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F. Barbarin, M. Dugay, A. Piovesan, D. Guillon, A. Skoulios. Phase transitions between single- and double-layered smectic structures in binary mixtures of cyano-mesogens. *Journal de Physique*, 1988, 49 (9), pp.1583-1591. 10.1051/jphys:019880049090158300 . jpa-00210839

**HAL Id: jpa-00210839**

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Submitted on 4 Feb 2008

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Classification  
 Physics Abstracts  
 61.30E

## Phase transitions between single- and double-layered smectic structures in binary mixtures of cyano-mesogens

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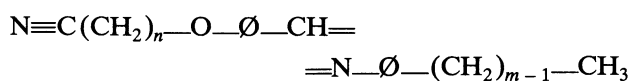
(Reçu le 17 février 1988, accepté sous forme définitive le 17 mai 1988)

**Résumé.** — Des mélanges binaires de mésogènes présentant respectivement des phases smectiques monocouches ( $A_1$ ), bicouches ( $A_2$ ) et partiellement bicouches ( $A_d$ ) permettent de mettre en évidence en fonction de la concentration des transitions brusques  $A_2$ - $A_1$  ou  $A_2$ - $A_d$ . La structure bicouche implique un processus de dimérisation des entités mésogènes qui est discuté en fonction du caractère amphipathique des molécules (molécules polaires symétriques et dissymétriques). La stabilité de la phase bicouche est également analysée lorsque l'on introduit une perturbation au niveau de l'interface polaire par adjonction de molécules non polaires.

**Abstract.** — Binary mixtures of mesogens which exhibit respectively single-layered ( $A_1$ ), double layered ( $A_2$ ) and partially double layered ( $A_d$ ) smectic phases show abrupt  $A_2$ - $A_1$  or  $A_2$ - $A_d$  transitions as a function of concentration. Double layered structures imply the formation of dimerized entities and the possibility of dimerization is discussed in terms of the amphiphilic nature of the molecules in the binary mixture (symmetrical and dissymmetrical polar mesogens). The results are analysed with respect to the thermal stability of the  $A_2$  phase when defects are introduced in the polar interface by adding non-polar symmetrical mesogens.

### Introduction.

Some aspects of the liquid crystalline polymorphism of a series of 4-cyanoalkoxybenzylidene-4'-alkylanilines (abbreviated to  $N\equiv C - nO \cdot m$  in the following) :



$$n = 3, 4, 6 \quad \text{and} \quad m = 4, 5, 8.$$

were recently reported in the literature [1, 2]. In this novel series of mesogenic compounds, the cyano endgroup is mechanically and electrically decoupled from the rigid and polar aromatic core through a flexible and non-polar aliphatic chain. Using X-ray diffraction, the structure of the observed smectic phases was found to correspond either to single or to double layers of molecules.

From the standpoint of chemical architecture,  $N\equiv C - nO \cdot m$  mesogens fall into the category of the so-called symmetrical mesogens, for their molecules contain two aliphatic chains of comparable lengths, attached to the two ends of the central aromatic core. As such, they should produce smectic layers corresponding to single layers of molecules set side by side [3], with the aromatic cores in lateral register so as to form well defined aromatic sublayers covered on both sides by the disordered aliphatic chains [4]. From the standpoint of electrical properties, on the other hand, these mesogens fall into the category of polar mesogens, for their molecules contain a strongly dipolar cyano endgroup. As such, they should lead to molecular associations due to an antiparallel coupling of the cyano endgroups. Associations of that sort have already been described to occur [5, 6] with highly polar and dissymmetrical mesogens whose molecules contain a single aliphatic chain and a polar group directly attached to the

aromatic core [7]; the smectic behaviour of these mesogens has been shown to be rather complex. Depending upon the case, the smectic layers can have thicknesses corresponding to one or to two molecular lengths, as in smectic  $A_1$  and  $A_2$  respectively, or still have thicknesses intermediate between one and two molecular lengths, as in smectic  $A_d$  [8]. In  $A_1$ , the molecules are oriented antiparallel to one another and set side by side with the aromatic cores arranged in single layers (see Fig. 4 in Ref. [6b]). In  $A_2$ , the molecules are associated head to head through their polar endgroups with the aromatic cores arranged in double layers (see Fig. 3 in Ref. [6b]). In  $A_d$ , the molecules are incompletely associated, and the aromatic sublayers are formed of a mixture of paired and unpaired aromatic cores juxtaposed in lateral register as well as possible (see Fig. 2 in Ref. [6b]).

In the single-layered smectic phases observed with the  $N\equiv C-nO.m$  series, the smectic layers were described [1, 2] to correspond to single layers of molecules arranged side by side, with the aromatic cores in lateral register — as reported above for the symmetrical mesogens —, and with the cyano endgroups randomly and equally located on the two faces of each individual layer (see Fig. 2 in Ref. [2]). In the double-layered phases, on the other hand, the basic structure was described to still correspond to the stacking of single layers of molecules arranged side by side; however, the cyano endgroups were described to no longer be equally located on both faces, but significantly accumulated on only one of the two faces of the single layers — which then get *polarized*. The Bragg spacing measured, equal to twice the molecular length, simply reflects the (anti-ferroelectric) stacking mode of the *polarized* single layers which tend to have their cyano-covered faces in close contact with one another (see Fig. 2 in Ref. [2]). Though similar to it, this structure is not strictly identical to the  $A_2$  structure presented above for the highly polar and dissymmetrical mesogens; indeed, it is not necessarily perfectly double-layered, because the domains of ferroelectric intralamellar arrangement of the molecules and antiferroelectric interlamellar stacking of the monolayers are not necessarily infinitely extended in space.

The occurrence of single- or double-layered smectic structures with  $N\equiv C-nO.m$  mesogens depends essentially on the length ( $n, m$ ) of the aliphatic chains; in the special case of  $N\equiv C-6O.8$ , both structures can be observed as a function of temperature [2]. It is the aim of the present paper to investigate the kind of smectic layers obtained in binary mixtures containing at least one  $N\equiv C-nO.m$  mesogen and, also, the phase transitions between different types of layering, that could eventually take place as a function of concentration.

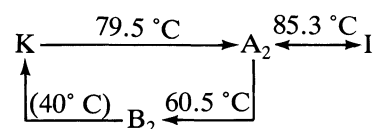
### Experimental.

All the mesogens studied in the present work are 4-4' derivatives of the same benzylideneaniline aromatic core; they differ from one another only by the nature of their endgroups. Their chemical nature and their polymorphic behaviour are reported in the following.

The 4-cyanobutoxybenzylidene-4'-octylaniline (abbreviated to  $N\equiv C-4O.8$ ):



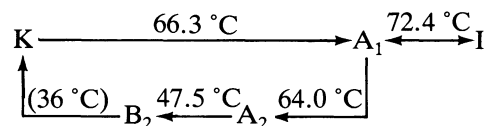
contains a cyano endgroup decoupled from the aromatic core through a tetramethylene aliphatic chain. Its polymorphic scheme [1] is:



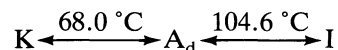
The 4-cyanohexyloxybenzylidene-4'-octylaniline (abbreviated to  $N\equiv C-6O.8$ ):



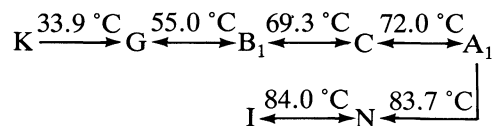
is formed of molecules almost identical to those of  $N\equiv C-4O.8$ , the flexible cyanoalkoxy chain being only slightly longer. Its polymorphic scheme [2] is however notably different:



The 4-hexadecyloxybenzylidene-4'-cyanoaniline (abbreviated to  $16-O.C\equiv N$ ) is dissymmetrical; it contains only one aliphatic chain and a cyano endgroup directly attached to, and hence mechanically and electrically coupled with the aromatic core. Its polymorphic scheme [9] is:



The 4-heptyloxybenzylidene-4'-heptylaniline (abbreviated to  $7O.7$ ) is a symmetrical mesogen, for it carries the same aliphatic chain at both ends. As such, it produces only single-layered smectic phases. Its polymorphic scheme [10] is:



The experimental techniques utilized are differential scanning calorimetry (Perkin-Elmer DSC IV), polarizing optical microscopy (Leitz-Orthoplan with FP-82 hot stage), and X-ray diffraction (Guinier camera equipped with a bent-quartz monochromator

and an electric oven). Some of the smectic phases considered being monotropic in nature, care was taken to study all the samples only by cooling from the melt. Strictly speaking, the phase diagrams obtained in this way are not true phase diagrams corresponding to thermodynamic equilibrium. They can just be considered as *phase maps*, showing at the worst the temperature range of reproducible occurrence of the various phases observed under given experimental conditions; as such, they are very useful for practical purposes.

### Results.

\*  $\text{N}\equiv\text{C}-4\text{O} \cdot 8 / \text{N}\equiv\text{C}-6\text{O} \cdot 8$  BINARY MIXTURES. — The molecules of the two mesogens used in this binary system are almost identical from the standpoint of their chemical composition and architecture; the aliphatic chain carrying the cyano endgroup is longer by two methylene groups in  $\text{N}\equiv\text{C}-6\text{O} \cdot 8$  than it is in  $\text{N}\equiv\text{C}-4\text{O} \cdot 8$ . The lengths of the fully extended molecules are 32 and 30 Å, respectively. Both mesogens give rise to  $B_2$  and  $A_2$  smectic phases,  $\text{N}\equiv\text{C}-6\text{O} \cdot 8$  producing an extra  $A_1$  phase prior to melting. The study of the present system was intended to give details about the transition from  $A_1$  to  $A_2$  as a function of concentration and molecular length.

As shown in figure 1,  $\text{N}\equiv\text{C}-4\text{O} \cdot 8$  and  $\text{N}\equiv\text{C}-6\text{O} \cdot 8$  are miscible in all proportions for both  $A_2$  and  $B_2$  smectic phases. On the contrary, the  $A_1$  smectic phase observed with pure  $\text{N}\equiv\text{C}-6\text{O} \cdot 8$  extends only very little in the phase diagram as it can dissolve only small amounts of  $\text{N}\equiv\text{C}-4\text{O} \cdot 8$  without disruption, figure 1b. From optical data no significant differences between  $A_1$  and  $A_2$  textures are evidenced. Moreover, the I- $SA_1$  transition line is very flat but no minimum can be clearly evidenced.

The single- and double-layered nature of A and B has been established as mentioned in a previous

paper [1-2] by comparing the measured spacing of the first Bragg harmonic with the known length of the molecules. The  $B_2$  phase observed with pure  $\text{N}\equiv\text{C}-6\text{O} \cdot 8$ , and the  $A_2$  and  $B_2$  phases observed with pure  $\text{N}\equiv\text{C}-4\text{O} \cdot 8$  being monotropic in nature, the mixtures of the two mesogens are not stable over sufficiently long periods of time to be easily studied by X-ray diffraction. X-ray investigations have therefore been performed only in the  $A_2$  phase at  $t \geq 60^\circ\text{C}$ . The experimental data obtained (Fig. 2) confirm the total miscibility of the two components in the  $A_2$  phase and show that the Bragg period changes monotonically as a function of concentration between the values measured with pure  $\text{N}\equiv\text{C}-4\text{O} \cdot 8$  and  $\text{N}\equiv\text{C}-6\text{O} \cdot 8$ , respectively.

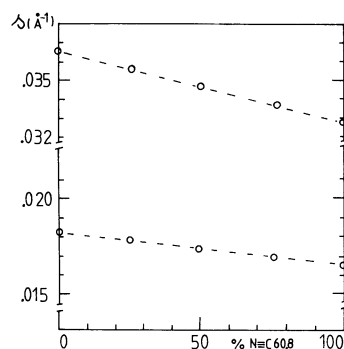


Fig. 2. — Reciprocal spacings  $s = 2 \sin \vartheta / \lambda$  of the small-angle Bragg reflections observed at  $62^\circ\text{C}$  for the smectic  $A_2$  phase of the  $\text{N}\equiv\text{C}-4\text{O} \cdot 8 / \text{N}\equiv\text{C}-6\text{O} \cdot 8$  binary system, as a function of molar concentration.

\*  $\text{N}\equiv\text{C}-4\text{O} \cdot 8 / 7\text{O} \cdot 7$  BINARY MIXTURES. — Although the two mesogens used to prepare this binary system have the same chemical architecture and almost the same molecular length in a fully extended conformation (30 Å for  $\text{N}\equiv\text{C}-4\text{O} \cdot 8$ , and 31 Å for  $7\text{O} \cdot 7$ ), they present entirely different electrical properties: one carries a cyano endgroup, while the other does not. The study of the mixtures of  $\text{N}\equiv\text{C}-4\text{O} \cdot 8$  with  $7\text{O} \cdot 7$  was intended to show how the double-layered smectic structure observed with the cyano compound transforms into a single-layered one where the cyano content of the system decreases upon addition of the non-polar compound.

In contrast to the binary system considered previously, the two mesogens here are not miscible in all proportions in the mesomorphic state (Fig. 3). Because the textures shown by the  $A_1(B_1)$  and  $A_2(B_2)$  smectic phases are similar and because the molecular lengths of the two components are almost the same, both optical microscopy and X-ray diffraction could not provide conclusive information about the mixing of the two species as a function of concentration. However, the existence of eutectic points in the phase diagram clearly demonstrates

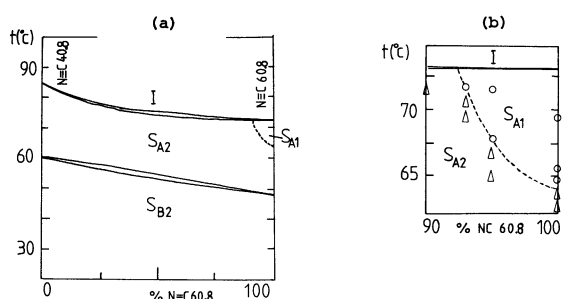


Fig. 1. — (a) Phase map of the  $\text{N}\equiv\text{C}-4\text{O} \cdot 8 / \text{N}\equiv\text{C}-6\text{O} \cdot 8$  binary system observed upon cooling. (b)  $A_1$ - $A_2$  transition as a function of temperature for different values of molar concentration. Triangles indicate the presence and circles the absence in the X-ray patterns of the Bragg reflection corresponding to the double-layered structure.

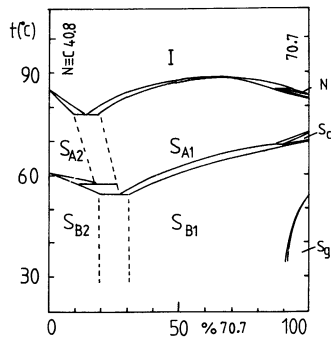


Fig. 3. — Phase map of the  $\text{N}\equiv\text{C}-4\text{O}.8/7\text{O}.7$  binary system observed upon cooling. Dashed lines stand for the demixion region.  $A_1$  ( $B_1$ ) and  $A_2$  ( $B_2$ ) phases are identified from X-ray experiments.

that the single- and double-layered smectic phases observed are separated by domains of demixion. It is of interest to note that the thermal stability of the  $A_1$  phase is slightly enhanced upon mixing, as evidenced in the existence of an azeotropic point for the mixture containing 65 % of  $7\text{O}.7$  — and as frequently observed in mixtures of mesogenic compounds [11]. It is also worthwhile to point out that the non-polar mesogen dissolves large amounts of the second mesogen, while the polar one does not.

From the X-ray observations (Fig. 4), it is clear, first, that the reciprocal spacings measured correspond exactly to layer thicknesses equal either to one or to two molecular lengths, but not to intermediate thicknesses as would be the case if the smectic layers were partially bilayered ( $A_d$ ); and second, that, within the stability concentration domain of the single- or double-layered smectic phase considered, the spacings hardly change with concentration, the two mesogenic molecules being of comparable length. This behaviour holds for the smectic A as well as for the smectic B phases.

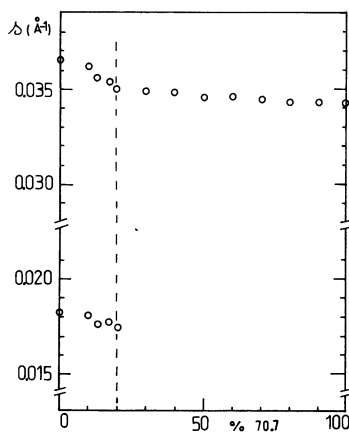


Fig. 4. — Reciprocal spacings  $s = 2 \sin \vartheta / \lambda$  of the small-angle Bragg reflections observed at  $74^\circ\text{C}$  for the smectic A phases of the  $\text{N}\equiv\text{C}-4\text{O}.8/7\text{O}.7$  binary system as a function of molar concentration.

\*  $\text{N}\equiv\text{C}-6\text{O}.8/16\text{O}.8/\text{C}\equiv\text{N}$  BINARY MIXTURES. — The molecules of the two mesogens used to prepare this binary system both contain a cyano endgroup and, when fully extended, are of about the same length ( $32 \text{ \AA}$  for  $\text{N}\equiv\text{C}-6\text{O}.8$  and  $34 \text{ \AA}$  for  $16\text{O}.8/\text{C}\equiv\text{N}$ ); they possess, however, architectures which are fundamentally different. Indeed,  $\text{N}\equiv\text{C}-6\text{O}.8$  contains two aliphatic chains of comparable length with the cyano group attached to the end of one of them, while  $16\text{O}.8/\text{C}\equiv\text{N}$  contains only one long aliphatic chain with the cyano endgroup directly attached to the aromatic core. As stated above,  $\text{N}\equiv\text{C}-6\text{O}.8$  gives rise to either single- or double-layered smectic structures, while  $16\text{O}.8/\text{C}\equiv\text{N}$  gives rise to smectic structures partially bilayered. The study of the mixtures of  $\text{N}\equiv\text{C}-6\text{O}.8$  with  $16\text{O}.8/\text{C}\equiv\text{N}$  was intended to provide information about the transition from a single- or a double-layered to a partially bilayered smectic.

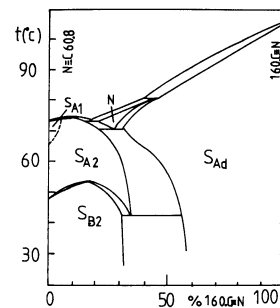


Fig. 5. — Phase map of the  $\text{N}\equiv\text{C}-6\text{O}.8/16\text{O}.8/\text{C}\equiv\text{N}$  binary system observed upon cooling. The domain of existence of  $A_1$  phase is very little extended in concentration. As for  $\text{NC } 6\text{O}.8/\text{NC } 4\text{O}.8$  mixture, dashed line indicates the disappearance of the  $L = 2d$  Bragg reflection. The boundaries of the  $A_2$ - $A_d$  biphasic region are also obtained from X ray measurements.

The phase diagram shown in figure 5 suggests the following comments. First, the domain of existence of  $A_1$  phase is very little extended in concentration, as for  $\text{N}\equiv\text{C}-6\text{O}.8/\text{N}\equiv\text{C}-4\text{O}.8$  mixtures. Second both  $A_2$  and  $B_2$  phases show positive azeotropic points indicative of enhanced thermal stability. At high temperatures the domain of existence of the  $A_d$  phase is very large scaling up to about 70 % of  $\text{N}\equiv\text{C}-6\text{O}.8$  at  $70^\circ\text{C}$ . At lower temperatures ( $t = 60^\circ\text{C}$ ) the  $A_2$  phase, rich in  $\text{N}\equiv\text{C}-6\text{O}.8$  is apt to dissolve amounts of  $16\text{O}.8/\text{C}\equiv\text{N}$  up to 30-35 % while a large biphasic region appears between the  $A_2$  and  $A_d$  phases. Third, the transition from  $A_d$  to  $A_2$  or  $B_2$  is first order and proceeds through the occurrence of two-phase systems, as evidenced in the presence of deep eutectic points. Finally an induced nematic phase is formed at about  $70^\circ\text{C}$  as the  $A_d$  phase grows richer in  $\text{N}\equiv\text{C}-6\text{O}.8$ .

The  $A_2$  and  $B_2$  phases observed with pure  $N\equiv C-6O.8$  being monotropic in nature, and the  $A_d$  phase observed with pure  $16O.C\equiv N$  being easily supercooled below  $68^\circ C$ , the binary mixtures of the two mesogens are not sufficiently stable at low temperatures for their X-ray diffraction patterns to be registered conveniently, in particular in the  $B_2$  phase. The X-ray study of the mixtures as a function of concentration showing the  $A_2$ - $A_d$  transition has therefore been carried out only at  $t > 60^\circ C$ .

Experimental data obtained (Fig. 6) show that, in the  $A_2$  concentration range, the spacings keep constant (first and second Bragg harmonic at about  $31 \text{ \AA}$  and  $62 \text{ \AA}$ , respectively) and correspond to a Bragg lamellar period of twice the average molecular length. In the  $A_d$  concentration range, the Bragg period measured decreases slightly, but significantly, with increasing concentration of  $C\equiv N-6O.8$  and corresponds to a lamellar thickness which is intermediate between one and two molecular lengths. Finally, in the concentration range where demixion occurs, the X-ray patterns contain simultaneously the diffraction signals of both  $A_2$  and  $A_d$  phases.

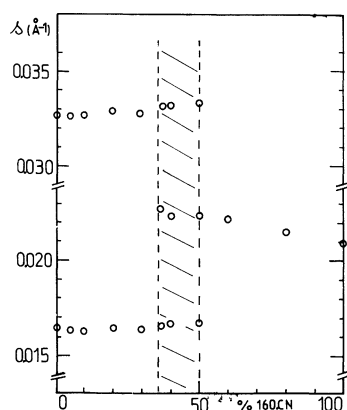


Fig. 6. — Reciprocal spacings  $s = 2 \sin \vartheta / \lambda$  of the small-angle Bragg reflections observed at  $60^\circ C$  for the smectic A phases of the  $N\equiv C-6O.8/16O.C\equiv N$  binary system as a function of molar concentration. Shadow in the graph stands for the demixion region.

### Discussion.

The above results and experimental observations suggest several comments which will be presented in the following. First we discuss the case of binary mixtures of  $N\equiv C-4O.8$  with  $N\equiv C-6O.8$  and  $7O.7$ , that is, the case of mixtures formed of molecules which are all symmetrical from the standpoint of chemical architecture; then we discuss the case of  $N\equiv C-6O.8/16O.C\equiv N$  mixtures which contain molecules having different architectures, some being symmetrical, and others dissymmetrical.

**BINARY MIXTURES OF SYMMETRICAL MOLECULES.** — Both  $N\equiv C-4O.8/N\equiv C-6O.8$  and  $N\equiv C-4O.8/7O.7$  binary systems, entirely formed of symmetrical mesogens, show smectic phases which are either single- ( $A_1, B_1$ ) or double-layered ( $A_2, B_2$ ) (Figs. 1 and 3). The transition between the two types of layering as a function of temperature and concentration is always abrupt, without the formation of partially bilayered structures ( $A_d$  or  $B_d$ ). This is easy to understand because both  $A_1(B_1)$  and  $A_2(B_2)$  are, in fact, the same as far as the one-dimensional smectic distribution of the molecular centers is concerned, their only difference as stated above being related with the presence or the absence of the cyano endgroups. In these systems, the amphiphilic character of the molecules is totally satisfied, the local segregation of the aromatic cores from the aliphatic chains being kept unchanged when the type of layering is modified. It is of interest to compare the single- and double-layered structures presented in this paper with the ideas developed recently [12] to describe the partially bilayered smectic phases of highly polar and dissymmetrical mesogens, involving a competition between two periodicities, one related with the molecular stacking (molecular density wave), the other with the distribution of the dipole moments (polarization wave). While, in the latter case, the two periodicities are supposed to be incommensurate with one another so as to explain the formation of  $A_d$  smectic structures, they are strictly commensurate in the present work as they correspond to either one or two molecular lengths.

In the  $N\equiv C-4O.8/7O.7$  system, the transition between single- and double-layered structures is clearly first order as it takes place through a concentration range where the two structures coexist. Figure 7 gives a schematic picture of the arrangement of the  $N\equiv C-4O.8$  and  $7O.7$  molecules in the smectic  $A_1(B_1)$  and  $A_2(B_2)$  phases. In the single-layered structure, the terminal methyl groups of the aliphatic chains of the  $7O.7$  molecules may be viewed as located predominantly at the external surface of each smectic layer, forming reasonably well defined methyl planes; the cyano endgroups of the  $N\equiv C-4O.8$  molecules added to the system also locate themselves at the external surface of each smectic layer, acting as *defects* in the methyl planes. In the double-layered structure, on the other hand, two types of endgroup planes alternately superposed may be defined, one containing methyl groups and the other a mixture of methyl and cyano groups; the methyl groups in the planes which contain the cyano endgroups act as *defects* and modify the lateral thermodynamic interactions.

In the  $N\equiv C-4O.8/N\equiv C-6O.8$  system, the transition is much more difficult to characterize as to its exact physical nature because the concentration

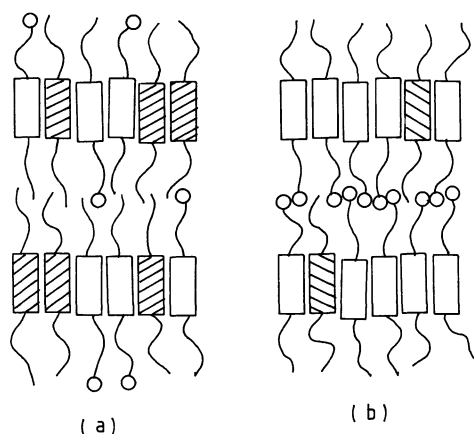


Fig. 7. — Schematic view of the lamellar structure of  $N\equiv C-4O.8/7O.7$  mixture (a) in the monolayered state; (b) in the  $A_2$  state. Wavy lines represent the aliphatic chains, circles the cyano endgroups, empty rectangles the aromatic cores of polar molecules and filled rectangles the aromatic cores of non-polar symmetrical molecules.

range of  $A_1$  is narrow and the molecular lengths of the two components too much the same, it is hard to detect whether or not  $A_1$  is surrounded in the phase diagram by a two-phase region. Previous high resolution X-ray diffraction studies on similar binary mixtures, presenting as a function of temperature a large stability domain for an  $A_1$  phase inserted between an  $A_2$  and a nematic phase, have shown that the  $A_2 \leftrightarrow A_1$  transition is first or second order depending upon the concentration [13]. The first observation of the  $A_2 \leftrightarrow A_1$  transition is first or second order depending upon the concentration [13]. The first observation of the  $A_2 \leftrightarrow A_1$  transition is first or second order depending upon the concentration [13]. The first observation of the  $A_2 \leftrightarrow A_1$  transition is first or second order depending upon the concentration [13]. A detailed X-ray diffraction study of the  $A_1 \leftrightarrow A_2$  transition as a function of temperature in pure  $N\equiv C-6O.8$ , including measurements of the relative intensities of the smectic Bragg reflections, is currently in progress [15].

\* BINARY MIXTURES OF A SYMMETRICAL WITH A DISSYMMETRICAL MESOGEN. — The  $N\equiv C-6O.8/16O.C\equiv N$  binary system contains mesogens of different architectures, one being symmetrical, the other dissymmetrical; in interpreting its liquid crystalline behaviour, one is hence faced with specific problems stemming from a possibility of getting mixed end to end associated dimers of the two mesogens through their cyano terminal groups.

For the  $A_2(B_2)$  smectic phase, the structural behaviour is easy to analyse. Starting from the pure  $N\equiv C-6O.8$ , and progressively adding small amounts of  $16O.C\equiv N$ , one sees immediately that the dissymmetrical mesogen can be introduced into each elementary layer of the bilayered structure either as individual molecules (monomers), or as head to head dimers formed exclusively of dissymmetrical molecules (abbreviated as dd-dimers in the

following), or else as mixed dimers formed of one symmetrical and one dissymmetrical mesogen (abbreviated as sd-dimers in the following). It helps to consider, now, how the layer spacing may be affected by the presence of dimers in the mixture. By assuming that the aromatic and the aliphatic moieties of the molecules tend to segregate, regardless of whether they belong to monomers or dimers, it is possible to calculate the layer spacing,  $d$ , as a function of concentration and degree of end to end association of the molecules.

It is useful to point out here that the degree of association of the cyano endgroups of the symmetrical molecules does not come into play, because these cyano groups are located on the outer faces of the smectic layer. Indeed, let  $x$  be the mole fraction of the symmetrical molecules in the mixture,  $\tau$  the mole fraction of the dissymmetrical molecules participating in the formation of dd-dimers, and  $t$  the mole fraction of the symmetrical molecules participating in the formation of sd-dimers. Clearly, a mixture of  $N$  symmetrical and dissymmetrical molecules globally contain  $xN(1-t)$  non-associated symmetrical molecules,  $xNt$  mixed sd-dimers,  $(1-x)N\tau/2$  dd-dimers of dissymmetrical molecules, and  $(1-x)N(1-\tau) - xNt$  non-associated dissymmetrical molecules. The total volume of the mixture is  $V = xNV_s + N(1-x)V_d$ , where  $V_s$  and  $V_d$  are the volumes of a symmetrical and a dissymmetrical molecule, respectively. Spread out in a single smectic layer and arranged side by side with an individual lateral molecular area  $\sigma$  (which may safely be taken as being the same for all of them), the monomeric and dimeric species will have a surface extension of

$$\Sigma = [xN(1-t) + (1-x)N\tau/2 + (1-x)N(1-\tau)]\sigma.$$

As, on the average,  $d$  is equal to  $V/\Sigma$ , it is clear that the thickness of each elementary layer of the bilayered smectic phase is:

$$d = \frac{xV_s/\sigma + (1-x)V_d/\sigma}{x(1-t) + (1-x)(1-\tau/2)} \quad (1)$$

where  $V_s/\sigma$  and  $V_d/\sigma$  give a measure of the lengths  $L_s$  and  $L_d$  of the symmetrical and dissymmetrical molecules, respectively. In the specific case of the mixture under consideration, the symmetrical and dissymmetrical molecules are both of almost the same length ( $L_s \approx L_d = L$ ); the above expression may, therefore, be written:

$$d = \frac{L}{1 - \tau(1-x)/2 - xt}. \quad (2)$$

The experimentally observed invariance of  $d$  with respect to  $x$  ( $d \approx L$ , see Fig. 6) clearly suggests that both  $\tau$  and  $t$  are zero; apparently, the dissymmetrical molecules are not involved in the formation of

dimers at all. This behaviour is easy to understand. Indeed, the smectic  $A_2(B_2)$  phase being rich in symmetrical molecules, its smectic structure must basically correspond to the double-layered structure of the pure symmetrical mesogen (see Fig. 2a in Ref. [2]), with only small modifications due to the presence of the dissymmetrical molecules (Fig. 8). Because of their low concentration, the dissymmetrical molecules do not appreciably associate with each other to give rise to dimers ( $\tau = 0$ ). This is in agreement with previous observations about the dimerization of highly polar and dissymmetrical mesogens in the presence of large amounts of non-polar and symmetrical mesogens (see Fig. 10 in Ref. [6b], see also Ref. [11]); this behaviour merely reflects the entropic contribution of the overcrowding of the aliphatic chains. The dissymmetrical molecules do not associate with the cyano-ended symmetrical molecules ( $t = 0$ ) either, because the amphiphilic character prevents the aromatic cores that carry the cyano endgroup of the dissymmetrical molecules from entering the aliphatic sublayers where the cyano endgroups of the symmetrical molecules are located. Owing however to the fact that the cyano endgroups of the dissymmetrical molecules are located not far from the cyano endgroups of the symmetrical ones, and also to the thermal agitation and longitudinal motions of the molecules, the formation of sd-dimers with short lifetimes should not be entirely neglected.

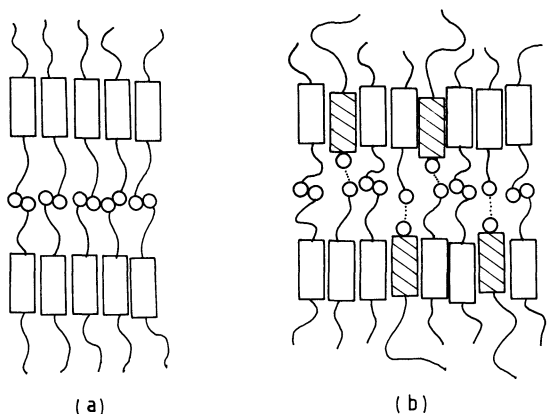


Fig. 8. — Schematic view of double-layered smectic  $A_2$  structure of  $N\equiv C-6O.8/16O.C\equiv N$ . a) Pure  $N\equiv C-6O.8$ . b) In the presence of dissymmetrical molecules: wavy lines represent the aliphatic chains, circles the cyano endgroups, empty rectangles the aromatic cores of the symmetrical molecules, and filled rectangles the aromatic cores of the dissymmetrical molecules.

For the  $A_d$  smectic phase, on the other hand, the structural behaviour is much more complex to analyse, at least quantitatively, as will be seen below. From a qualitative point of view, however, it no

doubt corresponds to the evolution of the partially bilayered smectic  $A_d$  structure of the pure  $16O.C\equiv N$  (see Fig. 2 in Ref. [6b]), brought about by the addition of increasing amounts of symmetrical  $N\equiv C-6O.8$ . A similar evolution has already been reported in the literature for another binary mixture of a dissymmetrical cyano-mesogen (4-cyanobenzylidene-4'-octyloxyaniline) with a symmetrical, but non-polar compound (bis-4,4'-heptyloxyazobenzene) [11]. The structural behaviour of the latter mixture was analysed [6] following equation (3), which had been established using the same arguments as those just presented in connection with equations (1) and (2):

$$d = 2 \frac{xL_s + (1-x)L_d}{2 - \tau(1-x)} \quad (3)$$

There was found a dramatic decrease of the degree,  $\tau$ , of head to head association of the polar molecules (down to  $\tau = 0$ ) as a function of increasing concentration,  $x$ , of the non-polar compound (up to  $x \neq 0.5$ ). This was interpreted as being due to the overcrowding of the aliphatic chains with respect to their average molecular area in the plane of the smectic layers.

The X-ray study of  $A_d$  in the present work (Fig. 6) has shown that the layer spacing of the mixture decreases from 48.5 to 44.0 Å when  $x$  varies from 0 to 70%. Although real, the observed decrease is much too small to be interpreted with equation (3), in terms of a simple change of the degree of association of the dissymmetrical molecules alone, as if  $N\equiv C-6O.8$  were simply playing the same role as a non-polar and symmetrical mesogen. Indeed,  $\tau$  is found to increase abnormally with  $x$  and to reach values far beyond unity (from  $\tau = 0.64$  for  $x = 0$  to  $\tau = 1.4$  for  $x = 0.65$ ), which is unacceptable. Of course, this is due to the fact that the symmetrical molecules added to the binary system can act either in the form of individual molecules, or in the form of sd-dimers, or else in the form of ss-dimers containing exclusively symmetrical molecules.

On the contrary, by taking into account the formation of ss- and sd-dimers, in addition to that of dd-dimers considered in equation (3), it becomes possible to explain the small decrease of  $d$  as a function of increasing  $x$  in a reasonable way. If  $\tau$  is the mole fraction of molecules involved in the formation of dimers, whatever their nature (ss, sd or dd), the layer thickness may be written as:

$$d = \frac{2L}{2 - \tau} \quad (4)$$

where  $L$  is the weighted average length of the molecules. With this equation, the experimental data of  $A_d$  lead to values of  $\tau$  which decrease from



0.64 to 0.49 when  $x$  goes from 0 to 65 %. Now, this result is quite satisfactory, because  $\tau$  has reasonable values included in the range from 0 to 1, and also because it reflects correctly the lateral overcrowding of the aliphatic chains. On the whole, such a behaviour is similar to that reported above for a system in which the symmetrical mesogen is non-polar, but here the degree of association does not fall to zero. Quite evidently, it would be interesting to determine quantitatively the  $x$  dependence of the chemical composition of the dimeric species, in ss-, sd-, and dd-dimers, but this is impossible to perform with only the experimental data available.

Figure 9 represents schematically how the different monomeric and dimeric species can arrange themselves in the smectic layers. To discuss this model, it is worthwhile to begin with the mixtures rich in dissymmetrical molecules. As already mentioned in a previous paper concerned with the partially bilayered smectic phases of highly polar and dissymmetrical mesogens (see Sect. 3.1 in Ref. [6b]), dissymmetrical molecules tend to form clusters of *monomers* and *dimers* within the layers, in such a way as to better satisfy the amphiphilic character of the system. For the same reason, the symmetrical molecules dissolved in the mixture considered in this paper tend to locate themselves either within the clusters of *dimers* or else within the clusters of *monomers* depending on whether they are involved in the formation of dimers or they remain in the form of monomers. Of the two dimers containing symmetrical molecules, the mixed sd-dimers must be overwhelmingly easier to incorporate into the system than the ss-dimers, because the aliphatic chain in the

dimers between the two aromatic cores (which must be inserted within the aromatic sublayers) is shorter. At any rate, the presence of sd- ss-dimers in the mixture must be unfavored as far as the amphiphilic character is concerned. This is no doubt why, beyond a certain concentration of symmetrical molecules, the  $A_d$  phase turns into either an isotropic liquid, or an  $A_2(B_2)$  phase, or still, quite interestingly, a nematic phase, depending upon the temperature.

### Conclusion.

The present work gives a general description of the phase diagrams of the binary mixtures of polar end group mesogens ( $N\equiv C$  4O . 8,  $N\equiv C$  6O . 8) with a non-polar one (7O . 7) or with a dissymmetrical polar mesogen (16O .  $C\equiv N$ ) the location of the single-layered, double-layered and partially bilayered smectic phases observed is specified. In the  $A_1$  and  $A_2$  smectic structures, the amphiphilic character of the molecules seems to be consistently satisfied, the surfaces of the elementary molecular layers containing the vast majority of the endgroups. The exchange of methyl and cyano endgroups as a function of concentration in binary mixtures of polar and non-polar symmetrical molecules corresponds to the creation of *chemical defects* in the endgroup planes, and modifies the thermodynamical interactions therein. In the  $A_d$  smectic structure, the amphiphilic character plays an important role, and has a prominent influence over the formation of dimers by the end to end association of the molecules through their cyano endgroups.

Up to this point, the phase transitions between single-layered, double-layered and partially bilayered smectic phases have been analysed exclusively from a static point of view. It is clear, however, that the dynamical aspect of the problem must also be taken into account. The end to end association of the polar molecules must, indeed, be significantly affected by the local mobility of the species. NMR measurements of the order parameter of the aromatic core ( $S \approx 0.7$  for a smectic A phase and  $S \approx 0.9$  for a smectic B phase) and of the methylene groups of the aliphatic chains ( $S$  decreases importantly with the distance to the aromatic core) [16] indicate that the mobility of the cyano endgroups must be different depending upon whether these are attached directly to an aromatic core or to the end of an aliphatic chain. Further experiments on the actual mobility and the dipolar coupling of the cyano endgroups are necessary to clarify this point.

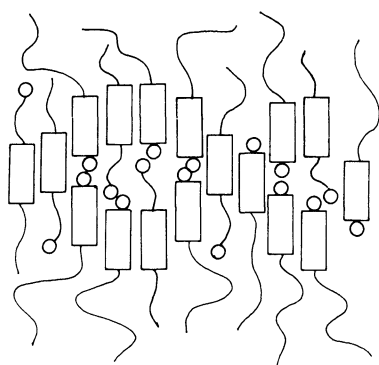


Fig. 9. — Schematic view of the partially smectic  $A_d$  structure of  $N\equiv C-6O . 8/16O . C\equiv N$  mixture: wavy lines represent the aliphatic chains, circles the cyano endgroups, empty rectangles the aromatic cores of the symmetrical molecules, and filled rectangles the aromatic cores of the dissymmetrical molecules.

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