and dimer), very little change in the excluded volume of the monomers, and a strong increase of the anisotropy of the excluded volume of the dimers. Provided that the monomer–dimer equilibrium does not shift much, the latter effect might dominate, which explains the order of T_{NI}. Compound **9** is very different from the others in that it has a strongly polarizable benzene ring separated from the strong CN dipole by a saturated ring. This allows for two types of dimers. Of these **9b** can be expected to be more stable because of the added interactions at two 'contact points' (Vorländer). But with respect to the anisotropy of the excluded volume **9b** differs little from **7**. Then the decrease in polarizability compared with **7** will dominate, leading to a decrease of T_{NI}.

TABLE 3. POSSIBLE TYPES OF DIMER WITH THE COMPOUNDS OF TABLE 1



The explanation given for the order of T_{NI} of compounds **7–10** is rather qualitative, and several points should be made more precise. In particular the equilibrium constants of the monomer–dimer equilibrium should be determined from careful measurements of the permittivities over a wide temperature range. Such measurements are in progress in Leuven (Belgium). However, to the best of my knowledge no other explanation is yet available for the rather unexpected order of the clearing points of these four compounds. Quite generally it has been found that separation of polar or polarizable groups in a molecule (benzene, cyano, oxygen with its lone-pair electrons) by a saturated ring or group, tends to reduce T_{NI}. Perhaps this can again be attributed to an unfavourable short-range structure, due to the possibility of interactions at two 'contact points'.

(*b*) *Re-entrant nematic behaviour*

Another aspect of the association between strongly polar molecules is the possible occurrence with decreasing temperature of the phase sequence nematic–smectic A–re-entrant nematic. This was first observed by Cladis (1975) in a mixture of two *p*-cyano-substituted compounds. Later it was also observed in a pure compound at high pressure and finally even in pure compounds at atmospheric pressure. Recently a microscopical model has been proposed for these two subsequent phase transitions, one that makes explicit use of the monomer–dimer equilibrium (Longa & de Jeu 1982).

The first phase transition nematic–smectic A can be understood from a simple extension of McMillan's theory of the smectic A phase. In his treatment the smectic layering is stabilized if a quantity r_0/l is small enough, where r_0 is the length of the central aromatic core (which is assumed to be strongly polarizable) and l the total length of the molecule. In its original form this applies only to approximately symmetrical molecules. With increasing molecular asymmetry the smectic phase can be expected to be destabilized. As a consequence the monomers of, for example, the cyanobiphenyls will have only weak smectic tendencies. However, if pairing occurs, the dimers are again symmetric and can fulfil the condition of small r_0/l. Hence a smectic phase can be expected if there is (1) sufficient pairing (low temperatures or high pressures), together with (2) long alkyl chains (small r_0/l of the dimers). The phase transition is percolation-like: above a certain threshold concentration of dimers the smectic order becomes long-range.

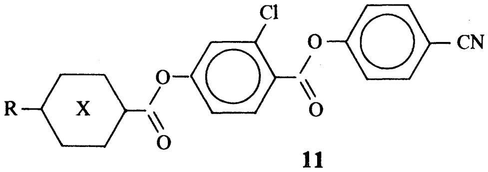
Interestingly the model calculations show that from the point of view of packing, the monomers help to stabilize the smectic A phase with a layer spacing equal to the length of the dimer. In the presence of monomers, space is better filled than when a dimer is surrounded by only dimers. The smectic order parameter increases with decreasing temperature or increasing pressure. At the same time the equilibrium shifts to the dimer side. At a certain stage this will cause an increasingly difficult packing of the bulky dimers in the smectic planes, while less and less monomers are available to fill the outer regions of the smectic layers. Because of the unfavourable packing entropy, dimers then have to move out of the smectic planes. The smectic order parameter thus decreases and finally the nematic phase re-enters.

Independently of model parameters re-entrant behaviour is predicted to be strongly favoured for length ratios of dimer and monomer of the order of 1.3–1.5. This is in agreement with experiments, where layer spacings of this magnitude are often found. For dimers of type **10** (table 3) this ratio is larger, and indeed for these types of compound no re-entrant behaviour has been observed so far.

5. APPLICATIONS TO PHYSICAL PROPERTIES

Dielectric studies are an important means of obtaining information about molecular association. Well studied are the CB series (Dumnur & Miller 1980; Parneix 1982). For a more quantitative approach results for the permittivity over a wide temperature range are required. This means necessarily measurements high up into the isotropic phase until the temperature dependence is close to (5). Though the monomer–dimer equilibrium will be determined mainly by the short-range structure, a small discontinuity in $\bar{\epsilon}$ at T_{NI} is well known. Moreover some dependence of $\bar{\epsilon}$ in the nematic phase on the order parameter can be observed close to T_{NI} (Schad & Osman 1981). The dynamics of the permittivity might provide additional information (Wacrenier *et al.* 1981).

The importance of differences in short-range correlations can be demonstrated once more with the example of compound **11**.



11

when X is benzene, $\epsilon_{\parallel} \approx 35$, $\epsilon_{\perp} = 7$; when X is cyclohexane, $\epsilon_{\parallel} \approx 20$, $\epsilon_{\perp} = 7$. In spite of the similar group moments there is a large difference in $\epsilon_{\parallel}$ of the two molecules. This example also illustrates the problems if we want to interpret the permittivity results quantitatively. In the first place there is a difference in conjugation between the two molecules, leading to somewhat different total dipole moments. Secondly one can expect a difference in short-range antiparallel correlation. The first effect should be exactly known to make the second one more quantitative.

In connection with applications, much work has been done lately on the elastic properties of various classes of compounds. There is interest especially in K_3/K_1, which should be low for a steep threshold of twisted nematic displays. Because of the required positive $\Delta\epsilon$, compounds with a terminal CN group are again often considered. Comparison of the results for various compounds is sometimes hindered by the fact that the same alkyl chain length cannot always be used. This mixes up the two trends described in § 2*c*. Nevertheless, even if this is taken into account it is clear that the simple relation between K_3/K_1 and length/width of the molecules does not hold generally. In particular two effects have been observed.

(i) Replacements of a benzene ring by a saturated ring tends to increase K_3/K_1 (Bradshaw & Raynes 1981; Schad & Osman 1981; Schadt & Gerber 1982). A bicyclo(2,2,2)octane ring has a more pronounced effect than cyclohexane (Bradshaw *et al.* 1981).

(ii) Introduction of heterocyclic rings (whether saturated or not) tends to decrease K_3/K_1 (Scheuble *et al.* 1981; Schadt & Gerber 1981; see also **6** in figure 1).

Schad & Osman (1981) have tried to explain the first point by incorporating the influence of the dimers on the effective length/width ratio. For compounds **7**, **8** and **10** the length/width ratio of the monomer is about the same, while that of the dimer increases in the order given. Hence, provided that the number of dimers does not decrease strongly in this order, the results for K_3/K_1 then fit in with Leenhouts's general trend. The second effect could in principle be rationalized along similar lines. For the systems investigated the hetero atoms give an extra dipole moment that adds up with the cyano dipole. This could increase the degree of dimerization. Taking the relatively unfavourable leng/thwidth ratio of the dimers (compared with the monomers) into account, this lowers K_3/K_1. However, at this stage I feel that explanation and speculation are no longer very well distinguished.

In conclusion it still remains to be seen whether the relation between K_3/K_1 and length/width of the molecule can be saved by incorporating the short-range correlations described above. More importantly the other trend of K_3/K_1 decreasing with increasing alkyl chain length is still not fully understood.

Coming finally to the viscosities one can point out two effects that are probably related to short-range correlations and that would be worth further investigation. In the first place for various compounds some important differences have been observed in the activation energy, which governs the temperature dependence (equation (7)). This is again somewhat unexpected for molecules of similar size and with similar clearing points. However, if a monomer–dimer equilibrium is involved it would be very natural that the viscosity is also influenced by this equilibrium. Secondly, the flow alignment angle θ_0 (see equation (6)) is usually small. The few substances for which κ_2 is known to change sign (see figure 6) are again compounds with a terminal CN group. In fact Gähwiller (1972) speculated already that the special shape of the dimer is responsible for this effect. At present we are comparing in Groningen the flow alignment of compounds with and without a CN group, that are otherwise as similar as possible, to verify whether this is indeed so.

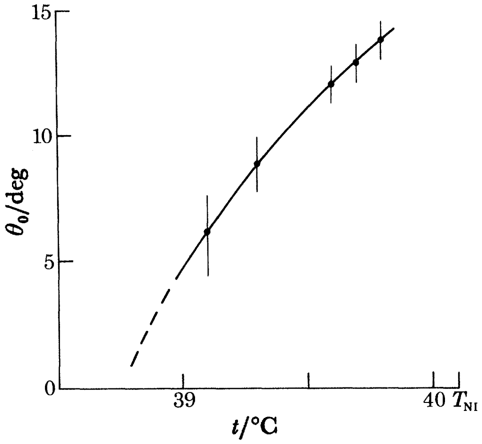


Figure 6. Region of existence of the flow alignment angle for 8CB (after Beens & de Jeu 1983).

In this paper I have tried to show that for mesogenic compounds with a strong terminal dipole moment, short-range antiparallel dipole correlation is of decisive influence both for the phase behaviour and for the various physical properties. It is somewhat disappointing that this cannot be made more quantitative yet. A key question is whether the monomer–dimer description is valid. However, if one chooses not to believe in dimers, it is possible to reformulate the various arguments in terms of direct correlation functions. To obtain quantitative information on these will then be as difficult as to describe the monomer–dimer equilibrium more precisely.

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Discussion

E. P. RAYNES (*R.S.R.E., Malvern, U.K.*). I have two comments on Dr de Jeu's attempt to relate clearing point to the extent of dimerization.

(1) His discussion considered only the geometry of the dimer; I would have thought that the strength of the dimer (in other words the value of g) would be at least equally important.

(2) Evidence from X-rays and electric permittivities indicates that the antiparallel ordering (dimerization) in cyano nematics is reduced to negligible proportions by adding non-cyano material (for example dialkyl esters). However, contrary to your model there is no corresponding decrease observed in the clearing point of the mixtures.

W. H. DE JEU. A full quantitative model, if one were possible, would require a description of the equilibrium process monomer–dimer, in which the strength of the dimer is an important factor. I agree that in principle dilution studies could provide valuable tests of the ideas presented, but the interpretation of the results might be not as simple as suggested. Adding a non-cyano material to cyano nematics can do more than just breaking up the dimerization of the cyano compound. Often induced smectic phases are observed, probably indicating specific interactions between the cyano compound and the other one.

A. H. PRICE (*Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, U.K.*). Two major points of interest arise from this paper. The first concerns the assumption regarding the predominance of dimers in the nematic phase. The dielectric evidence for molecular association arises from the Kirkwood g factor being less than unity (as is found in some 'normal' polar liquids such as nitrobenzene) but this only tells us that antiparallel dipolar association exists and very little about the number of dipoles involved. From the results of Kirkwood g factor calculations one would not conclude that nitrobenzene associates into 'dimers'. Why do so for the nematogens mentioned?

The second point concerns the relative magnitude of dipole–dipole and dipole–induced-dipole interactions. The forces responsible for molecular association are not easily evaluated and the resulting molecular configuration of minimum potential energy is a balance between all the forces involved. Calculations of the magnitude of dipole–dipole and dipole–induced-dipole interactions invariably show that the former dominate. What evidence is available that this does not occur in the nematogens discussed in this presentation?

W. H. DE JEU. The g factor as obtained from permittivity measurements can be interpreted either in terms of direct correlation functions or as a monomer–dimer equilibrium. In strongly terminally polar liquid crystals the occurrence of a smectic A phase with $d \approx 1.4l$ leads to some preference for considering an associated pair of molecules as a separate entity. This concept has been very useful in a molecular model of re-entrant nematic behaviour.

I quite agree that the various contributions to the intermolecular forces are not easily evaluated. The main point I wanted to make is that for the systems under consideration here, often emphasize has been on the interactions between permanent dipoles, overlooking possible interactions between dipole and induced dipole.

M. G. Clark (*R.S.R.E., Malvern, Worcs., U.K.*). It is well known that the coefficient κ_2, which is more commonly denoted α_3, changes from a small negative value through zero to a diverging positive value as one approaches a smectic A phase through a nematic phase. Furthermore, studies of flow alignment instability during oscillatory shear (M. G. Clark, F. C. Saunders, I. A. Shanks & F. M. Leslie, *Molec. Cryst. liq. Cryst.* **70**, 195–222 (1981)) have shown that κ_2 may also become positive in materials without smectic phases. Indeed, to our knowledge all ‘two-frequency’ nematics (having the lowest relaxation of $\epsilon_\parallel$ at audio frequencies) have κ_2 positive over part or all of their nematic range. Thus the phenomenon of κ_2 changing sign is actually quite common and occurs in compounds without terminal CN groups as well as those possessing them.