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Cyano Mesogens: A New Interpretation of the Structure of the Bilayer Smectic A Phase

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A new model describing the bilayer structure of the smectic A mesophases observed with cyano mesogens is proposed. Our interpretation is based upon recent experimental x-ray studies of binary mixtures containing a cyano mesogen on one hand and a non polar one, on the other, with either one or two aliphatic chains in the molecules. In this model, the smectic layers are formed of the intimate mixture of single molecules and of dimers described as being pairs of molecules associated head-to-head. As a result, the degree of dimerization is far from unity due to the steric hindrance of the aliphatic chains; it decreases notably when the average number of aliphatic chains in the system increases.

I INTRODUCTION

A new class of interesting liquid crystals was discovered when the first cyanobiphenyl mesogens were synthesized.[1] Substances belonging to this class consist of molecules with a highly polar cyano group at one end of the aromatic core and a single paraffin tail at the other end. Their liquid crystalline properties were found to be rather unusual, both for the smectic A and for the nematic states. The smectic layers have a thickness ranging from one to two molecular lengths, and were immediately claimed to be some kind of bilayer.[2] The nematic state was found to occur not only at temperatures above the temperature domain of the smectic phase, but also at temperatures below it, yielding what is now known as being the re-entrant nematic.[3]

In the structural model of the smectic A phase, proposed by Cladis and coworkers,[3,4] the highly dipolar aromatic cores of the molecules overlap one another within the layers in an antiparallel pairing (Figure 1a). The model accounts directly for the uniaxiality of the system, since all the molecules stand perpendicular to the layers. It also accounts for the amphiphilic character of the smectogens since the aromatic and aliphatic parts of the molecules segregate efficiently and fit separately into distinct sublayers. It has, nevertheless, a weak point, for it requires a highly compact packing for the aromatic cores. The molecular area calculated from the experimentally observed density and the layer thickness is much too small (σ = 16.5 Å^2) when compared with the corresponding molecular area (~20 Å^2) in the crystal. It should be pointed out that this model is different from that[5] proposed recently for similar smectogens in which the cyano end groups are replaced by chlorine atoms (Figure 1c). In the latter, the aromatic cores also overlap one another, but their packing density is comparable (~22 Å^2) to that in the crystal, and, therefore, the overall thickness of the layers is equal to one molecular length. The difference between the two models lies essentially in the packing of the aromatic cores. When these are packed in a dense way, the paraffin tails are squeezed out of the layers over a larger distance, and the thickness of the layers is larger than one molecular length. Quite obviously however, any increase of the packing density of the aromatic cores at constant length should imply a reduction of the molar volume, which has never been observed experimentally. It has been found instead that the molar volume of the cyano smectogens is very close to that of the chloro derivatives.[5,6]

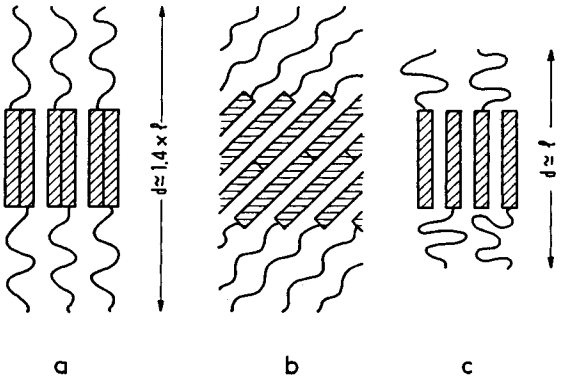


FIGURE 1 Models of the smectic A structure of cyano mesogens. The packing density of the cores is lower in model c than in model a.

In the model proposed by Leadbetter and coworkers[7,8] the aromatic cores overlap one another over a large distance, as illustrated in Figure 1c, and they show the same low density of packing as just mentioned for the chloro smectogens. The increased thickness observed for the smectic layers is achieved here by the longitudinal diffusion of the molecules which creates "free volume."[8] However, the substantial increase of the specific volume which is implied has not been observed experimentally so far.

In the model that we proposed recently (Figure 1b),[6] the molecules are associated head-to-head through the cyano end groups and are located within the layers in a bilayer configuration with a large tilt angle with respect to the normal. In this case, the molecular area of the aromatic cores calculated from the experimental data is reasonable (σ = 22 Å^2). This model implicitly involves the absence of rotational correlation between the layers in such a way as to make it possible for the smectic A phase to be uniaxial.

In addition to these models, one should mention those proposed recently by the Bordeaux group.[9] Involving such concepts as anti-ferro-electricity, commensurability and antiphases, these models have been elaborated to describe the smectic behavior of special smectogens consisting of molecules in which the aromatic core is made of three benzene rings connected through dipolar groups. However, they do not take into account the amphiphilic character of the smectogens; we will discuss this important point in a forthcoming paper.

II PROPOSAL OF A NEW MODEL

Our former model[6] (Figure 1b) is characterized by a structural homogeneity on the molecular level which is unduly pronounced. Moreover, it is in contradiction with the fact that the smectic phase of the cyano compounds (where the molecules are tilted) is miscible in all proportions with the conventional smectic A phases (where the molecules stand perpendicular to the layers). As already reported in the literature,[2] and as we will see below, the x-ray patterns of the binary mixtures of a cyano compound with a classical A smectogen contain Bragg reflexions, which are sharp whatever the composition. In contradiction with the assumption of the segregation of the species within distinct layers randomly superposed, this observation implies a mixing on the molecular level.

In an attempt to propose a new model for the smectic A mesophases of the cyano liquid crystals, we thought we should renounce the assumption of structural homogeneity, which we feel is responsible for the imperfection of the models described above. This procedure was strongly suggested to

us by a recent paper,[10] where the variation of the thickness of the smectic A layers was interpreted as being due to the association of the cyano molecules which depends upon the concentration. In that paper,[10] the main idea was to consider the smectic layers as formed by the intimate mixture of single molecules on one hand, and of dimers identical to those described in Figure 1a, on the other. The thickness of the layers was thought to be related to the average length of the species present.

In the model that we now propose (Figure 2), the basic idea of the existence of dimers and monomers within the smectic layers is totally preserved. The only modification is that the dimers are now described as being associated head-to-head. The dimers are therefore twice as long as the monomers, and their molecular area, σ_2, is very close, if not identical to that, σ_1, of the monomers. The mesophase is, of course, uniaxial since all the species are understood to stand normal to the layers.

In order to better characterize the model, it is of interest to calculate explicitly the thickness, d, of the smectic layers as a function of the degree of association, τ, representing the fraction of cyano molecules involved in the creation of the dimers. Assuming that the molar volume, V_1, of the product is independent of the degree of association (at least to a first approximation) it is easy to show that:

$$d=\frac{V_1}{(1-\tau)\sigma_1+(1/2)\tau\sigma_2}\simeq\frac{V_1/\sigma_1}{1-(1/2)\tau}=\frac{2l}{2-\tau} \tag{1}$$

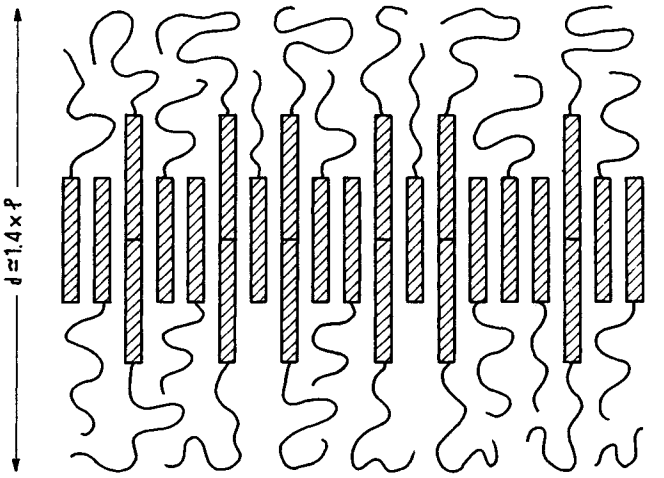


FIGURE 2 New model of the smectic A structure of cyano mesogens.

where l is the length of the molecule. From this relationship it is clear that d is equal to l when $\tau = 0$; i.e. when there is no association of the molecules at all, and that d is twice as large when $\tau = 1$; i.e. when all of the molecules are dimerized. Very often, d is found to be equal to $1.3 \times l$ or $1.4 \times l$ indicating a degree of association of about 0.5

It is useful to further characterize the geometry of the model by calculating the parameter S which represents specifically the molecular area of the paraffin tails. Dealing now with a binary mixture of the cyano compound with a non polar smectogen, and knowing the mole fraction, x, of the non polar smectogen along with the number, ε, of aliphatic chains in its molecules, one can calculate:

$$d = \frac{xV_0 + (1-x)V_1}{x\sigma_0 + (1-x)(1-\tau)\sigma_1 + {}_{1/2}(1-x)\tau\sigma_2} \tag{2}$$

$$S = 2 \cdot \frac{x\sigma_0 + (1-x)(1-\tau)\sigma_1 + {}_{1/2}(1-x)\tau\sigma_2}{(1-x) + x\varepsilon} \tag{3}$$

where V_0 is the molar volume of the non polar compound and σ_0 the molecular area of its aromatic stems.

Finally, it is of interest to note that the description of the model given in Figure 2, and that the calculation of the structural parameters presented above, might suggest the absence of any longitudinal motion of the molecules. Actually, Figure 2 should be understood as a mere over-simplified representation of the ideal structural situation where the distribution of the centers of the aromatic cores along the normal to the smectic layers (Figure 3) is infinitely sharp (delta function). It is clear however, that depending upon the molecular interactions, the segregation of the aromatic and the aliphatic moieties of the molecules is more or less pronounced, and that the distribution curves illustrated in Figure 3 are, as a consequence, more or less wide. It is clear in addition that on top of the unusual lateral diffusion of the molecules within each layer, one should also expect further motions on a local scale related to the equilibrium reaction of dimerization. Now, as for the structural parameters, their calculation remains perfectly compatible with the presence of molecular motions, provided there is no creation of extra free volume. It is important to add by the way that, regardless of whether the longitudinal diffusion of the molecules is weak or intense, the x-ray diffraction patterns of systems the degree of dimerization of which is about $\tau = ½$ would hardly contain more than one Bragg reflection. This is due to the presence both of single and associated molecules, resulting in a diffuse interface between adjacent sublayers and in rather smooth an electron density distribution.

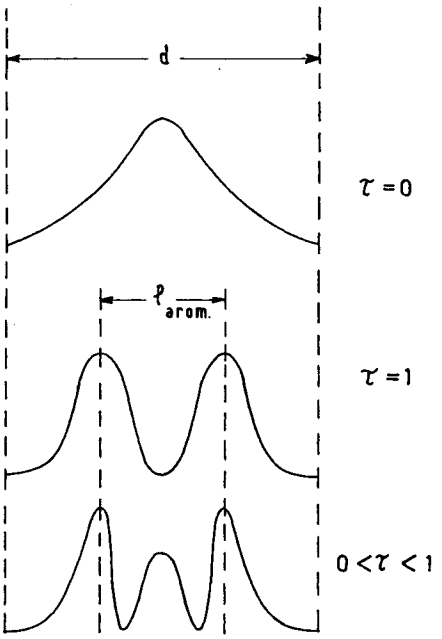
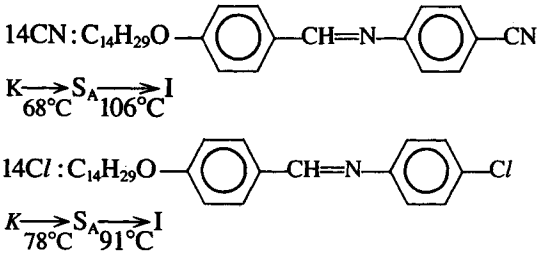


FIGURE 3 Distribution of the centers of the aromatic cores of the molecules along the normal to the smectic layers. Cases $\tau = 0$, $\tau = 1$ and $0 < \tau < 1$ respectively correspond to the structural situations of single layers of aromatic cores (Figure 1c), of double-layers of aromatic cores (Figure 1b), and of composite layers of aromatic cores (Figure 2).

III. RESULTS AND DISCUSSION

A. Binary mixtures 14CN/14Cl

We studied, first, the binary mixture of the following two smectogens:



In this case, both molecules are almost identical from the standpoint of their geometry; they have the same length (33.3Å), the same molecular area

of the aromatic stems (21.7 Å^2 at 90°C) and the same molar volume (440 cm^3 · mole^{-1} at 90°C).[5,6] The sole difference lies in the fact that the chloro compound shows a single layer smectic structure with a layer spacing of d = 33.7 Å, while the cyano compound shows a bilayer structure with a spacing of d = 45.2 Å.

Thermal analysis (DSC) measurements enabled us to draw the phase diagram illustrated in Figure 4. This was obtained using the transition temperatures determined on heating. The two types of smectic A mesophase appear to be perfectly miscible.

The miscibility of the two smectics was further confirmed and proved to occur on a molecular level using x-ray diffraction. As already observed by Lydon and coworkers[2] for another mixture, the Bragg reflection characteristic of the smectic ordering remains sharp throughout the whole range of stability of the mixed smectic mesophase, and the spacing varies almost linearly with concentration (Figure 5).

From these experimental diffraction data, the degree of association of 14CN was calculated (Figure 6) using Eq. (2). The molar volumes V_0 and V_1 were taken equal to 440 cm^3 · mole^{-1} and the molecular area of the aromatic stems equal to 21.7 Å^2. The molecular area S of the paraffin tails was then calculated (Figure 7) using Eq. (3). The results obtained show that the degree of association of the pure 14CN is only 0.50. This is easy to understand for if τ were to be equal to 1, the paraffin tails would then have

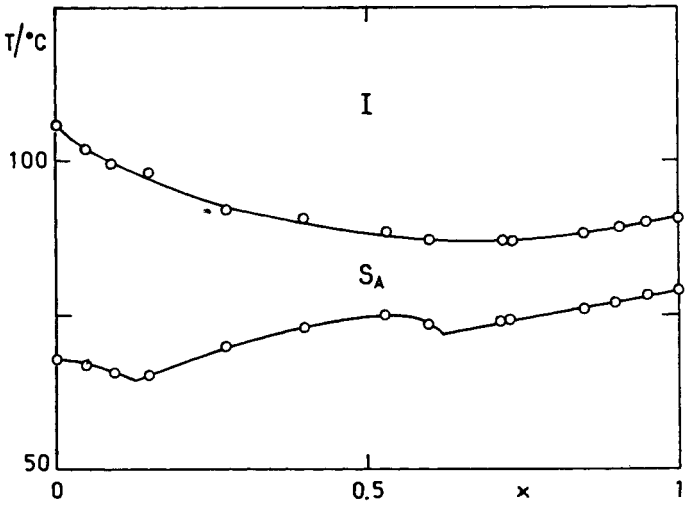


FIGURE 4 Phase diagram of the 14CN/14Cl binary mixture.

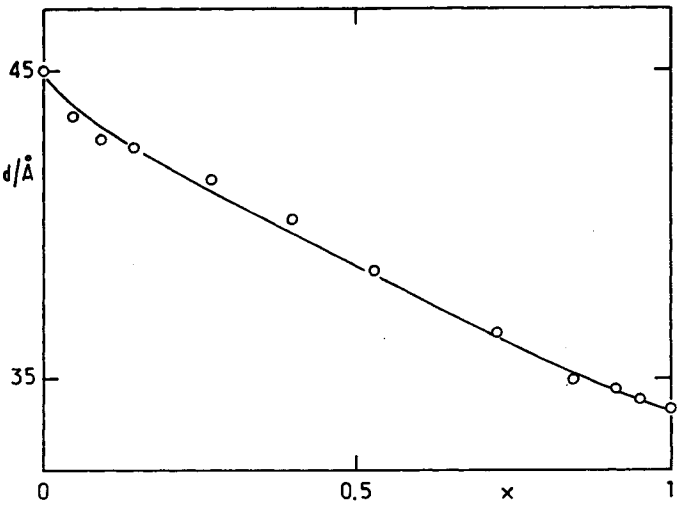


FIGURE 5 Bragg spacing as a function of concentration in smectic A phase of the 14CN/14Cl binary mixture.

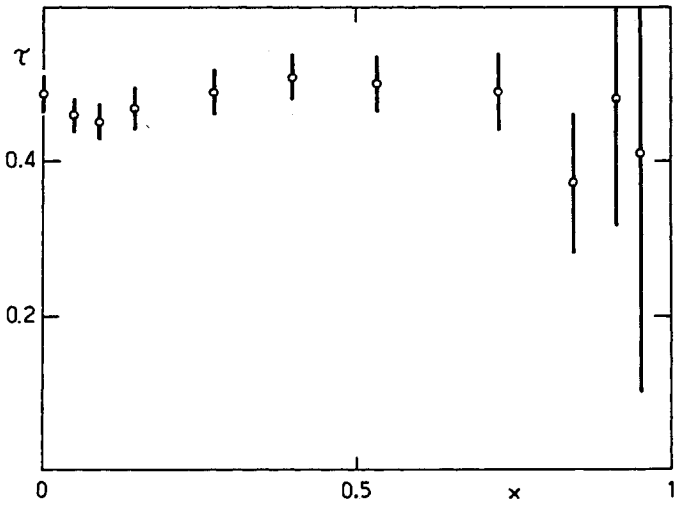


FIGURE 6 Degree of association of the cyano molecules as a function of concentration in the smectic A phase of the 14CN/14Cl binary mixture.

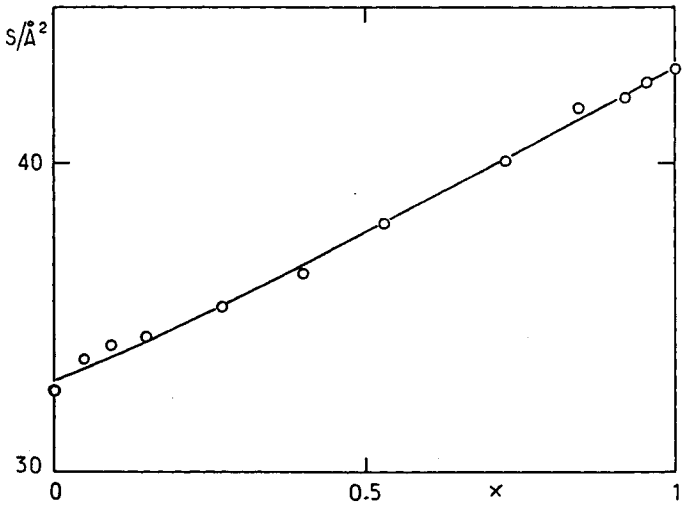


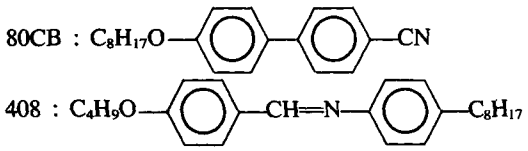
FIGURE 7 Molecular area of the paraffin tails as a function of concentration in the smectic A phase of the 14CN/14Cl binary mixture.

to exhibit a molecular area of only $S = \sigma_1 = 21.7$ Å^2, which is totally insufficient for them to adopt the disordered configuration. The presence of non associated molecules around each dimer contributes to reducing the interfacial density of the aliphatic tails and ensures their ability to adopt the disordered configuration. The results show, on the other hand, that the degree of association is little affected by the composition. Normally, one would have expected the degree of association to decrease beyond a certain amount of non polar compound added to the system. However, for strongly interacting systems, such a dilution effect usually occurs at high "solvent" contents, which we have not been able to explore with precision in this work. Furthermore, the "ceiling" effect due to the steric hindrance of the aliphatic chains also contributes to maintaining τ constant over a large concentration range of the mixture. It is also of interest to note that S smoothly increases with x all the way up to the value of 43 Å^2 which is characteristic of the pure non-polar compound.

B. Binary mixtures 80CB/408

To complete our discussion using the same procedure described above, we analyzed the experimental data obtained recently by other authors who used additives with two aliphatic chains in the molecules. The variation with

concentration of the layer spacing was found to be rather peculiar.[10-12] More specifically, we considered the case of the following mixture[10]:



As previously, the degree of association τ and the molecular area S of the paraffin tails were calculated (Figures 8 and 9) using Eqs. (2) and (3). The molecular area of the aromatic stems were assumed to be identical for all of the species present in the system ($\sigma_0 = \sigma_1 = \sigma_2$), and the molar volumes were supposed to be equal to $V_0 = \sigma_0 l_0$ and $V_1 = \sigma_1 l_1$ respectively, with $l_0 = 28$ Å and $l_1 = 24.0$ Å.[10] Of course, ε was taken equal to two.

It is of special interest to note that τ decreases rapidly as a function of composition and that it reduces to zero beyond a molar concentration of 408 equal to $x = 0.5$. This remarkable effect is no doubt due to the presence of the two aliphatic chains in the non-polar molecules. Whereas the addition of a non-polar smectogen with a single aliphatic chain in its molecule contributes to reducing the overall interfacial density of the paraffin tails (Figure 7), the addition of 408 on the contrary tends to increase that density

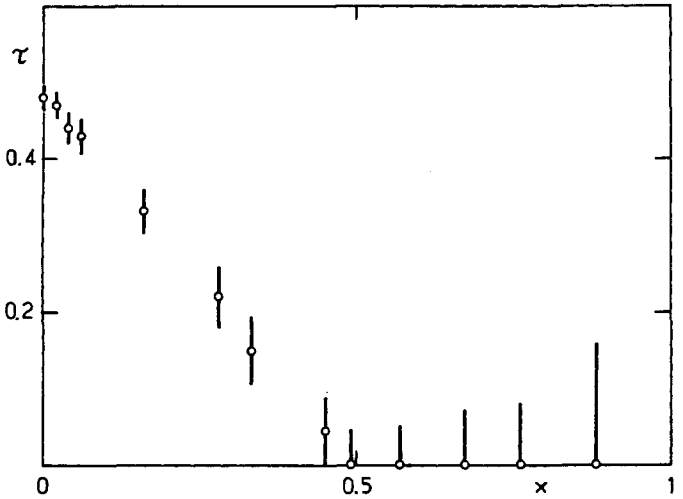


FIGURE 8 Degree of association of the cyano molecules as a function of concentration in the smectic A phase of the 80CB/408 binary mixture, following the experimental data in Ref. 10.

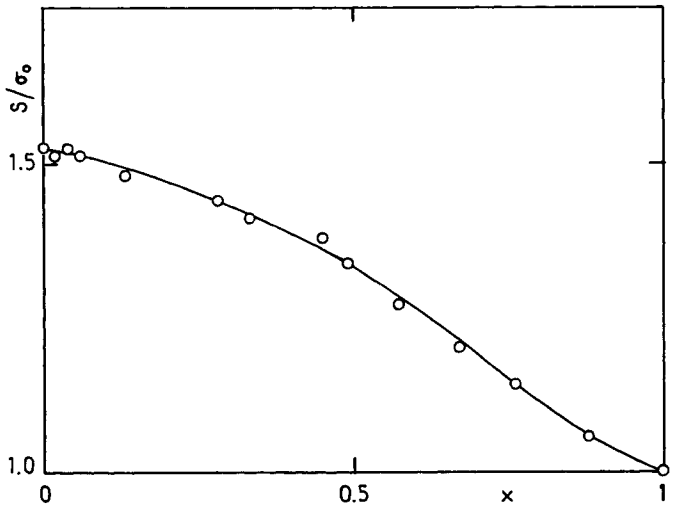


FIGURE 9 Molecular area of the paraffin tails as a function of concentration in the smectic A phase of the 80CB/408 binary mixture, following the experimental data in Ref. 10.

significantly. This trend is counterbalanced by the dissociation of the dimers. Indeed, as long as τ is different from zero, S decreases slowly starting from a value of $1.5 \times \sigma_0$ (33 Å^2) and as soon as τ cancels out, S begins to decrease rapidly as a function of composition (Figure 9). The degree of association of the cyano molecules seem therefore to be much more dependent upon the steric hindrance of the aliphatic chains than upon the specific interactions of the cyano dipoles. This effect is probably also responsible for the re-rentrant nematic behavior.[3] The natural tendency of the asymmetric mesogens with a strong dipolar end group to form dimers is efficiently counter-balanced in the smectic phase by the resulting increase of the interfacial density of the paraffin tails.

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