Binary Smectic Systems Including Trinuclear Pyrimidines with and without Nematic Gap

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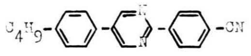
Phase diagrams of binary mixtures are presented in which one component has been selected from among four trinuclear isomeric pyrimidines forming a nematic or smectic A_1 phase, and the second one from cyanocompounds forming an A_d smectic phase. Depending on the molecular structure of pyrimidine, mixtures were obtained that show or show not a nematic gap between the A_1 and A_d smectic regions. In the latter case it was found that the relation $T_{S_A \to N} = f(x)$ has two independent branches in different ranges of the concentration x. The measured spacing of the smectic layers in such mixtures points to the possibility of the pyrimidine monolayer being transformed into a bilayer.

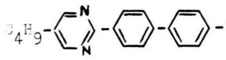
1. Introduction

In earlier works [1, 2] it was shown that in binary mixtures composed of compounds with polar terminal groups forming A_1 and A_d smectic phases a nematic gap is observed which separates a smectic A_1 region with an excess of one component from a smectic A_d region with an excess of the other component. So far this behaviour was observed for pairs of compounds for which the smectic layer spacing ratio is at least 1.36. This brings up the questions: (i) is the observed behaviour specific for mixtures composed of polar A_1 and A_d smectics when the components differ significantly as regards the spacing of their smectic layers? (ii) is the nematic gap observed if the above condition is fulfilled together with other conditions so far unknown? The binary mixtures showing a nematic gap which is not accompanied by an enhancement of the smectic phase included one of the following compounds: isothiocyanatophenyl alkylbenzoate or alkylcyclohexylbenzoate, or else 5-alkyl-2-(p-isothiocyanatophenyl)-1,3-dioxane (all smectics A_1), and one of the following compounds: cyanophenyl or nitrophenyl alkylcyclohexylbenzoate, or else 4-alkoxy-4-cyanobiphenyl (smectics A_d) [1, 2]. A common feature of these compounds is the presence of two polar groups located in the terminal and central parts of the molecule so that the components of the dipole moments parallel to the long axis of the molecule add. It was therefore interesting to check whether the nematic gap between the smectic phases A_1 and A_d is also observed in binary mixtures if the polar groups are located oppositely while the smectic layer spacing ratio is preserved. In the present work the first results regarding this question are given.

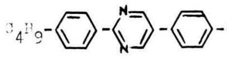
The properties have been tested for binary mixtures consisting of one of the isomeric pyrimidines



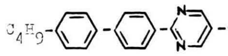
Cr 93.5 N 244 I, **1**



Cr 112 S_{A_d} 212.5 N 262 I, **2**

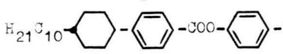


Cr 138 S_{A_1} 180 N 260 I, **3**

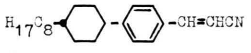


Cr 126.5 S_{A_1} 216.5 N 274.5 I, **4**

and one of the compounds:



Cr_1 65 Cr_2 84 Cr_3 94 S_{A_d} 167 N 183 I, **5**



Cr 48 S_{A_d} 128 N 137.5 I, **6**

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Compound **1** forms only a nematic phase which, according to X-ray tests carried out by Jha et al. [3], consists at 90 °C of molecules having the average length 2.24 nm. Their length increases above 170 °C, reaching 3.24 nm at 230 °C. Compounds **2, 3** and **4** form a smectic phase A which, as will be shown, is of monomolecular structure (of A_1 type). Compounds **5** and **6** form a partially bimolecular smectic phase (of A_d type).

2. Experimental

Trinuclear pyrimidines, compounds **1, 2, 3** and **4,** were supplied by Hoffmann La Roche. Their phase transition temperatures are given in [4]. Compounds **5** and **6** have been synthesized in our laboratory. The synthesis has been described in [5, 6].

The smectic A phases of compounds **2–6** were identified by the standard small-angle X-ray scattering, and by the miscibility method using selected standard substances. The spacing d of the smectic layers was determined from the location of the internal reflexes on the X-ray pattern, and the intermolecular distance *D* was estimated from the location of the external reflex. The lengths of the isolated molecules were calculated under the assumptions that the lengths of the bonds and the valency angles are the same as in smaller molecules, the alkyl chain assuming the trans configuration, the Van der Waals radii of the terminal atoms having been accounted for. The dipole moments of the pyrimidines **1–4** have been estimated by adding the contributions of the particular parts of the molecule as well as from the dielectric permittivity of the binuclear analogs given in [7], and for compound **1** after [8]. The phase transition temperatures were determined by the thermomicroscope method with use of the VEB Analytic Dresden device. The samples of the mixtures were placed between two thin microscope glasses. Separate weighed portions were used for every composition, and the samples were heated to the clearing point to ensure good mixing of the components. The significant details of the phase diagrams of the tested mixtures appear in the temperature range far below their melting points; so it was not possible to observe them during slow cooling of the sample. In order to determine the phase transition temperatures in the strongly supercooled state we proceeded as follows: the microscope stage was brought to a temperature close to that at which the phase transition was expected to occur while the sample was heated on a separate heater to a temperature much above the melting point. Then the sample was quickly transported to the measuring stage. This procedure allowed rapid cooling of the sample to the anticipated temperature. The highest temperature of the stage at which it was possible to observe the lower-temperature phase (S_A or N_{re}) before crystallization took place was assumed as the phase transition temperature in the strongly supercooled state. For some mixtures with the smectic A phase we encountered difficulties in the accurate determination of the end melting temperature. Then the solidus lines were calculated from the CSL equation and presented on the diagrams by dashed thin lines.

3. Results

3.1. Identification of the smectic phases

The X-ray scattering patterns of the substances **2–6** are characteristic of smectics A. They all reveal one pair of sharp internal spots located symmetrically in the vicinity of the primary beam, and one pair of diffused external spots located externally oriented perpendicular to the internal spots. From these patterns the interlayer spacings, *d*, and intermolecular distances, *D*, were calculated. They are summarized in Table 1.

The three pyrimidines with a smectic phase A (compounds **2–4**) show the same temperature independent spacing of the smectic layers ($d = 2.1$ nm). The measured spacings are only insignificantly smaller than the lengths of the isolated molecules in

Table 1. Calculated maximal lengths (*l*) of the isolated molecules, measured smectic layer spacings (*d*), and intermolecular distances (*D*).

Compound	*l* nm	*d** nm	*D* nm
1	2.18		
2	2.18	2.1	0.457
3	2.18	2.1	0.455
4	2.18	2.1	0.459
5	3.16	4.1	0.492
6	2.54	3.4	

* These values are temperature independent.

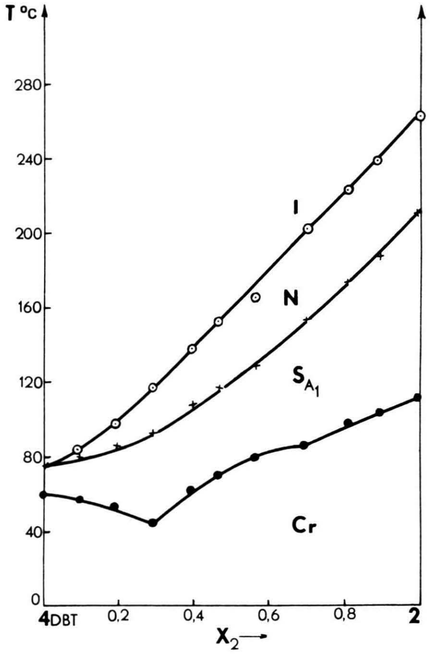


Fig. 1. Phase diagram of binary mixture composed of pyrimidine **2** and 4-n-butyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane (4DBT) showing complete miscibility of the smectic phases A_1 of both compounds.

their longest conformation. On this basis one can conclude that the smectic layers are built of single molecules; so these compounds belong to smectics A_1. This conclusion is further confirmed by the fact that the smectic A phases of the pyrimidines **2, 3** and **4** mix in the whole concentration range with the smectic A_1 phase of 4DBT (5-n-butyl-2-(p-isothiocyanatophenyl)-1,3-dioxane, $d = 1.8$ nm). One phase diagram of such mixtures is shown in Figure 1. The $S_{A_1} \leftrightarrow N$ phase transition in the pyrimidines **2, 3** and **4** is a transition of the second kind. The Unipan 600 microcalorimeter with the DSC device did not reveal any liberation or absorption of energy in the transition region even if the maximum sensitivity (10^{-3} J) was applied. The smectic layer spacing of compounds **5** and **6** is greater than the respective lengths of their isolated molecules, and the d/l ratio amounts to 1.32 and 1.34, respectively, which is in accordance with the dimensions of the dimers if side overlapping of the rigid cores takes place on the whole length. Such smectic layers are referred to as partially bimolecular and are denoted as A_d [9, 10].

3.2. Phase diagrams of cyanopyrimidines with dipole moments of the polar groups oriented in the same direction

Figures 2a and 2b show the phase diagrams of the systems **1** + **5** and **1** + **6**.

These diagrams are quite similar. They reveal a virtual $S_{A_d} \rightarrow N_{re}$ transition in compounds **5** and **6**. The shape of the A_d smectic region of system **1** + **5** is parabolic with the summit at $x_1 = 0.3$ and $T = 105$ °C. The A_d phase neighbours at higher temperatures the normal nematic phase and at lower temperatures the reentrant nematic phase in a fairly wide concentration range. Extrapolation of the lower branch of the parabola to $x_5 = 1$ allows us to estimate the temperature of the virtual $S_{A_d} \rightarrow N_{re}$ transition in the pure compound **5** to be at about 50 °C. The phase diagram in Fig. 2a shows the typical shape of the phase boundary often observed for mixture of other cyanocompounds consisting of one A_d smectic and one nematic usually chosen from the same homologous series [11]. The reentrant nematic phase of the mixture **1** + **6** occupies a narrower concentration interval which makes it difficult to estimate the temperature of the virtual $S_{A_d} \rightarrow N_{re}$ transition in the pure compound **6,** but it surely lies below 0 °C. The summit of the parabola limiting the smectic A_d region is at $x_1 = 0.48$, $T = 60$ °C. The A_d smectic phase in the mixture **1** + **6** occupies a wider concentration and temperature interval due to the differences in the properties of **5** and **6.**

Figures 3a and 3b show the phase diagrams of the mixtures **2** + **5** and **2** + **6.** Here all the components show the smectic A phase. In both diagrams the A_d and A_1 smectic regions are fully separated by a nematic region. The shapes of the smectic A_d regions (left-hand parts of the diagrams) are similar to those in Figs. 2a and 2b but the parabola summits are flattened. This is a characteristic feature of systems with a nematic gap in which the destabilization of the smectic phase A_d in the vicinity of the nematic gap is very strong [1, 2]. The lowering of the stability of the smectic A_1 phase (see right-hand parts of the diagrams) proceeds more gradually and is greater in the mixture **2** + **5** than in **2** + **6.**

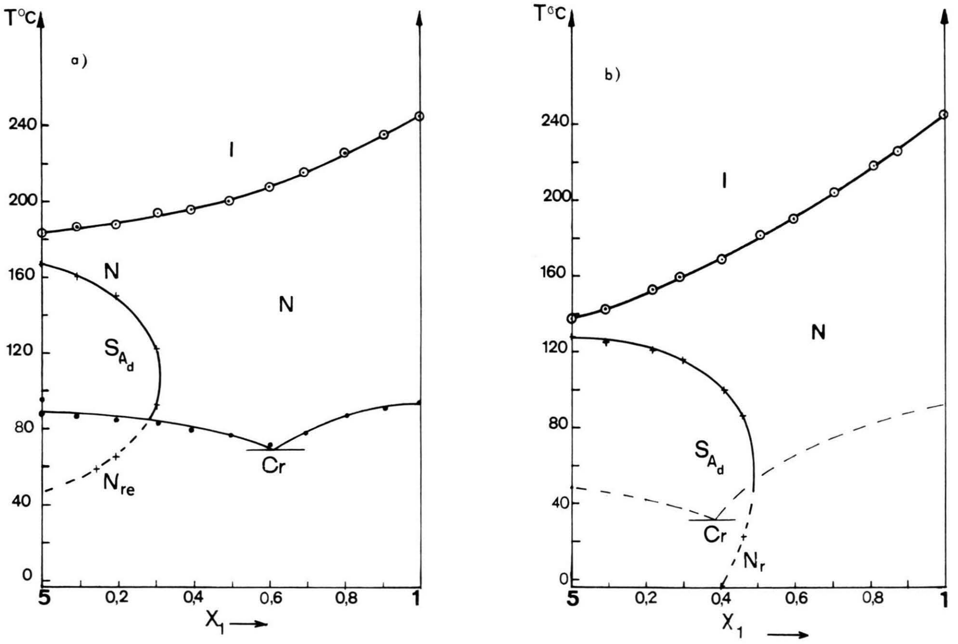


Fig. 2. Phase diagrams of binary mixtures including nematic pyrimidine **1** showing the presence of the virtual nematic reentrant phase of compounds **5** and **6.**

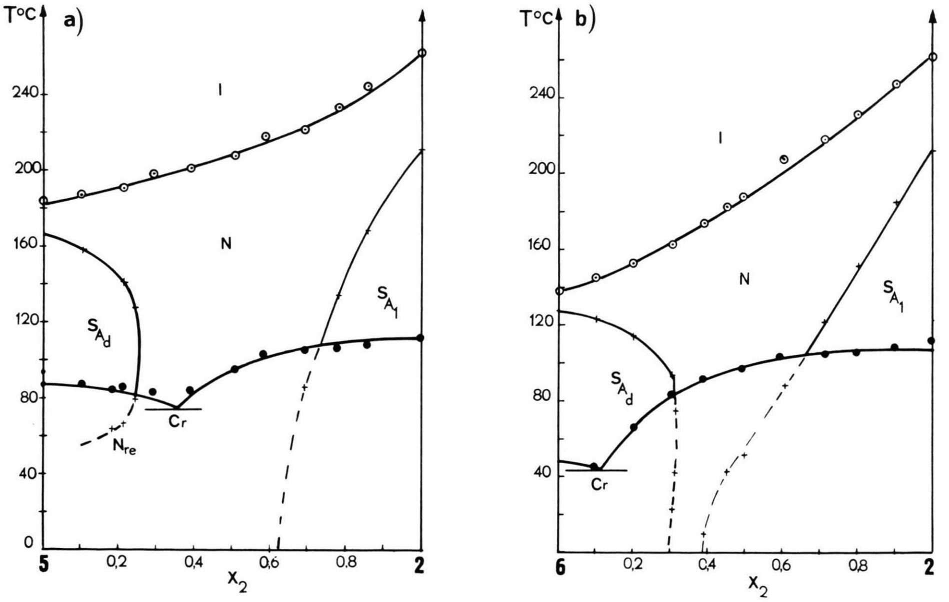


Fig. 3. Phase diagrams of binary mixtures including smectic A_1 pyrimidine **2** showing a nematic gap between the A_1 and A_d smectic regions.

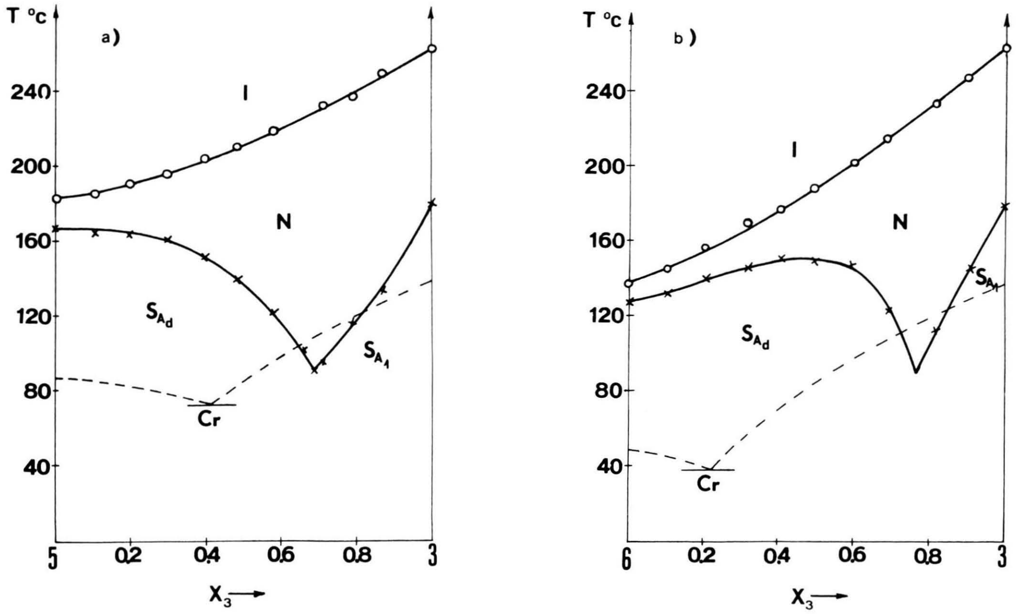


Fig. 4. Phase diagrams of binary mixtures including smectic A_1 pyrimidine **3** with no nematic gap between the A_1 and A_d smectic regions.

3.3. Phase diagrams of cyanopyrimidines with opposite orientation of the dipole moments of the polar groups

Figures 4a and 4b show the phase diagrams of the systems **3** + **5** and **3** + **6.** These diagrams are very similar but differ in some details. The $S_{A_d} \rightarrow N$ transition temperature in the system **3** + **5** decreases monotonically with increasing concentration of **3** up to $x_3 = 0.7$. As regards the system **3** + **6,** the transition temperature $S_{A_d} \rightarrow N$ increases somewhat up to $x_3 = 0.4$. In the range of $x_3 = 0.4$ to 0.6 it remains practically constant and then it decreases assuming the lowest value at $x_3 = 0.75$. The most characteristic features of both mixtures including **3** as compared to those including **2** are the strong shift of the smectic phase A_d towards higher concentrations of **3** and the absence of the nematic gap separating the smectic regions A_d and A_1. The shape of the $S_{A_d} \rightarrow N$ and $S_{A_1} \rightarrow N$ phase boundaries reminds the solidus of solids in the absence of mutual solubility of the mixture components. By analogy to a eutectic point we can anticipate that at the point of intersection of the $S_{A_d} \rightarrow N$ and $S_{A_1} \rightarrow N$ transition branches two non-miscible smectic A phases may coexist. The shape of the $S_A \rightarrow N$ phase boundaries shown in Figs. 4a and 4b is very similar to that observed for the mixture DB5 + TBBA [12], where the former compound form a smectic A_2 phase and the latter a smectic A_1 phase.

The diagrams of mixtures including pyrimidine **4** are shown in Figs. 5a and 5b. In both mixtures with **4** the stability of the smectic phases is greater than in the mixtures with **3**; the $S_{A_d} \rightarrow N$ and $S_{A_1} \rightarrow N$ phase boundary curves intersect at a greater angle.

When observing the mixtures **4** + **5** from $x_4 = 0.55$ to $x_4 = 0.7$ under a microscope in the cooling cycle we found that a new smectic phase is generated from the A_d smectic at temperatures on the extension of the right-hand branch of the $S_{A_1} \rightarrow N$ phase boundary; see also X-ray data in Table 2. The separation of the components proceeds fairly slowly and in heating disappears at a temperature higher than that at which it began to appear. In the temperature range of 70 − 140 °C for $x_4 = 0.55$ we obtain from X-ray scattering experiments patterns characteristic of smectic phase A. In the range 90 − 140° the smectic layer spacing is constant, $d = 3.78$ nm. Below 90° we observe two pairs of spots to which spacings $d = 4.12$ nm and $d = 2.0$ nm can be assigned. Thus the microscopic observations are in agreement with the X-ray ones. The observed

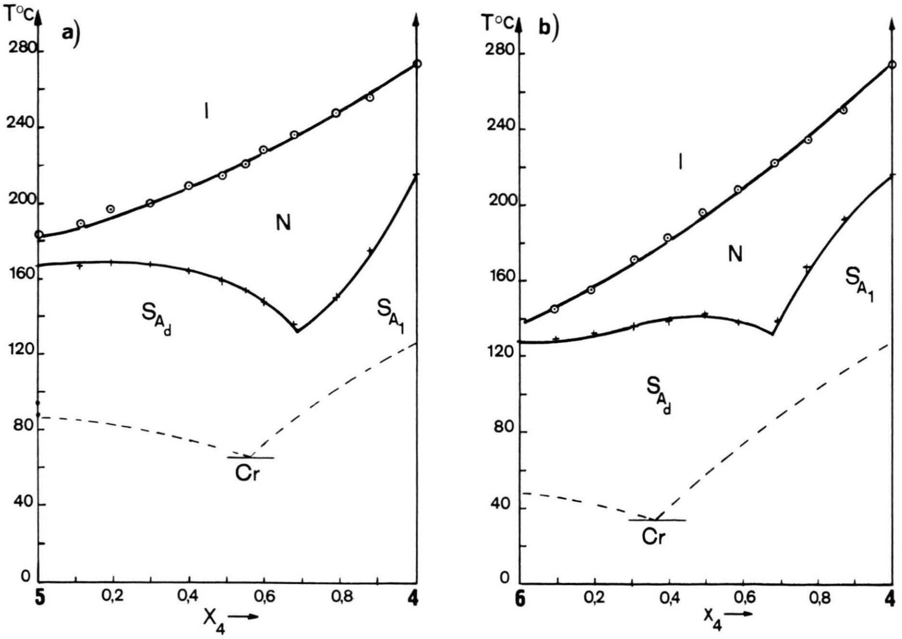


Fig. 5. Phase diagrams of binary mixtures including pyrimidine **4** with no nematic gap between the A_1 and A_d smectic regions.

Table 2. Temperature dependence of smectic layer spacings (d) in nm of binary mixture **4** + **5** for two concentration **4**.

	Mole fraction of **4**			
Temp, °C	0.55		0.65*	
140	3.78		3.47**	2.20**
128	3.78		3.55	2.17
120	3.78		3.63	2.14
110	3.78		3.67	2.05
90	4.12	2.0	crystallization	
80	4.12	2.0	below 100 °C	
70	4.12	2.0		

* Intensity of spots in X-ray pattern decreasing with increasing temperature and more quickly for the second one than for the first one. They are not observable for this concentration above 150 °C at all.
** In nematic phase.

behaviour may be explained as follows:

(i) either the A_d smectic mixture separates at a given temperature into the pure compounds **4** and **5**,

(ii) or the smectic A_d mixture transforms into a mixture of smectics A_2 and A_1.

The above properties of the mixture **4** + **5** require more detailed studies, in the present work we only draw attention to the observed anomalous behaviour.

4. Discussion

From the phase diagrams of the binary mixtures of four isomeric pyrimidines **1**–**4** and the cyanophenyl compounds **5** or compound **6** it follows that relatively small changes in the molecular structure of the pyrimidines affect significantly the thermal stability and miscibility of the smectic phases. All four pyrimidines have molecules of the same length and geometry, the dipole moments of the polar groups **1** and **2** add and result the high dipole moment of the molecules. Its value estimated from the principle of additivity is $\mu = 6.5 \pm 1$ D, while that calculated according to [13] from the experimentally measured dielectric constants of the binuclear analogs [7] is $\mu = 6$ to 7 D. Dielectric constants of compound **1** are available in [8]; the dipole moment estimated then by us is somewhat smaller, viz. $\mu \cong 5$ D. This allows us to suppose that in the nematic phase the molecules of compound **1** form to a small degree an antiparallel dimer. The results of X-ray investigations presented in [3] allow us to conclude that dimerization becomes more effective at above 185 °C. The dipole moments of the pyrimidines **3** and **4** are smaller by about 4.5 D since their two polar groups have an opposite orientation. The resultant dipole moment of **3** and **4** was estimated as $\mu = 1.7 \pm 0.7$ D, and that calculated from the dielectric constants is $\mu = 2$ to 3 D. In **5** both polar groups give concordant contributions to the dipole moment of the molecule. The value of its longitudinal component calculated from dielectric measurements for the pentyl analog [13] is $\mu = 4.7$ D, and that estimated from the additivity principle is $\mu = 5.3$ D, which allows us to conclude that the nematic phase of this compound is associated to a small degree. Compound **6** has only a strongly polar group at the end of the molecule; its dipole moment was estimated as $\mu = 4.2$ D. The dielectric constants measured for the propyl analog points to a dielectric anisotropy $\Delta\varepsilon_{70°} = 13.6$ ($\mu = 3.9$). This indicates that antiparallel pairing of the molecules takes place in this homologous series.

The shapes of the phase diagrams of the mixtures **1** + **5** and **1** + **6** as well as **2** + **5** and **2** + **6** are such as they could have been expected from the properties of the pure components. The compounds **5** and **6** in mixtures with the nematic **1** confirm that they have a smectic phase of A_d structure, since the S_{A_d} phase boundary bends at low temperatures revealing the reentrant nematic phase. The observed greater stability of the smectic phase A_d in the mixtures including **6** as compared with those including **5**, especially on the low temperature side, is probably due to the greater liability of **6** to dimerization. The disappearance of the smectic phase in the mixtures of **2** with **5** or **6** may be explained by the very pronounced incomeasurability of the spacings of their smectic layers. The smectic layer spacing ratios in the pairs **2** + **5** and **2** + **6** are $d_5/d_2 = 1.95$, and $d_6/d_2 = 1.6$, respectively.

Compounds **5** and **6** in mixtures with **3** and **4**, which also are smectics A_1 of the same smectic layer spacing as in **2**, do not reveal a nematic gap between the S_{A_1} and S_{A_d} regions. In these mixtures, **3** and **4** behave so as if there were no smectic present in the system with layer spacing $d = 2.1$ nm and S → N phase transition temperature of 180 °C or 216 °C but one of greater smectic layer spacing d and lower S → N phase transition temperature.

Such a behaviour was a surprise for us. It suggests the possibility of a virtual $S_{A_1} \rightarrow S_{A_d}$ or $S_{A_1} \rightarrow S_{A_2}$ transition taking place in **3** and **4**, or that **3** and **4** yield intermolecular complexes with **5** or **6**.

The lack of the nematic gap in the mixtures **3** + **5**, **3** + **6**, **4** + **5**, and **4** + **6** can be explained by considering one of the following hypotheses:

(i) The nematic gap occurs only if the smectic layer ratio of the compounds making up the mixture is high and, simultaneously, the orientation of the dipole moments of the polar groups present in the molecule is concordant.

(ii) A structural transformation of compounds **3** or **4** takes place in the matrix of compounds **5** or **6** leading to a change of the state of association, which in consequence neutralizes the differences of the smectic layer spacing between the mixture components.

In order to evaluate the above hypotheses we measured for the mixture **4** + **5** the variation of the smectic layer spacing with the concentration of **4** (Fig. 6). Pure compound **4** and a mixture with $x_4 = 0.9$ yield X-ray patterns with one pair of spots, the corresponding smectic layers spacing being $d = 2.1$ nm. For $x_4 = 0.8 - 0.65$ (region still belonging in the diagram to phase S_{A_1}) we have two pairs of spots to which the spacings $d_1 = 2.1$ nm and $d_2 = 3.4 - 3.6$ nm correspond. For the remaining concentrations (region of phase S_{A_d}) we observe again one pair of spots, and the smectic layer spacing ranges maximally from 4.14 nm to 3.51 nm. In the region of $x_4 = 0$ to $x_4 = 0.4$ the A_d smectic layer spacing varies in a moderate way, so as if the components of

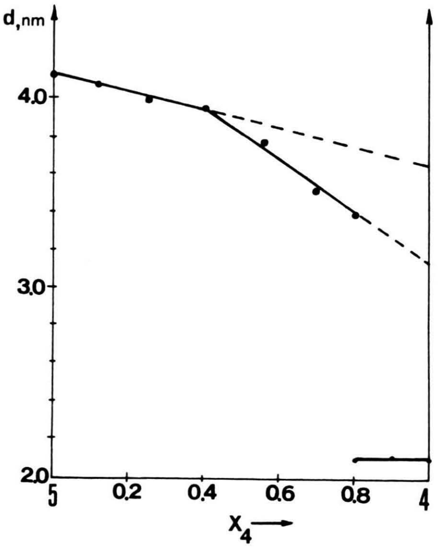
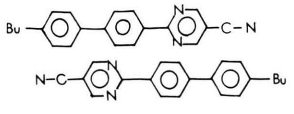
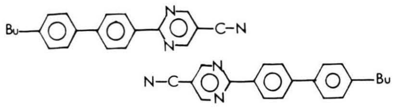
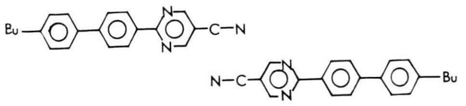
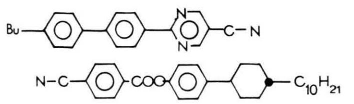
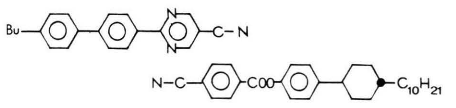
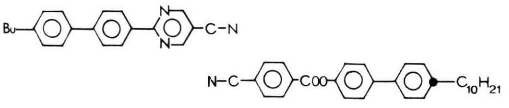


Fig. 6. Dependence of the smectic layer spacing on the concentration of the mixture including pyrimidine **4** and ester **5** at 128 °C.

Table 3. Conformation dependence of the lengths l_d of dimers of pyrimidine **4** and of associates of pyrimidine **4** with ester **5**.

Dimers	l_d, nm
	2.63
	3.44
	3.91
Associates	
	3.77
	4.63
	5.06

the mixture had smectic layer spacings differing very little. The value of the hypothetic smectic layer spacing for pure compound **4** extrapolated from the linear part of the upper curve in Fig. 6 is $d_2 \approx$ 3.6 nm.

The lengths of dimers of different conformation made up of compound **4** and the associates of compounds **4** and **5** are summarized in Table 3. We see that the dimer consisting of molecules **4** reveals values closest to the estimated value of $d = 3.6$ nm. Here the intermolecular interaction is realized by the overlapping of only the end CN groups (structure corresponding to a smectic layer of A_2 type, $d = 3.9$ nm). The associate composed of **3** and **5** molecules is produced by complete side overlapping of the rigid cores (structure corresponding to the smectic layer A_d, $d = 3.77$ nm). Taking account of the results reviewed in [10] that the $S_{A_2} \rightarrow S_{A_1}$ transition is observed in esters with opposite orientation of the dipole moments and that phase S_{A_2} lies below phase S_{A_1}, we can guess that a virtual $S_{A_2} \rightarrow S_{A_1}$ transition takes place in pure compound **4.** The X-ray investigations of **4** up to 100 °C have not revealed in this compound the presence of phase A_2. If this phase existed, perhaps it would be observed at a lower temperature.

The X-ray data given in Fig. 6 allow us to believe that the lack of the nematic gap not only in the case of the **4** + **5** mixture but also in the cases of **3** + **5,** **3** + **6,** and **4** + **6** mixtures is due to compounds **3** and **4** changing their molecular structure in the matrix of compounds **5** or **6** so that their characteristic dimensions increase. It follows that adequately high smectic layer spacing ratios are decisive for the appearance of the nematic gap between the two smectic regions, whereas the distribution of the polar groups in the molecule may be decisive for the formation of association, which may vary with the environment and affect indirectly the shape of the phase diagrams.

Acknowledgements

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