



ON THE NEMATIC, SMECTIC, AND REENTRANT NEMATIC PHASE IN CYANOBIIPHENYLS*)

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Some experimental results are discussed in relation to the phase transition sequence nematic-smectic A-reentrant nematic. The first phase transition can be understood by a combination of pairing of the terminally strongly polar molecules and a simple extension of McMillan's theory of the smectic A phase to asymmetric molecules. The reentrant nematic phase is proposed to result as an escape from the unfavourable packing of paired molecules in layers, which becomes more and more difficult with increasing value of the smectic order parameter.

1. Introduction

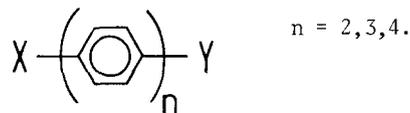
A considerable amount of evidence has become available that liquid crystals consisting of molecules with a strongly polar endgroup (usually -CN, but also -NO₂, -Cl), differ in many aspects from the more classical liquid crystals. These differences refer to the physical properties, or even to the very existence of the liquid crystalline phases. The most spectacular effect is the occurrence with decreasing temperature of the phase sequence nematic-smectic A-reentrant nematic, first observed by Cladis in a mixture of two *para*-cyano substituted compounds.¹ Later it was also observed in a pure compound² at high pressure, and finally even in pure compounds at atmospheric pressure.³ In the cases studied up to now, the period of the density wave of the intermediate smectic A phase is not commensurate with the molecular length ℓ (as is usually the case for classical liquid crystals), but varies for different compounds from 1.1ℓ up to 1.9ℓ .⁴ These results are related to the existence of association between the strongly polar molecules. In these compounds the induced polarization contributes much less to the dielectric permittivity ϵ than the orientation polarization. One would thus expect ϵ in the isotropic phase and $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ in the nematic phase to be proportional to $\mu^2/k_B T$. Here μ is the permanent dipole moment and k_B is Boltzmann's constant. Hence the normal behaviour would be that $\bar{\epsilon}$ increases with decreasing temperature. In practice either the slope is much smaller than expected for a large dipole moment (~ 4.5 D in case of a CN-group), or even has the opposite sign.⁵ This indicates that μ is not constant but decreases with decreasing temperature (anti-parallel association of the dipole moment). Formally, one can describe this association as a monomer-dimer equilibrium, where we emphasize that the asso-

ciated pairs or dimers need not exist on a human time scale, but that a dynamic equilibrium is involved. This anomalous behaviour of $\bar{\epsilon}$ has been observed through all phases, including the isotropic phase. Recently it has been shown to slow down near the transition smectic-reentrant nematic.⁶

A phenomenological Landau theory has been given to account for the reentrant behaviour.⁷ This involves the notion of an optimum density for stabilization of the S_A phase. However, in this way no explanation is offered for the microscopic origin of the effect, which can also not be obtained from some thermodynamic arguments.⁸ It is the purpose of this letter to present a microscopic model for the two phase transitions nematic-smectic A and smectic A-reentrant nematic. As far as we know it gives for the first time a consistent molecular picture of the rather complicated experimental facts observed so far. Some ingredients of the model can be found at other places, in particular in Cladis' work,^{2,9} but often used in a rather different way.

2. Smectic Behaviour of *p,p'*-substituted Biphenyls

Schubert and coworkers¹⁰ have synthesized a large number of terminally substituted oligophenyls with molecular structure



This includes for X and Y many of the usual substituents like alkyl, alkoxy, acyloxy, etc. Without hardly any exception only smectic mesophases are observed, and no nematic phases. This includes the completely non-polar *p,p'*-dialkylbiphenyls, that possess S_B and S_E phases, and the corresponding terphenyls with S_A and S_B phases. Smectic A and nematic phases have also been observed for other non-polar molecules like the *p,p'*-dialkylazobenzenes¹¹ and the *p,p'*-*trans*-alkylcyclohexyl-biphenyls.¹² For the biphenyls it is only when an endgroup

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like -CN is introduced that a nematic phase appears, and for longer alkyl chains at the other *para*-position also again a smectic phase.¹³ These compounds will be indicated as nCB (nOCB) where n gives the number of carbon atoms in the alkyl (alkoxy) chain.

The above results can at least qualitatively be understood from McMillan's theory of the nematic-smectic A transition.¹⁴ In his model a parameter $\alpha = 2\exp[-(\pi r_0/\ell)^2]$ is introduced, where ℓ is the length of a molecule, and r_0 a length of the order of the dimension of the central aromatic core (Fig. 1a). For $0.98 < \alpha < 2$ (small values of r_0/ℓ) no nematic phase is predicted and the smectic A phase clears directly into the isotropic liquid. For $\alpha < 0.98$ a smectic A-nematic phase transition is obtained, which becomes second order for $\alpha < 0.70$. Compared with other typical mesogenic molecules, the terminally substituted biphenyls possess two benzene rings that are directly linked together, and not *via* a bridging group. This will make r_0 smaller, and - for a fixed ℓ - promote smectic behaviour at the expense of the nematic phase, in agreement with the experimental findings described above.

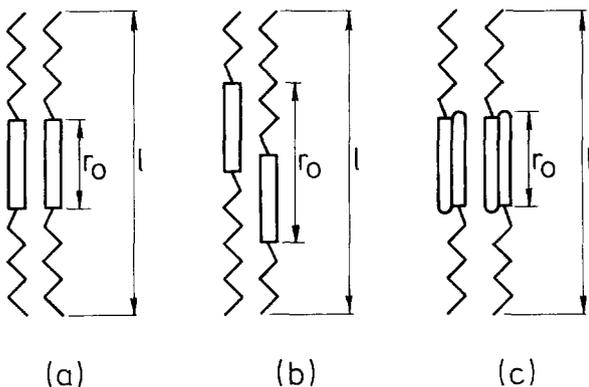


Fig. 1. Definition of r_0 and ℓ for a perfectly ordered layer in the case of (a) symmetric molecules, (b) asymmetric molecules, (c) paired molecules.

In McMillan's theory implicit reference is made to approximately symmetrically substituted molecules, and the question arises how these ideas can be extended to asymmetric molecules. As long as the molecules have no preference to be "up" or "down", it seems reasonable to take for r_0 an average value in the way indicated in Fig. 1b.¹⁵ In the case of extreme asymmetry, as for the nCB and nOCB series, we thus have $r_0 \approx \ell$, and only nematic behaviour is predicted. However, if some pairing of the molecules occurs, the dimers again have the possibility to fulfill the condition of small α (see Fig. 1c). Hence for the nCB and nOCB series we can expect in the first place a nematic phase. A smectic A phase is again possible if two conditions are fulfilled: (1) sufficient pairing (low temperature or high pressure), (2) long alkyl chains (small r_0/ℓ for the dimers). These predictions are in excellent agreement with the experimental situation for the cyanobiphenyls, where for $n \geq 8$ again smectic phases are observed.

If a mixture of two mesogenic molecules gives a smectic phase, quite generally the layer spacing varies roughly linearly between ℓ_1 and ℓ_2 , the length of molecule 1 and 2, respectively.¹⁶ Hence, in the present case we expect layer spacings in between the length of a monomer and that of a dimer. Because of requirement (1) given above, in practice it will be closer to that of the dimer. In our discussion so far the polarity of the molecules is assumed to be important only for the degree of pairing; it is not assumed to play a direct role in the forces leading to the nematic or smectic phase.

3. The Smectic A-reentrant Nematic. Phase Transition

First we note that the layer structure in the bilayer smectic A phases is rather weak. This is evident from the absence or weakness of higher-orders of the 001-reflection in X-ray experiments.¹⁷ Furthermore, for example, the conductivity is hardly anisotropic, in contrast to the situation in classical smectics.¹⁸ What usually is called a layer is in fact only a small density modulation. Consequently, the smectic order parameter:¹⁴

$$\sigma = \langle P_2(\cos\beta) \cos(2\pi z/\ell) \rangle,$$

will also be small, and similarly the free energy difference between the nematic and the smectic A phase.

The phase transition nematic-smectic is observed to be second order for both 8CB¹⁹ and 8OCB.²⁰ In such a situation the usual behaviour below the transition temperature is that σ increases relatively strongly with decreasing temperature. However, this sharpening of the density modulation would force the bulky central cores of the paired molecules more and more in one plane. As already noted by Cladis *et al.*² this would lead to an overall unfavourable packing because the alkyl chains alone cannot fill the rest of space. This effect can be made quantitative by adding to the free energy a packing entropy that - taking the relatively bulky central parts of the paired molecules into account - favours the nematic phase above a bilayer smectic one. Increasing the pairing is in principle a means of decreasing the energy of the smectic phase. Once this effect is approximately saturated and the temperature is lowered further, the packing term will force σ to decrease, and finally cause a transition back to the nematic phase. In order to observe this effect obviously no other phase transition, like solidification, or a transition to another smectic phase, should intervene.

The above ideas also nicely account for the effect of pressure on the phase behaviour. As the electrostatic forces involved in the dipole association are long-range, one expects little effect from the pressure on the degree of pairing. However, if packing effects are involved in the smectic-reentrant nematic transition, a pronounced effect of pressure is inevitable. In agreement with the experimental results an increase in pressure will shift the transition to the reentrant nematic phase to higher temperatures. The effect of pressure on the high-temperature nematic-smectic phase transition is much smaller, and above a cer-

tain pressure the smectic phase is not stable anymore.

To get a rough estimate of the order of magnitude of the effect, we calculate with the model of Fig. 1c the hypothetical difference in packing between a smectic with $\sigma = 1$ and with $\sigma = 0$. Following note 17 of Ref. 9 we associate with the dimer a molecular area perpendicular to the long axis of 31 \AA^2 . For the monomer this is 25 \AA^2 . From Fig. 1c the "free space" per molecule is calculated for $\sigma = 1$ as approximately $(31 - 25) \times (\ell - r_0) \approx 100 \text{ \AA}^3$. This should be compared with the volume of the dimer (or two monomers) which is approximately 1200 \AA^3 (again using the numbers of Cladis *et al.*⁹). We conclude that increasing the smectic order parameter will create an appreciable amount of free space. Evidently this will not occur and σ is forced to remain small. When either the temperature is further lowered or the pressure increased a phase transition back to the nematic phase is a possible escape.

If we consider the reentrant behaviour of a homologous series^{3e,21} (see Fig. 2), we find

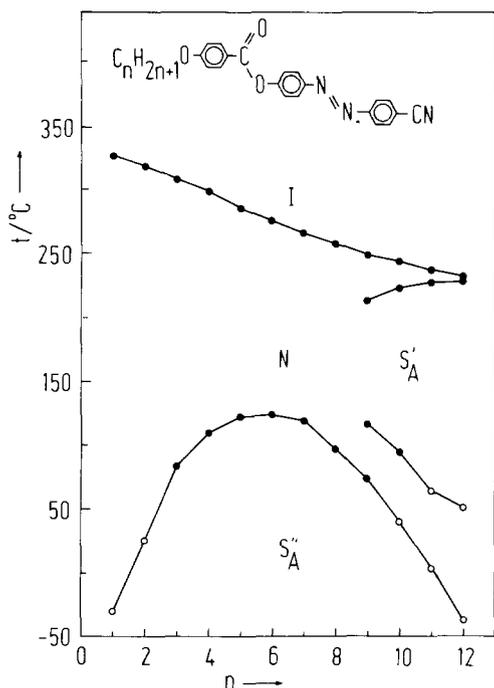


Fig. 2. Typical reentrant behaviour in a homologous series (from Ref. 3e).

that an increase of the length of the alkyl chains stabilizes the intermediate smectic phase. In fact only for $n \geq 9$ the reentrant nematic phase is observed. Now the longer the alkyl chains, the more possibilities for *gauche-trans* conformations which make the chain effectively bulkier and shorter. In this way the alkyl chains are able to fill the available space better, in agreement with the above model. Finally there is in all cases a second smectic A phase, with a spacing commensurate with the molecular length, which will not be discussed here.

Very recently Luckhurst and Timimi²² have obtained reentrant polymorphism by introducing in McMillan's theory of the smectic A phase a temperature dependence of the parameter α . By assuming that α decreases with decreasing temperature a phase sequence nematic-smectic A-reentrant nematic-reentrant smectic A is obtained. It is not understood, however, why α should decrease with decreasing temperature. In that situation the monomer-dimer equilibrium shifts to the dimer side, and one expects on average r_0/ℓ to decrease, and thus α to increase.

4. Conclusions

- (i) Terminally substituted biphenyls usually give smectic phases, with the exception of the strongly asymmetric nCB and nOCB series that are nematic. This can be understood from a simple extension of McMillan's theory of the nematic-smectic A phase transition.
- (ii) The molecules of the nCB and nOCB series associate with anti-parallel dipole moments. In order for smectic phases to occur for the higher homologues of these series the symmetry of the molecules must be restored, which means sufficient pairing. The layering in the resulting smectic A phase is extremely weak; the spacing approaches the length of the paired unit.
- (iii) An increase of the smectic order parameter would force the bulky central parts of the paired units in one plane, thus creating an unfavourable packing at the position of the alkyl chains. Once the pairing is saturated this makes the smectic A phase unstable towards the nematic state. Reducing the temperature or increasing the pressure then leads to a phase transition to the reentrant nematic phase.

As far as we know no other microscopic model is available that accounts well for the rather wide range of effects discussed so far. A more quantitative elaboration of this work is in progress.

Finally we note that several other remarkable effects have been observed in connection with terminally polar liquid crystals. As already noted at the end of Sec. 3 the reentrant nematic phase may give way at lower temperatures to a second smectic A phase, with a layer spacing commensurate with the molecular length. A direct phase transition between the two types of smectic phase is also possible.²³ At present it is not clear how this can be incorporated into the general picture, but we note that Hardouin *et al.*²⁴ have given a model for the structure of this second smectic phase. Secondly, in mixtures of a terminally strongly polar compound and an "ordinary" compound an induced smectic phase may appear.²⁵ By "ordinary" we mean a non-polar or relatively weakly polar compound. Cladis²⁶ has attributed this induced smectic phase to the decrease of association of the terminally polar compound due to the dilution with the less polar compound. However, the real situation must be much more complicated because the existence of charge-transfer complexes between the terminally strongly polar compound

and the "ordinary" compound has been demonstrated.²⁷

All the effects described above indicate that the association between polar mesomorphic compounds has a profound influence on both the

phase behaviour and the physical properties. In analogy with the situation in the physics of ordinary liquids we propose to call them *associated liquid crystals* to distinguish them from the more classical liquid crystalline systems.

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