Dimerization of polar smectics A₁ with a terminal cyano group in the matrix of smectics A₁ of lower polarity

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Dimerization of polar smectics A_1 with a terminal cyano group in the matrix of smectics A_1 of lower polarity

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Binary mixtures have been studied of polar compounds with smectic A_1 phases belonging to the following series: 4-cyanobiphenyl 4-yl 4'-n-alkylbiphenyl-4-carboxylate (CBnAB) and 4-(trans-4-n-decylcyclohexyl) benzoates (10XPCHB) with $X =$ F, NCS, COCH$_3$. In these systems a strong destablization of the smectic A_1 phase is observed on the side of the CBnAB component and an enhancement of the smectic A_1 phase on the side of 10XPCHB. It is shown that the anomalous behaviour of the mixtures of two A_1 smectics with a similar layer spacing is due to the dimerization of CBnAB in the matrix of 10XPCHB which is of lower polarity.

1. Introduction

It has been observed that binary mixtures composed of polar compounds with a smectic A_1 phase, one of which belonged to the 4-cyanobiphenyl 4-yl 4'-n-alkylbiphenyl-4-carboxylate homologous series (CBnAB)

$$H_{2n+1}C_n-\bigcirc-\bigcirc-CO.O-\bigcirc-\bigcirc-CN \qquad (I)$$
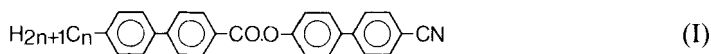
and the other to the halogenophenyl 4-(trans-4-n-decylcyclohexyl)benzoate (10XPCHB) series:

$$H_{21}C_{10}-\bigcirc-\bigcirc-CO.O-\bigcirc-X \qquad (II)$$
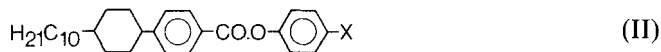
reveal an anomalous behaviour. That is the smectic phase is strongly destabilized on the side of the CBnAB component while that on the side of 10XPCHB is enhanced [1]. The extent of destabilization and enhancement of the smectic regions in the mixture depend on the kind of substituent X; in the CB7AB-10FPCHB system the two smectic regions are completely separated by a nematic gap. In this mixture a reentrant nematic phase is observed in a wide range of concentrations. In binary systems that are characterized by an almost identical spacing of the smectic layers the smectic A–nematic transition temperatures should vary, in accord with the results of [2, 3, 4, 5], approximately as for ideal solutions. It has been suggested that the observed anomalous behaviour is due to the dimerization of the CBnAB molecules in the 10XPCHB matrix. Here experimental proof is provided supporting this hypothesis and further examples are given of binary mixtures of similar behaviour composed of compounds (I) and compounds (II) with other terminal groups such as NCS (10TPCHB) or COCH$_3$(10APCHB).

2. Experimental

2.1. *Materials and methods*

Compounds (I) and (II) were synthesized in Professor Dabrowski's laboratory according to the method described elsewhere [6, 7]. The following series of binary mixtures were studied (i) CB7AB–10XPCHB where X = F (10FPCHB)^x, X = NCS (10TPCHB), x = COCH₃ (The binary mixture CB7AB-10FPCHB is described in [1].) (II) CBnAB–10APCHB where n = 5, 6, 7, 8, (10APCHB). The binary mixtures were prepared by weighing out the pure compounds in suitable proportions. The phase diagrams of all the binary mixtures studied were obtained by determining the transition temperatures by the thermomicroscopic method (heating stage and VEB Analytik, Dresden, polarization microscope), and for series (i) also by the calorimetric method using a Perkin-ELMER DSC 2 calorimeter. The mixtures were prepared, and thermomicroscopic and calorimetric measurements carried out as in [1].

The smectic layer spacings of the pure compounds and of the CB7AB–10FPCHB

(*a*)
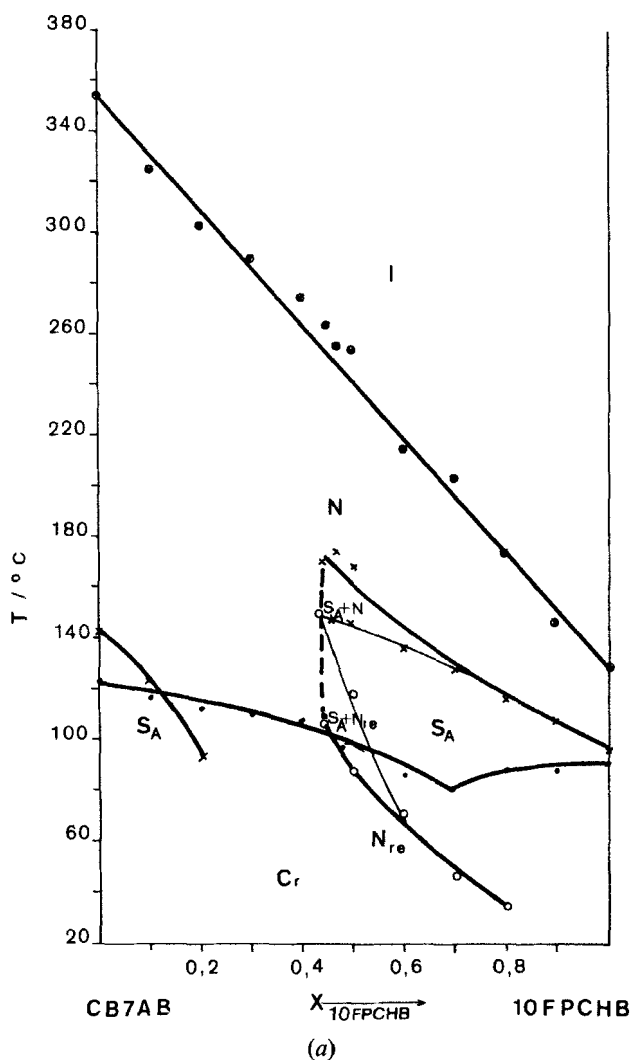
Figure 1.

and CB7AB–10APCHB binary mixtures were determined in Professor Przedmojski's laboratory using a Guinier camera according to his free standing sample method [8].

2.2. *Results*

2.2.1. *The phase diagrams*

In figure 1 the phase diagrams for the binary mixtures CB7AB–10FPCHB from [1], and CB7AB–10TPCHB and CB7AB–10APCHB are compared. The character of the phase diagrams is similar though not identical for all the binary systems studied with all three kinds of terminal groups: $X =$ F, NCS, and $COCH_3$. Above the concentration $x_{10XPCHB} = 0.15$ to 0.20 the smectic phase disappears completely and so only the nematic phase is observed. The width of the nematic gap depends on the nature of the substituent X, and is smallest for $COCH_3$ (see figure 1 (*c*)) and increases successively for NCS (see figure 1 (*b*)) and F (see figure 1 (*a*)). A further increase in the

(*b*)

Figure 1.

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(c)
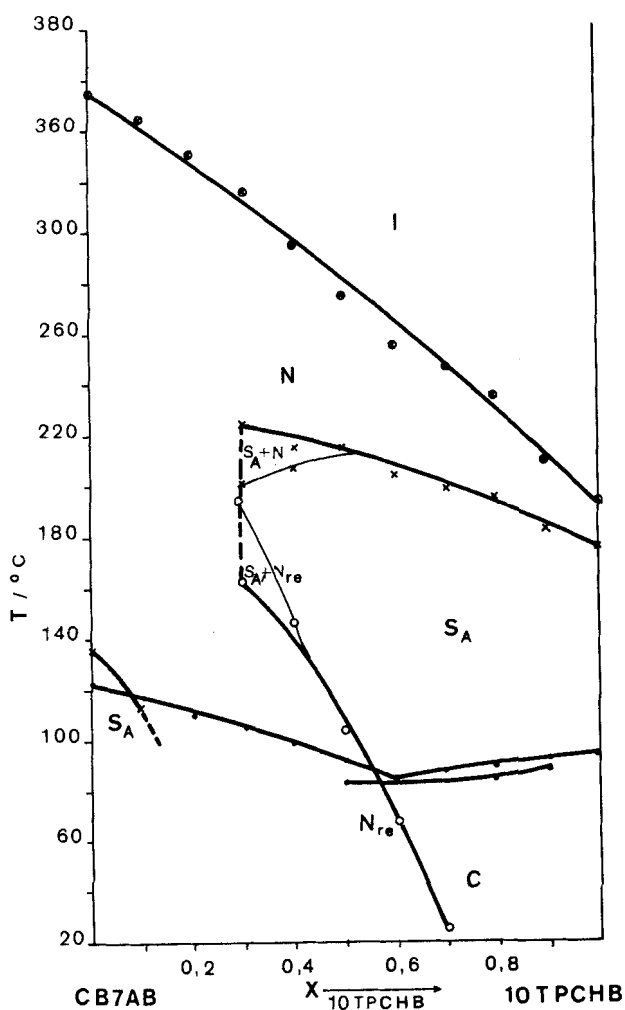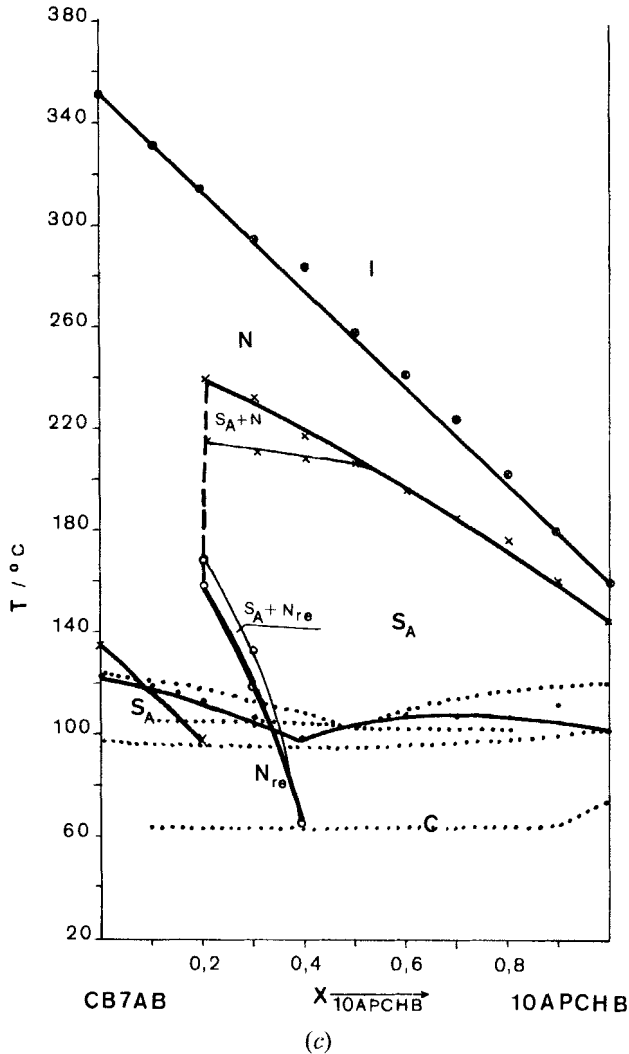
Figure 1.   Phase diagrams for the binary mixtures of the series CB7AB–10XPCHB (a) X = F, (b) X = NCS, (c) X = COCH$_3$. The dotted line in (c) represent the phase transition in the solid state obtained by the calorimetric method.

concentration of 10XPCHB causes a stepwise change of the phase diagrams. At concentrations of 0·2, 0·3 and 0·45 mole fractions of 10APCHB, 10TPCHB and 10FPCHB, respectively, the smectic phase reappears and is observed in an extended temperature range. This extension also depends on the terminal substituent, being greatest for COCH$_3$ and decreases successively for NCS and F. At lower temperatures a reentrant nematic phase appears. This phase is enantiotropic for the CB7AB–10APCHB and CB7AB–10TPCHB mixtures for a wide range of concentrations. Differences are observed in the shape of the phase boundaries limiting the region of existence of the smectic phase between the nematic phases. For the CB7AB–10FPCHB mixture the S$_A$–N and N$_{re}$–S$_A$ phase boundaries are concave, while for the remaining two mixtures they are convex.

In all the mixtures studied, near the nematic gap wide diphase regions (nematic and smectic) are observed (see figures 1 (a), (b), (c)).

The nematic–isotropic transition temperatures for all the systems studied are in agreement with those calculated from the Schroder–van Laar equation [9] which indicates that there are no deviations in the nematic phase from the properties of ideal solutions. The liquidus curves show that the systems exhibit simple eutectics. Both branches of the liquidus are in accordance with the Schröder–van Laar equation except for the region close to the eutectic point.

The transition temperatures determined by the thermomicroscopic method are in agreement with the results of calorimetric measurements. Only the N_{re}–S_A phase transition is invisible on the D.S.C. plots since it is a second order transition. The transitions in the solid phase (see, the dotted line in the plot in figure 1 (c)) were determined solely by the calorimetric method since they are invisible under the microscope.

In figure 2 (a), the phase diagrams of the mixture CB5AB–10APCHB is shown and parts of those for the binary mixtures CB6AB–10APCHB and CB7AB–10APCHB along the boundaries of the S_A–N transition. It is seen that as the length of the terminal aliphatic chain decreases in CBnAB compounds from seven to five carbon atoms the destabilization of the CBnAB smectic phase decreases and the enhancement of the smectic phase on the side of 10APCHB decreases. In addition no reentrant nematic phase is observed for both compounds with $n = 5$ and $n = 6$, and the nematic gap reveals a sudden discontinuity on the side of 10APCHB.

The phase diagram for the CB8AB–10APCHB mixture (see figure 2 (b)) has a different character. Here we observe a complete miscibility of the smectic A_d phase of CB8AB with the smectic A_1 phase of 10APCHB. Similar effects of the length of the aliphatic chain were also observed for the CB8AB-10FPCHB and CB8AB-10IPCHB mixtures [1].

2.2.2. *X-ray studies*

The X-ray spacings of the smectogens CBnAB and 10XPCHB were studied earlier [10, 11]. In the present work, in order to preserve the same conditions of determination in the pure compounds and their mixtures, the spacings were measured again by a new method [8]. The results for the pure compounds and selected compositions of the binary mixtures: CB7AB–10APCHB and CB7AB–10FPCHB, are listed in tables 1, 2 and 3.

Table 1. Smectic layer spacings of the pure components.

Symbol for compound	Length of molecule/nm	Smectic layer spacing/nm		Temperature of measurement/°C	d/l
		From [10, 11]	this work		
CB5AB	2·97	2·75		150	0·92
CB6AB	3·06	2·85		150	0·93
CB7AB	3·21	3·00	3·08	130	0·96
			3·06	140	0·95
CB8AB	3·25	4·05		170	1·28
10FPCHB	2·9	3·0	3·34	95	1·15
10TPCHB	3·3	3·4	3·39	100	1·03
			3·43	120	1·04
			3·44	130	1·04
			3·50	150	1·06
10APCHB	3·1	3·1	3·44	107	1·11
			3·51	115	1·13
			3·54	120	1·14
			3·56	130	1·15

Table 2. (a) Measured smectic layer spacings for CB7AB–10APCHB mixtures.

Mole fraction of 10APCHB $x_{10APCHB}$	Temperature of measurement/°C	Smectic layer spacing d/nm
0·3	115	3·80
	125	3·79
	130	3·77
	155	3·77
	160	3·77
	170	3·77
0·8	130	3·65
	150	3·84
	160	3·98
	170	3·97

Table 2. (b) Calculated smectic layer spacings for the CB7AP–10APCHB mixture.

Mole fraction $x_{10APCHB}$	d/nm calculated according to the first method	d/nm calculated according to the second method
0·3	3·22	3·75
0·8	3·45	3·60

Table 3. (a) Measured smectic layer spacings for the CB7AB–10FPCHB mixtures.

Mole fraction $x_{10APCHB}$	Temperature of measurement/°C	Smectic layer spacing d/nm
0·6	110	3·67
	135	3·76
0·8	110	3·58

Table 3. (b) Calculated smectic layer spacings for the CB7AB–10FPCHB mixtures.

Mole fraction $x_{10FPCHB}$	d/nm calculated according to the first method	d/nm calculated according to the second method
0·6	3·22	3·60
0·8	3·36	3·51

For compound CB7AB we obtained good agreement with results of [11], and so we did not repeat the measurements for the remaining compounds of the CBnAB series. The compounds of this series are smectic A_1 for $n \leqslant 7$ ($d < 1$) and smectic A_d for $n = 8$ ($d/l = 1·23$).

For compounds 10FPCHB and 10APCHB we obtained somewhat greater layer spacings than those found in [10] and so we repeated the measurements for all the compounds studied of this series. The smectic layer spacing measured with the Guinier camera is somewhat greater than the length of the molecule and increases with temperature. The greatest d/l ratio was obtained at temperatures close to the S_A–N transition, e.g. for 10FPCHB $d/l = 1·15$ at a temperature lower than the $T_{S_A N}$ by only 2°C. The d/l ratios for all the compounds studied here lie in the range 1–1·15 and are significantly lower than those determined in [10] for smectics A_d of the same series of compounds with cyano and nitro terminal groups; this proves that the smectics examined may not be treated as smectic A_d.

The smectic layer spacings for selected compositions of the mixture CB7AB–10APCHB are given in table 2 (*a*), and those for the CB7AB–10FPCHB mixture in table 3 (*a*). The layer spacings of the mixtures are greater than those of the pure component and increase with the concentration of CB7AB. In addition a significant increase of the smectic layer spacing as a function of temperature is observed in the mixtures, especially in those having a composition far from the nematic gap region.

Tables 2 (*b*) and 3 (*b*) give the smectic layer spacings in the mixtures calculated by assuming that the smectic layer spacings are additive

$$d_m = x_{CB7AB} d_{CB7AB} + x_{10CPCHB} d_{10XPCHB}, \tag{1}$$

where d_m is the smectic layer spacing for the mixture, d_{CB7AB} and $d_{10XPCHB}$ are the smectic layer spacings for the pure components, and x_{CB7AB} and $x_{10XPCHB}$ are the mole fractions of the components. The smectic layer spacings in the mixtures were calculated in two ways. First this spacing was calculated by assuming that component CB7AB yields an A_1 structure, thus the spacing d_{CB7AB} was assumed to be equal to that measured for the pure component (see table 1). Secondly the layer spacing for the mixture was calculated by assuming that compound CB7AB yields a partly dimerized structure, so the smectic layer spacing of CB7AB was assumed to be equal to the hypothetical spacing for S_{A_d} of this compound calculated by subtracting from the smectic layer spacing S_{A_d} of compound CB8AB (see table 1) the lengths of two methylene groups.

The measured smectic layer spacings for both mixtures are much higher than the values calculated according to the first method but they are in agreement with the values calculated according to the second. This supports fully the hypothesis of the partial dimerization of CB7AB in the 10APCHB matrix.

The X-ray pattern of the CB7AB–10APCHB mixture with a mole fraction of $x_{10APCHB} = 0.3$ taken at 115°C shows reflections typical of a smectic phase, though studies of the optical texture carried out at the same temperature reveal the presence of the reentrant nematic phase. The presence of the reentrant nematic phase in this mixture at 115°C is supported by dielectric and conductivity studies [12]. The character of changes of conductivity in the mixture perpendicular and parallel to the director are analogous to those found for the reentrant nematic phase of pure CB8AB.

3. Discussion

The X-ray studies show that smectic A phases from both series of compounds CBnAB and 10XPCHB may be classified as smectic A_1, but they are not the same smectic A_1. This is confirmed by dielectric and conductivity studies [12]. The differences in conductivity perpendicular and parallel to the director are much smaller for the 10XPCHB than for the CBnAB.

From the work of Gramsbergen and de Jeu [13] concerned with thin layers of compounds it follows that two types of smectic A_1 phases may exist. In smectics with a strongly polar cyano group the molecules are arranged on the surface so that a layer with oriented dipoles is formed; this layer in turn orients the successive layer. In this way a structure similar to that of smectic A_2 is produced. The second type of smectic A_1, referred to by Gramsbergen and de Jeu as classical smectic A_1, exhibits a structure in which the dipoles of the molecules are arranged randomly. In [13] it has been shown that the compound 7TPCHB is indeed a classical smectic A_1. It may also be expected that other compounds from the *n*TPCHB homologous series, i.e. 10TPCHB and other
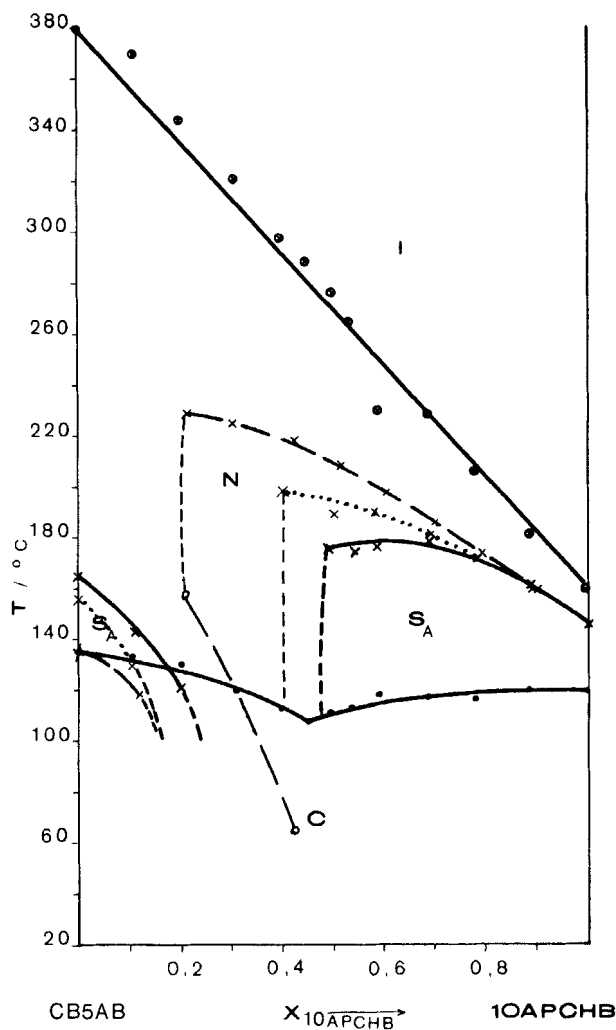
(a)

Figure 2.

compounds from the 10XPCHB series studied in the present work, are smectics with a disordered arrangement of the dipoles. Such compounds may be treated as smectics with a nematic ordering in the layer, their centres of gravity being slightly shifted. As the temperature increases the ordering of the centres of gravity decreases and the smectic layer becomes more and more extended. This may explain the observed increases of the smectic layer spacing as a function of temperature (see table 1).

The second reason for the increase of the smectic layer spacing with temperature may be the fact that the structure of the smectic A_1 phase of compounds $10X$PCHB is closer to the S_{A_d} structure and the normal association equilibrium takes place. The structure of the smectic A_1 phase of compounds $10X$PCHB which is closer to the S_{A_d} phase provide complete miscibility of these compounds with smectics A_d (the CB8AB–10APCHB mixture in figure 2 (b) as well as the CB8AB–10XPCHB mixtures described in [1]).
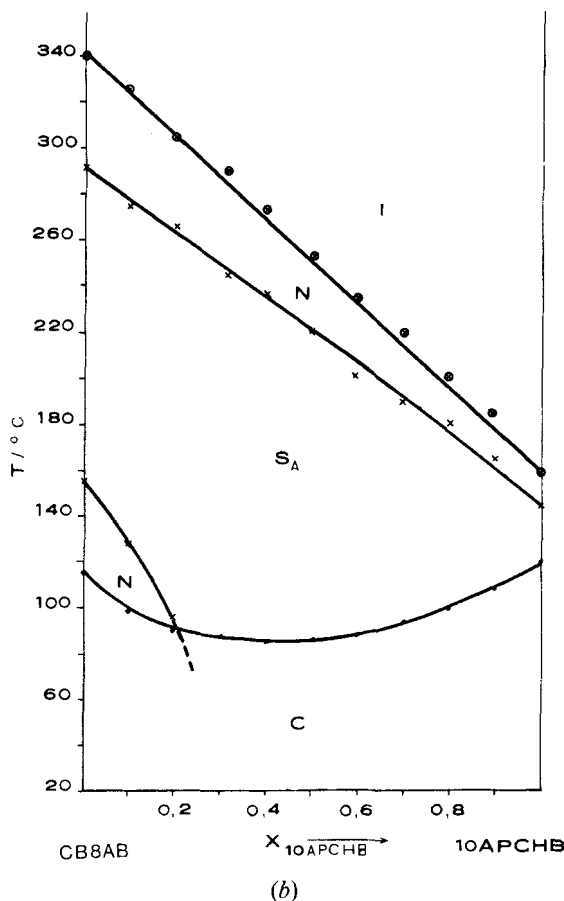
(*b*)

Figure 2. Phase diagrams for the binary mixtures of the series CB7AB–10APCHB (*a*) $n = 5$ (*b*) $n = 8$. The dotted line in (*a*) represents a fragment of the phase diagram for the CB6AB–10APCHB and the dashed line for the CB7AB–10APCHB mixtures.

In contrast, smectic A_1 of compounds CBnAB with $n \leqslant 7$ do not mix with smectic A_d of the same homologous series ($n = 8$) as shown in [11]. Smectic A_1 of compounds CBnAB with a strongly polar cyano group differ in structure from smectic A_d; perhaps they have oriented dipoles in the small region which prevents the increase of the layer spacing with temperature and the miscibility with smectic A_d phases.

The solution of compound CBnAB in the matrix of compound 10XPCHB of much lower polarity makes possible the rearrangement of the molecular structure of CBnAB to yield dimers. The rearrangement of the S_{A_1} layer to the S_{A_d} layer takes place when the dielectric constant of the medium assumes a sufficiently low value.

The dimerization of the CBnAB compounds in the 10XPCHB matrix explains all of the anomalous behaviour of the CBnAB–10XPCHB mixtures observed in the phase diagrams, i.e. the destabilization of the smectic phase of component CBnAB, the nematic gap, as well as the extension of the smectic region on the side of the 10XPCHB component which was discussed in [1].

The existence of the reentrant nematic phase may also be explained by the dimerization of CBnAB in the 10XPCHB matrix. According to [14, 15 and 16] the reentrant nematic phase always appears at temperatures below the existence of the A_d

smectic phase. The change of the monomer to dimer ratio at this lower temperature results in a lesser packing of the molecules in the layer and is the cause of the formation of the reentrant nematic phase [16]. Luckhurst and Timimi [17] claim that the reentrant nematic phase appears when a sufficiently large change of parameter α as a function of reduced temperature takes place. This parameter, defined by McMillan [18], depends on the smectic layer spacing who assumed that it is independent of temperature. Luckhurst and Timimi claim [17] that α may depend on temperature. The studies of smectic layer spacings in CB7AB–10APCHB and CB7AB–10PCHB mixtures have shown that the spacing may change with temperature quite significantly. In the light of Luckhurst–Timimi theory the latter may be due to the appearance of the reentrant nematic phase. Also in [15] it was observed that the smectic layer spacing varies as a function of temperature when the reentrant nematic phase appears.

The fact that the X-ray pattern of the reentrant nematic phase is analogous to that of the smectic phase may be due to the cybotactic groups [19, 20] which exist in this reentrant nematic phase.

In the light of these considerations it can be concluded that all the anomalies observed in the phase diagrams of CBnAB–10XPCHB mixtures are due to the dimerization of CBnAB compounds in the matrix of 10XPCHB compounds of lower polarity.

We shall present the results of studies on the effect of polarity of the medium on the phase diagrams in a subsequent paper.

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