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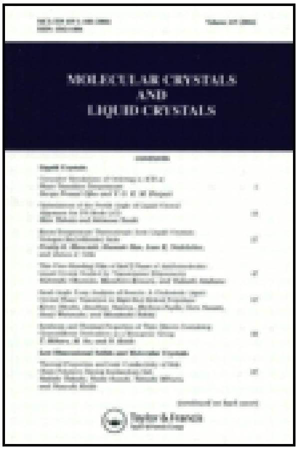

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Nematic Phases Created in Binary Mixtures of Smectics A

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Nematic Phases Created in Binary Mixtures of Smectics A†

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It is shown that the forming of nematic mixtures composed uniquely of compounds with the smectic phase A is possible. The nematic phase is created as a result of the weakening of intermolecular attraction forces in the disturbed smectic layers. Many examples are given of binary mixtures in which induction of the nematic phase is observed or an enhancement of the nematic phase at the cost of the smectic phase takes place. The effect of the molecular structure and of the properties of the smectic-phase A on its destabilization in a mixture and the creation of the nematic gap between the smectic A regions are discussed. The most characteristic features of the phase diagrams related to the S→I and S→N phase transitions and the accompanying changes of enthalpy of these phase transitions, of density and viscosity are shown in detail by way of example of binary mixtures composed of 5-n-alkyl-2-(4′-isothiocyanatophenyl)-1,3-dioxanes (smectic A_1) and 8OCB, or 12OCB or 12CB (smectic A_d).

Keywords: liquid crystals, polar smectic mixtures, induced nematic phases, dioxanes, biphenyls, esters

I. INTRODUCTION

The induction of the smectic phase usually of A_1 type is observed in binary or multicomponent mixtures composed of nematic or only potentially nematic compounds.[1–5] The induction of the smectic phase is often accompanied by an increase of the thermal stability of the nematic phase manifested by the occurrence of a maximum of the clearing point $T_{N\to I}$ or even complete decay of the nematic phase in the central part of the concentration range. A typical diagram for a binary mixture in which the smectic phase is induced is shown in Figure 1.

The strongest induction of the smectic phase is observed for mol-

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†Presented at the Eleventh International Liquid Crystal Conference, Berkeley, June 30–July 4, 1986.

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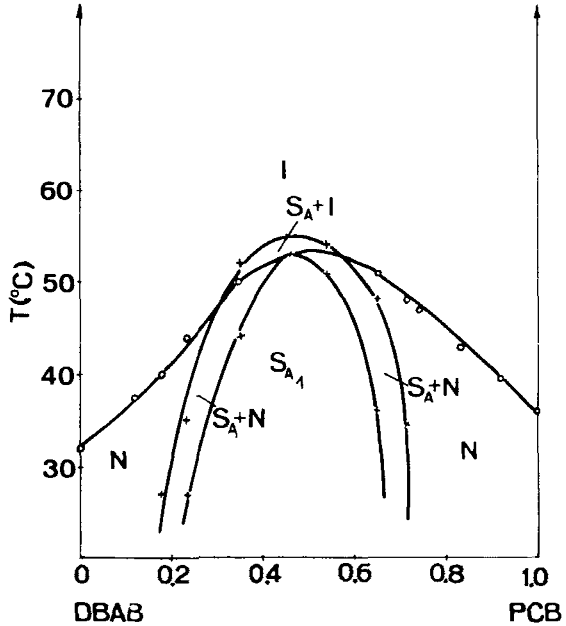

FIGURE 1 Phase diagram with the induced smectic A phase for the binary mixture of nematic compounds: PCB (4-pentyl-4'-cyanobiphenyl) and DBAB (4,4'-dibutylazoxybenzene).

ecules of similar length. This property of such systems is usually ascribed to intermolecular interactions of electron-donor-acceptor type,[6–8] though other intermolecular reactions and steric factors play a role that should not be neglected.

The opposite behavior is also possible and we have been studying it recently in detail. It consists in that in a mixture composed of two smectic compounds a nematic phase is created (Figure 2a) or even the smectic phases of both components are completely separated from each other by the nematic gap (Figure 2b).

The creation of the nematic phase in a narrow temperature interval was already sporadically observed earlier by several authors in mixtures of smectics A and C[9–12] or E.[13] The authors of these works refer to this nematic phase as "stabilized intermediate nematic phase." Its creation is ascribed to hypothetical phases of the pure compounds which lie in the metastable or unstable region. The conditions that a binary system should meet to allow the revealing of nematic properties in smectic compounds have not been determined so far.

In the present work we discuss the effects of various factors related to the structure of smectic layers and the chemical structure of the

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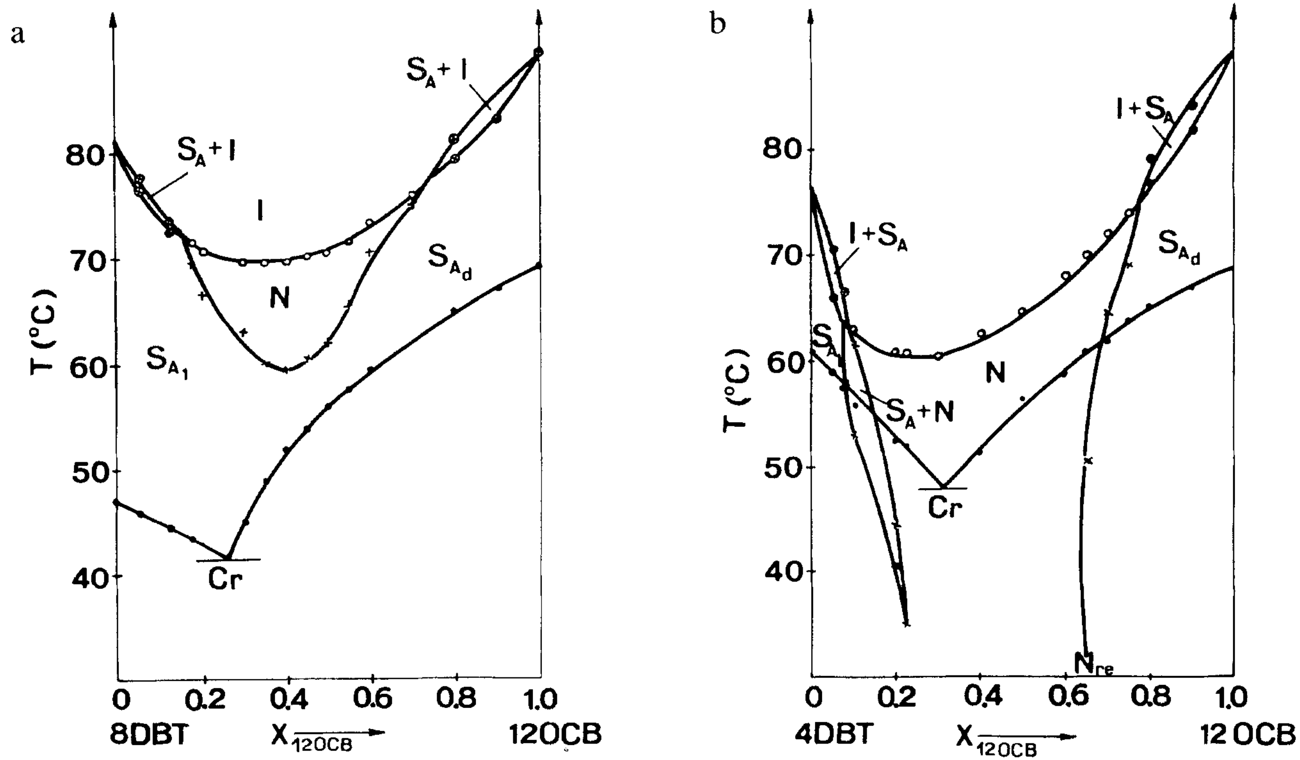

FIGURE 2 Phase diagrams of binary mixtures with lowered thermal stability of the smectic phase: (a) 8DBT-12OCB [5-n-octyl-2-(4′-isothiocyanatophenyl)-1,3-dioxane and 4-dodecyloxy-4′-cyanobiphenyl], and (b) 4DBT-12OCB; in (a) we see the creation of the nematic phase in a limited temperature interval, in (b) we have a system with the nematic gap.

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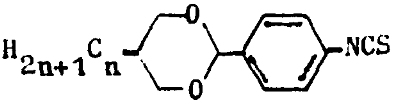
molecules on the ability of the smectic system A to convert into a nematic system. This is a recapitulation of the results of mostly our own works, some of which have already been published[14-17] but many have not.

II. EFFECT OF THE SMECTIC LAYER SPACING RATIO ON THE CHARACTER OF PHASE DIAGRAMS IN POLAR COMPOUNDS

The investigations conducted by us have shown that a strong correlation exists between the stability of the smectic phase in a mixture of compounds and the spacing of the smectic layers as measured for the pure components. The smectic layer spacing ratio of the components of the mixture is a factor decisive for the shape of the diagrams of binary mixtures composed of polar compounds.

2.1. Mixtures of A_1 smectics

In Ref. (15) we studied mixtures composed of compounds belonging to the same homologous series 5-alkyl-2-(4'-isothiocyanatophenyl)-1,3-dioxanes (compounds n-DBT, formula 1).

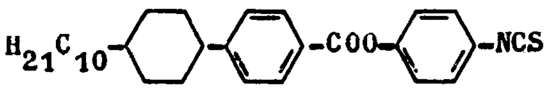


1

These compounds reveal only the A_1 smectic phase of spacing d slightly smaller than the length of their molecules $l > d \geqslant 0.9\, l$. The clearing points (phase transition $S_{A_1} \rightarrow I$) of the mixtures made up of two successive members of the homologous series (e.g. 4DBT and 5DBT when the smectic layer spacing ratio $r = d_{5DBT}/d_{4DBT} = 1.08$) are close to the theoretical values found from the CSL equation. However, since the $T_{N \rightarrow I}$ temperatures reveal a weak minimum in the central part of the system, a better agreement of their values with theoretical data is obtained when the latter are calculated from the theory of regular solutions.

For mixtures composed of more distant members of the n-DBT homologous series, when the difference of the smectic layer spacing of the components increases, the stability of the smectic phase in the mixture systematically decreases. In the case of the 7DBT-4DBT pair with the value $r = 1.23$ the nematic phase is also created in a narrow range of temperatures and concentrations. The temperature range in which the nematic phase is observed widens systematically with the increase of r; for instance, in the case of the 12DBT-4DBT mixture ($r = 1.64$) the nematic phase exists in the range of 15°C.

In view of the lack of homologs with a longer alkyl chain it was not possible to determine further diagrams of this series with greater values of r. However, by using the mixture 3DBT-2DBT as one component and 12DBT as the other one we obtained a mixture whose mean value of the smectic layer spacing ratio was $r = 1.78$. In this mixture the nematic phase was observed in an interval of 37°C. It could be expected that a further increase of r should lead to a complete separation of the smectic regions by the nematic gap. Such behavior of the system was observed in the mixture composed of 4DBT and 10TPCHB (formula 2) wherein the smectic layer spacing ratio was $r = 1.87$.



2

Cr 95 S_{A_1} 187 N 201 I **10TPCHB**

2.2. Mixtures of smectics A_1 and A_d

The spacings of smectic layers of smectics A_d are greater than the lengths of their molecules, usually $d/l \geqslant 1.3$.[18] Compounds with a large spacing of the smectic layers (high values of d) are easily available into smectics A_d. They may be used with smectics A_1 for obtaining mixtures of a ratio r greater than it would be possible in the case of mixtures composed solely of smectic compounds A_1 or A_d.

In Figures 3a-3h fragments of phase diagrams are presented relating to the phase boundaries $S_A \rightarrow I$, $N \rightarrow I$ and $S_A \rightarrow N$ of binary mixtures 12CB-n-DBT for n varying from 4 to 12 when $r = d_{12CB}/d_{n\text{-DBT}}$ varies from 1.34 to 2.19.

The mixture of compounds 12CB-12DBT, for which the ratio of molecule lengths is $l_{12CB}/l_{12DBT} = 0.92$ and the smectic layer spacing ratio $r = 1.34$, reveals a shallow minimum on the $S \rightarrow I$ phase transition curve which deepens for mixtures with greater r. In the case of 12CB-9DBT mixtures with $r = 1.57$ we observe the creation of the nematic phase in a narrow temperature interval in the concentration range of 0.2 to 0.6 X_{12CB} mole fraction. The complete separation of the smectic A_1 region from the smectic A_d region by the nematic gap is observed for the 12CB-6DBT ($r = 1.83$) mixture. Its width at a temperature

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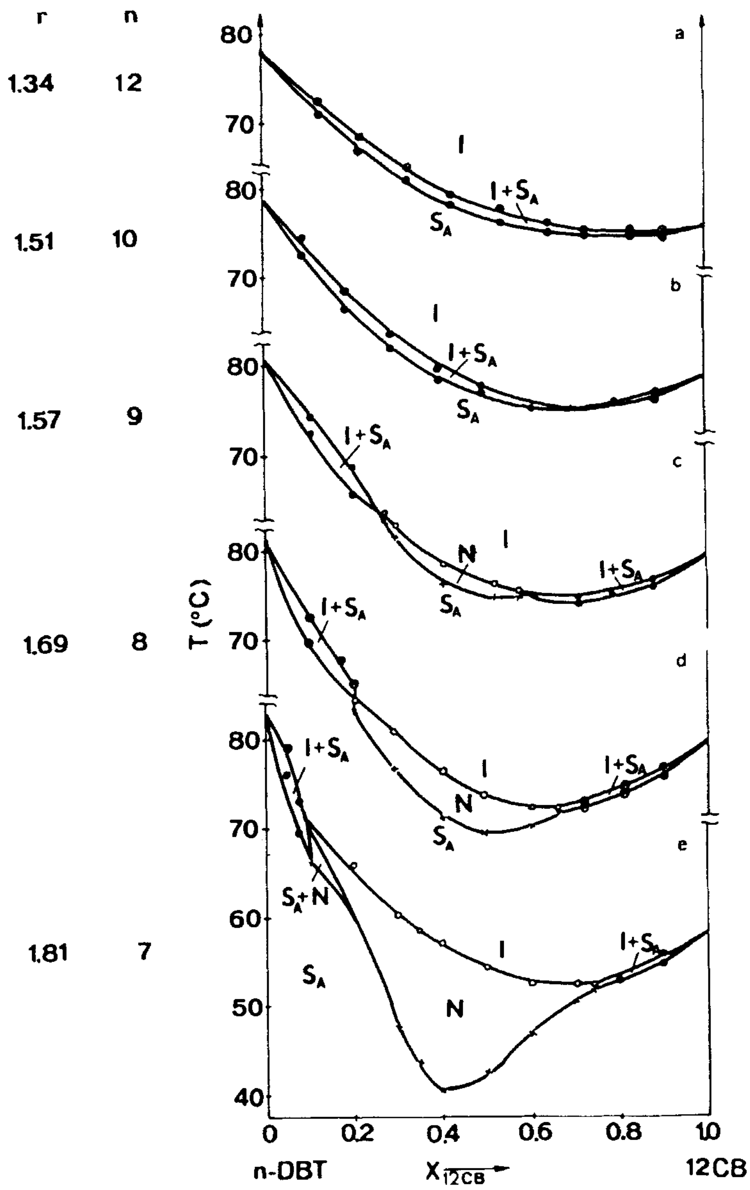

FIGURE 3 Effect of the smectic layer spacing ratio (r) on the phase transition in binary mixtures composed of one member of the DBT homologous series (formula 1) and 12CB (4-dodecyl-4′-cyanobiphenyl); the transitions $S_A \rightarrow I$, $N \rightarrow I$ and $S_A \rightarrow N$ are marked by circles with crosses, empty circles and crosses, respectively.

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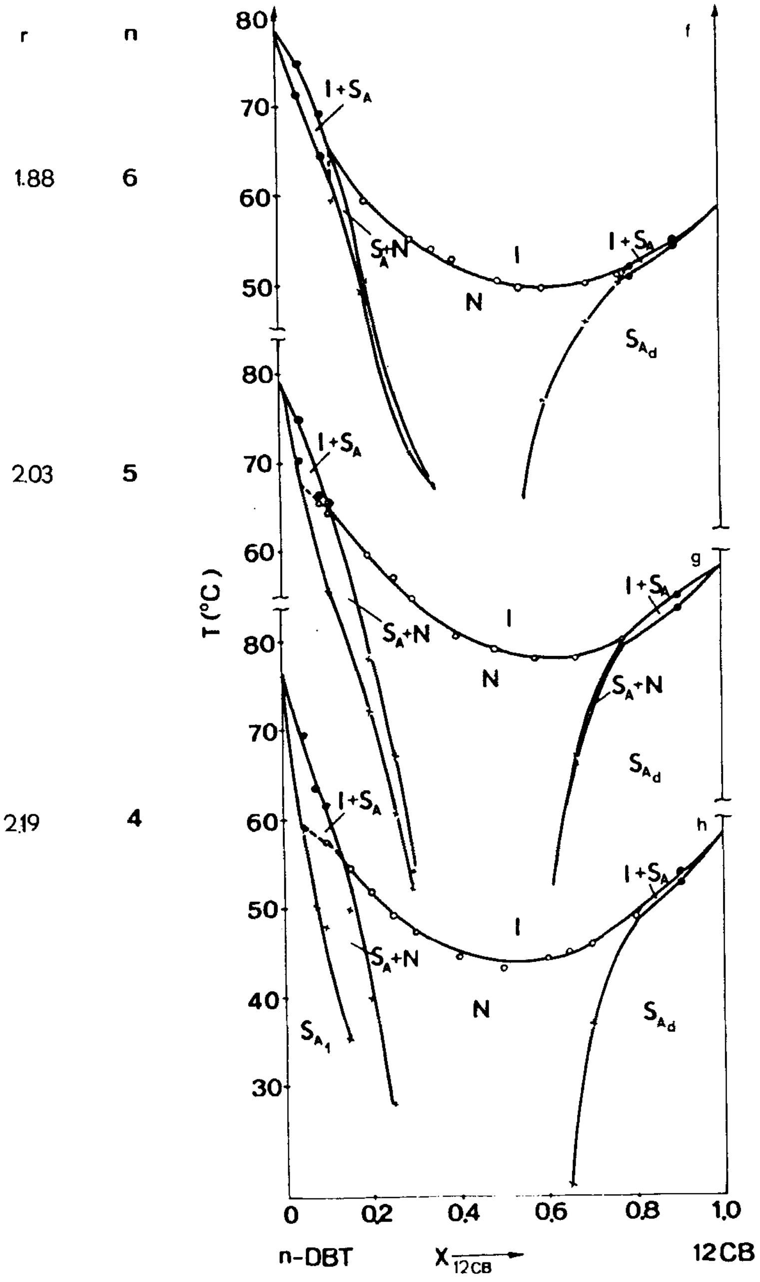

FIGURE 3 (*continued*)

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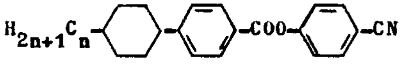
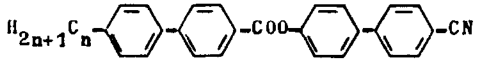
by 20°C lower than the lowest N→I transition temperature of this system is 0.28 mole fraction and increases moderately for the successive mixtures with increasing r and reaches the value of 0.4 for the 12CB-4DBT ($r = 2.19$) mixture. As soon as the nematic gap appears between the smectic regions characteristic changes are observed in the system. The temperature interval in which two phases: the smectic and the isotropic ones or the smectic and nematic ones coexist in equilibrium enhances even to several degrees (see Figures 3f, g, h). Such a behavior was observed by us for mixtures 80CB-n-DBT[16] and 120CB-n-DBT. This is probably a common feature of all smectic mixtures composed of compounds with differing smectic layer spacings and densities. In the mixtures of smectics 120CB-n-DBT the nematic phase is created at $r = 1.53$ (120CB-10DBT) and the nematic gap at $r = 1.86$ (120CB-7DBT).

The detection of the nematic gap in mixtures composed of compounds with smectic phase A_1 and A_d selected so that the lengths of their molecules are almost identical allows us to conclude that the smectic layer spacing difference is decisive for the creation of the nematic phase in smectic mixtures. We observed the nematic gap in the mixture of compounds 80CB and 7DBT [$l_{8OCB}/l_{7DBT} = 1.06$; $d_{8OCB}/d_{7DBT} = 1.46$, Ref. 16] and of compounds 9CPCHB and 5CBB [$l_{9CPCHB}/l_{5CBB} = 0.99$; $d_{9CPCHB}/d_{5CBB} = 1.46$, Ref. 19].



3

a	n=9	Cr 101 S_{A_d} 165 N 198 I	9CPCHB
b	n=10	Cr 94 S_{A_d} 167 N 183 I	10CPCHB



4

a	n=5	Cr 139 S_{A_1} 166.5 N 380 I	5CBB
b	n=6	Cr 140.5 S_{A_1} 158 N 360 I	6CBB
c	n=7	Cr 127 S_{A_1} 141 N 352 I	7CBB

The lengths of molecules in these pair are almost identical. The clearing temperatures of the N→I transition for the last pair of compounds lie approximately on a straight line (good agreement with the CSL equation). Thus the depature from the laws of ideal solutions takes place only in the smectic phase.

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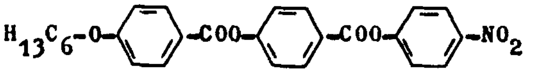
2.3. Mixtures of smectics A_d–A_d

An example of a mixture composed of two compounds with the A_d smectic phases in which a complete separation of the smectic phases by the nematic gap is observed has been described by Ratna *et al.*[20] These compounds are:

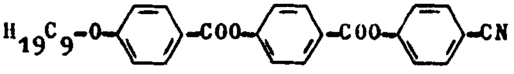


5

Cr S_{A_d} 151.5 N 238 I

6ONPBB

l=2.90 nm , d=3.02 nm, d/l=1.04 , ref. 20



6

Cr 120.4 N_{re} 116.4 S_{A_d} 194.8 N 226 I

9OCPBB

l=3.29 nm , d=3.79 nm , d/l=1.15 , ref. 21

Both compounds reveal the N_{re} phase that confirms that their layers are composed of molecules at least partially dimerized. The temperature interval in which the S_{A_d} phase is observed in the pure compounds is comparatively narrow. The S_{A_d} phase is unstable both at higher and lower temperatures (this relates especially to compound 5). This may be the reason why the nematic phase appears between the two smectic A_d regions at low values of $r = d_{9OCPBB}/d_{6ONPBB} = 1.25$.

III. THE EFFECTS OF THE STRUCTURE OF THE MOLECULES ON THE CREATION OF THE NEMATIC GAP BETWEEN THE SMECTIC REGIONS IN POLAR COMPOUNDS

The creation of the nematic phase and the presence of the nematic gap between the smectic regions in polar compounds are not observed after a given constant value of the ratio *r* is exceeded, this value varies, however, with the properties of the smectic phases and the chemical and geometrical structure of the components of the mixture. In mixtures whose components reveal only the smectic phase the

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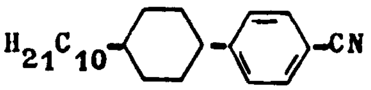
nematic gap was observed so far for fairly high values of $r (r > 1.8)$. In mixtures composed of compounds both of which or at least one reveal the smectic and nematic phases the nematic gap is observed for smaller values of $r (r \geqslant 1.25)$. Systems composed of 9CPCHB and 7CBB (formula 3a and 4c) can serve as an example of mixtures with the nematic gap that have the lowest ratio r so far observed in the $A_1 + A_d$ series ($d_{9CPCHB}/d_{7CBB} = 1.34$).

The situation is similar for mixtures of 10PCH and 8TPB ($d_{10PCH}/d_{8TPB} = 1.36$).



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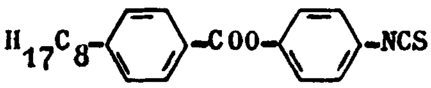
Cr 49 N 54.5 I / S_{A_d} 31.5 / **10PCH**



8

Cr 49 S_{A_1} 56.5 I **8TPB**

The reduced temperature $T_{S \to N}/T_{N \to I}$ may be considered as the criterion of the smectic phase stability. Its value depends on the length of the alkyl chain and on the character of the polar groups in the molecule. Smectics A_d are created only by compounds with terminal groups CN, NO_2 or CHO. Compounds with other terminal polar groups yield only smectics A_1.[22] The ratio $T_{S \to N}/T_{N \to I}$ in smectics A_d with molecules of similar structure decreases in the order

$$NO_2 > CN > CHO$$

This is why we observe in mixtures composed of compounds with the terminal group NO_2 a nematic gap between the two smectic regions that is narrower than in analogous compounds with the CN terminal group (see Figure 4).

Similar conclusions for smectics A_1 can be drawn from the work by Ziemnicka *et al.*[24] The quoted authors have observed the creation of the nematic phase in mixtures of 2-fluorenylmethylidene-4′-n-dodecylaniline (FC12A, smectic A_d) and 4-n-butoxybenzylidene-4′-n-halogenoanilines (40X, smectic A_1). They have found that the tem-

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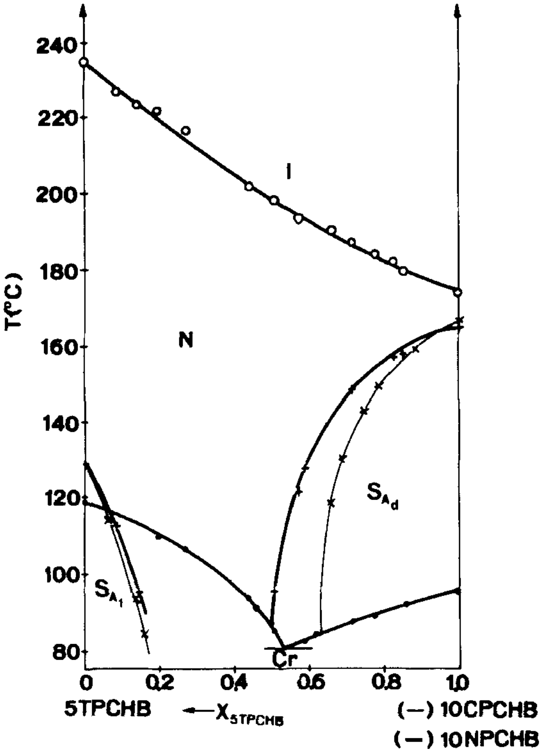

FIGURE 4 Effect of the properties of the smectic A_d phase on the width of the nematic gap between the smectic A_1 and A_d phases. The bold line presents the phase diagram of the mixture of 5TPCHB (formula 2, alkyl = pentyl) and 10NPCHB [analog of compound 3b with a nitro group, viz. 4″-nitrophenyl 4-(trans-4′-n-decylcyclohexyl) benzoate]. The thin line presents a fragment of the phase diagram of the binary mixture of 5TPCHB and 10CPCHB (formula 3b). The value of $T_{SA \to N}/T_{N \to I}$ is equal to 0.965 for 10CPCHB and 0.98 for 10NCPCHB; $d_{10CPCHB}/d_{5TPCHB} = 1.54$ and $d_{10NPCHB}/d_{5TPCHB} = 1.46$.

perature interval in which the nematic phase is created decreases in the order

$$\mathrm{Cl} > \mathrm{Br} > \mathrm{I}$$

The stability of the smectic phase in 40X varies in the opposite order.

The nematic gap between the A_1 and A_d smectic regions is usually shifted in the central part of the concentration range asymmetrically, i.e. towards the component of the mixture that reveals a lower sta-

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bility of the smectic phase (e.g. lower $T_{S_{A\to N}}/T_{N\to I}$ ratio). The lower value of the $T_{S_{A\to N}}/T_{clear.}$ ratio the wider is the region in which the nematic phase is observed (Figure 5).

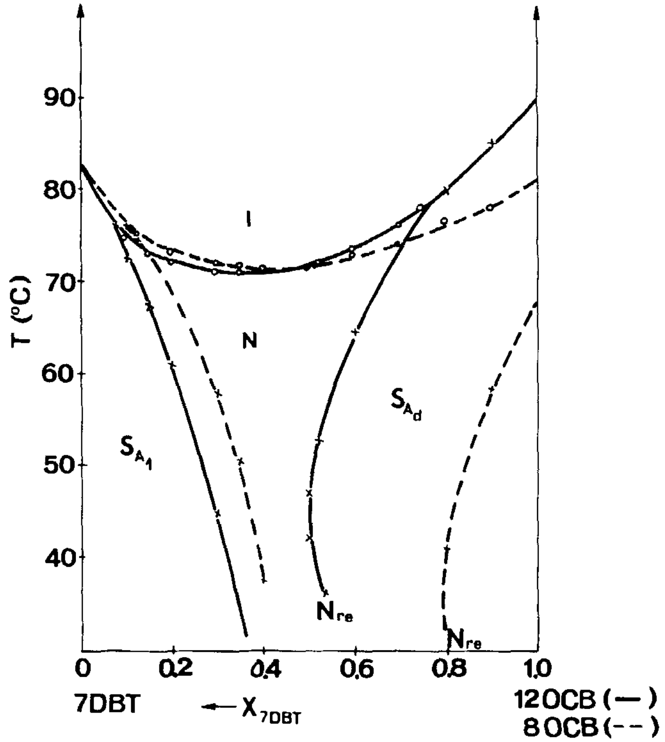

FIGURE 5 Effect of the properties of the smectic A_d phase on the width and position of the nematic gap. The solid line presents a fragment of the phase diagram for the 7DBT-12OCB mixture. The dashed line presents a fragment of the phase diagram for the 7DBT-8OCB mixture.

In Figure 5 fragments of phase diagrams are compared of binary systems: 12OCB-7DBT and 8OCB-7DBT. Compound 7DBT is the first in the *n*-DBT series for which in mixtures with 12OCB or 8OCB a complete separation of the smectic regions is observed. The lower stability of the 8OCB smectic phase as compared with 12OCB (the values of $T_{S\to N}/T_{N\to I}$ are 0.96 and 1, respectively) is manifested by the lower value of *r* necessary for the separation of the smectic regions to occur (*r* is equal to 1.46 and 1.83, respectively). The width of the nematic gap (in concentration units—mole fraction) as measured at

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a temperature by 20°C lower than the lowest clearing temperature of the system is 0.53 and 0.25, respectively.

Compound 7DBT causes a much stronger destabilization of the smectic A_d phase of 80CB than 120CB (see right-hand side of Figure 5). This is due to the lower values of the forces bonding the 80CB molecules in the smectic layers as compared with those bonding the 120CB molecules (the phase transition enthalpies $\Delta H_{S_A \to N \text{ or } I}$ are for these compounds equal to 22 J/mole and 4.6 kJ/mole, respectively).

In distinction, the 7DBT smectic A_1 phase is stronger destabilized by the 120CB molecules than by the 80CB ones. In this case the greater difference in the smectic layer spacing and densities between compounds 120CB and 7DBT than between compounds 80CB and 7DBT is decisive.

If the properties of the smectic phase of one of the components of the mixture change drastically in the homologous series with the change of length of the alkyl chain, then the changes in the phase diagrams are significant and the position of the nematic gap may undergo considerable shifts (see Figure 6).

Such a behavior was observed by us in mixtures of 9CPCHB with 5CBB, 6CBB or 7CBB. 5CBB, 6CBB, 7CBB belong to the homologous series revealing the property that up to $n \leqslant 7$ they have the smectic phase A_1 whose thermal stability decreases with increasing n (number of carbon atoms in the alkyl chain) when n varies from 5 to 7[19]. For $n > 7$ these compounds reveal at higher temperatures the smectic phase A_d, and at lower temperatures the latter is separated from the A_1 smectic phase by the N_{re} phase.

The mixture of 9CPCHB and 5CBB ($l_{9CPCHB}/l_{5CBB} = 0.99$, $d_{9CPCHB}/d_{5CBB} = 1.46$) reveals a wide nematic gap (see Figure 6). The mixtures of 9CPCHB and 6CBB, and 9CPCHB and 7CBB ($l_{9CPCHB}/l_{6CBB} = 0.96$, $d_{9CPCHB}/d_{6CBB} = 1.4$; $l_{9CPCHB}/l_{7CBB} = 0.92$, $d_{9CPCHB}/d_{7CBB} = 1.34$) are characterized by a significantly increased stability of the smectic A_d phase.

A widening is observed of the temperature and concentration ranges in which the smectic A_d phase of compound 9CPCHB exists, so this phase is strongly enhanced like smectic A_1 phase some of non-polar compounds with polar one.[23] The smectic A_d phase is enhanced at the cost of the nematic gap and the region of existence of the S_{A_1} phase.

Compounds: 5CBB, 6CBB, and 7CBB if are introduced into the matrix of compound 9CPCHB, reveal in an increasing extent the properties characteristic of the S_{A_d} structure as n brings closer 8 (when

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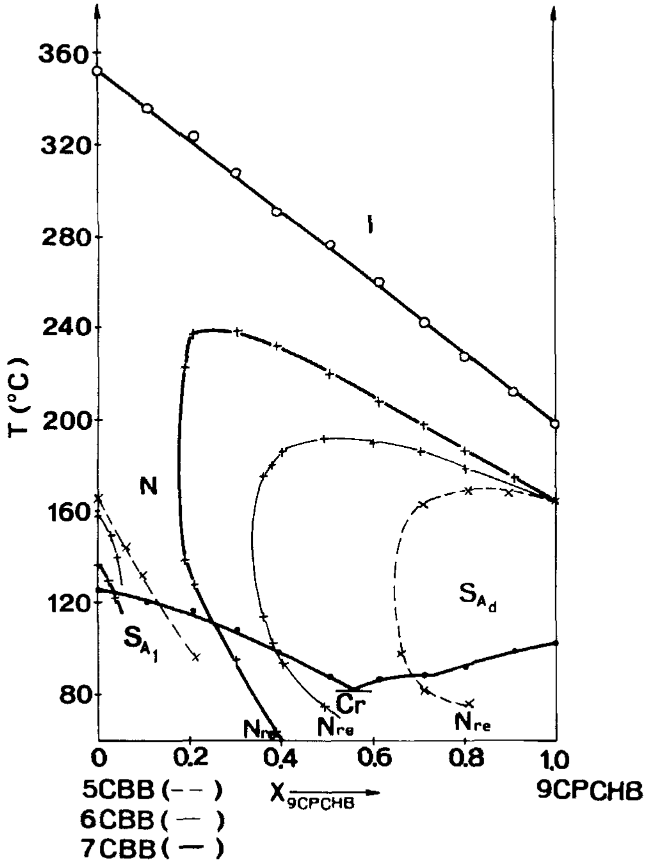

FIGURE 6 Effect of the smectic A_1 phase on the width and position of the nematic gap. The solid bold line presents the phase diagram of 7CBB (formula 4c)—9CPCHB (formula 2a). The solid thin line presents a fragment of the phase diagram of 6CBB-9CPCHB. The thin dashed line presents a fragment of the phase diagram of 5CBB-9CPCHB.

this value is reached the A_d smectic phase is created in this homologous series). The diagrams in Figure 6 indicate that the conversion of the internal structure of compounds 5CBB, 6CBB and 7CBB proceeds graudually and is observed much earlier than it is manifested by the appearance of the reentrant nematic phase.

The nematic gap was observed in smectic mixtures of polar compounds whose molecules have a polar group at least in the terminal position (CN or NO_2 in the case of smectics A_d, and CN, NCS or I in the case of smectics A_1). Polar groups may be also in other positions in the molecule, but their dipole moments were in the cases studied

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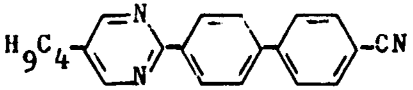
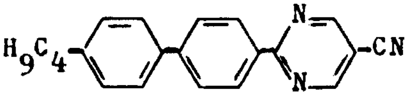
always in accordance with the dipole moment of the terminal group (so they added to the dipole moment of the terminal group). Is this a necessary condition, or is this observation the result of our studying incidentally molecules of such a structure? We tried to find an answer to this question by studying the phase diagrams of mixtures of three isomeric pyrimidines:



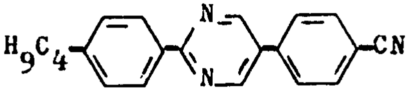
9

Cr 112 S_{A_1} 212.5 N 226 I



10

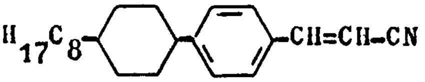
Cr 126 S_{A_1} 216.5 N 274.5 I



11

Cr 138 S_{A_1} 180 N 260 I

with the compounds: 10CPCHB and



12

Cr 48 S_{A_d} 128 N 137.5 I 8EPCH

selected in such a way that the ratio *r* ensures the creation of a nematic gap between the smectic regions. All three pyrimidines reveal the smectic A_1 phase of similar stability and similar spacing ($d = 2.1$ nm), the lengths of the molecules are also the same ($l = 2.18$ nm) but the dipole moments of the polar groups have a different orientation. Pyrimidine 9 has a large dipole moment $\mu \approx 6.5$ D since the moments of the CN group and the pyrimidine ring are concordant and therefore they add. Pyrimidines 10 and 11 have a much smaller dipole moment, $\mu \approx 1.7$ D since the moments of the cyano group and the pyrimidine ring are discordant and are deducted. Only pyrimidine 9 gives with compounds 10CPCHB (3b) and 8EPCH (12) phase diagrams with a nematic gap (thin solid line in Figure 7), while the two remaining ones have phase boundaries as shown by the solid line.

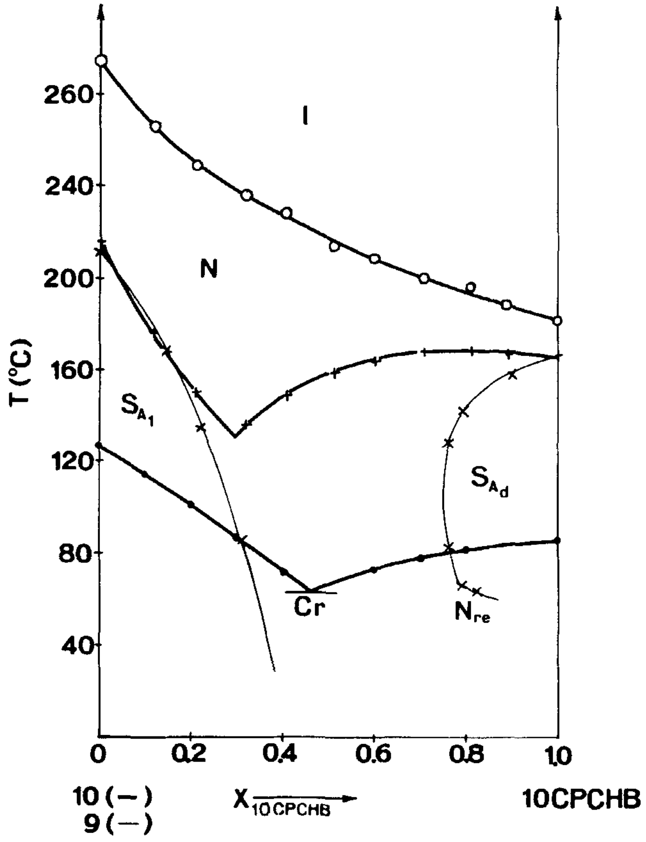


FIGURE 7 Effect of structure of the molecules on the character of the phase diagrams of binary mixtures of smectics A_1 and A_d: solid line—the phase diagram of 10CPCHB and 5-cyano-2-(4′-n-butyl-4-biphenylyl)pyrimidine (formula 10), thin solid line—fragment of phase diagram of 10CPCHB and 5-n-butyl-2-(4′-cyano-4-biphenylyl/pyrimidine (formula 9).

For pyrimidines 10 and 11 the $S_A \rightarrow N$ phase transition temperatures of their mixtures with 10CPCHB or 8EPCH give two independently varying curves which intersect at an acute angle and do not have the characteristic flat minimum occurring in other systems in which the destabilization of the smectic phase was observed. The $S_A \rightarrow N$ phase boundary had a similar character in the binary system 5DB-TBAA.[25]

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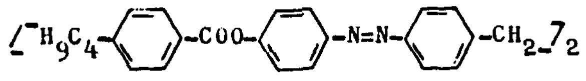
The lack of the nematic gap in mixtures of compounds 10 – 10CPCHB, 10 – 8EPCH, 11 – 10CPCHB, 11 – 8EPCH can be explained by the change of the molecular dimensions of compounds 10 and 11 in the 10CPCHB or 8EPCH matrix.[17] Probably the monomeric molecules of compounds 10 and 11 convert into associates or dimers existing only in a limited range of concentrations and temperatures. They can be assigned virtual temperatures of the S→N transitions in another temperature range and spacings of their smectic layers different from those observed for the pure compounds.

It is still difficult to prejudge whether the mixtures made up of other compounds with discordant dipole moments in the molecules will show a similar behavior, since more experimental data are necessary for drawing such conclusions.

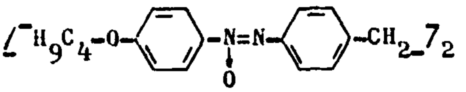
IV. CREATION OF THE NEMATIC PHASE IN WEAKLY POLAR COMPOUNDS

So far we have been studying one binary system composed of molecules that do not have strongly polar groups in the terminal position which is characterized by a very wide nematic gap between the smectic regions. It is composed of compounds 13 and 14:



13

Cr 165 S_C 184 N 303 I



14

Cr 137 S_A 290 N 330 I

The investigations of the properties of this system and its components have not as yet been concluded, however, the initial results of X-ray analysis have shown that probably it is the difference in the structure of the smectic layers and not so much the difference in their spacing that is the main factor responsible for the depression of the stability of the smectic phase in the mixtures of these compounds. Compound 13 reveals the smectic phase C with a very large angle of inclination of the molecules with respect to the normal layer (θ = 43°). Compound 14 is a smectic A (θ = 0). The great chemical similarity of compounds favors their mutual dissolution, whereas the difference

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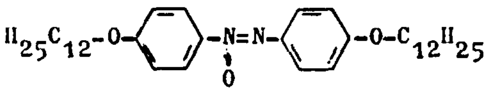
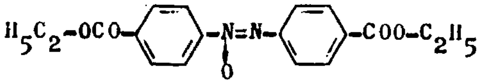
in the tilt of the molecules in the smectic layers and the difference in the lengths of the molecules do not permit the creation of a smectic layer composed of a mixture of these compounds.

It seems that there will be no greater difficulty in finding further examples of mixtures of non-polar compounds revealing a nematic gap since several pairs of smectic compounds in whose mixtures the nematic phase is observed have already been found. By way of example we can mention the following pairs: 15 and 16, 17 and 18, and 19 and 20.



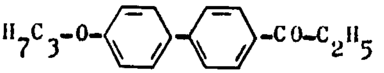
15

Cr 81.7 S_C 122 I



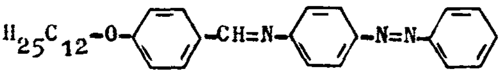
16

Cr 113.7 S_A 122.5 I



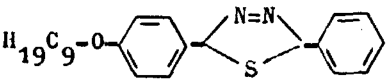
17

Cr 119 S_E 177.3 I



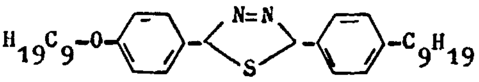
18

Cr 102.5 S_B 125 S_A 159 I



19

Cr 96 S_A 126 I



20

Cr 97 S_C 192 I

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Compounds 15–20 yield smectic layers built of single molecules, so their layer spacings should fulfill the condition $d \leqslant 1$. It should be expected that in similar mixtures but where the difference in the length of the molecules is greater the nematic gap between the smectic regions will be created. It follows from the examples presented that the creation of the nematic gap is particularly favored in mixtures of weakly polar compounds constituting smectics A and C. This is probably a result that the smectic C phase is particularly sensitive to destabilization. It seems to us that nothing stands in the way of mixtures composed of other smectics behaving in the same manner.

V. PHYSICAL PROPERTIES

5.1 Effect of the smectic layer spacing ratio on the phase transition enthalpies

The variation of the values of the S→I, S→N and N→I phase transition enthalpies in mixtures of polar smectics A with concentration is correlated with the changes observed in the phase diagrams (Figure 8). The enthalpy of the S→I phase transition in n-DBT-120CB mixtures is lowered drastically for both components as the concentration of the other component increases (Figure 8a). After the nematic phase is created in the system, the N→I phase transition enthalpy is almost independent of concentration but its value decreases for the successive pairs of compounds with increasing ratio *r* (Figure 8b). In distinction, the values of the enthalpy of the S→N phase transition depend strongly on concentration and on the ratio *r* (Figure 8c). In the case of the mixtures 9DBT-120CB, and 8DBT-120CB the S→N transition becomes a transition of the second kind in the range of concentrations close to $X_{120CB} = 0.4$.

In the successive mixtures revealing the nematic gap $\Delta H_{S\to N}$ decreases with the growing concentration even more drastically and the more rapidly the larger is the ratio *r*. In the 7DBT-120CB and 4DBT-120CB systems $\Delta H_{S\to N} = 0$ for concentrations X_{7DBT} and X_{4DBT} by about 0.1 to 0.15 mole fraction bigger than the concentration at which we observe by the microscope method the decay of the smectic phase. From the side of 120CB the gap determined by the thermo-microscopic method is narrower by 0.05 to 0.1 mole fraction as compared with that observed in the calorimetric method. In mixtures composed of n-DBT compounds only or else of *n*-DBT and 10TPCHB, or n-DBT and 80CB the enthalpy of phase transition varied in a similar way with the value of *r*. In our opinion this is a general property of

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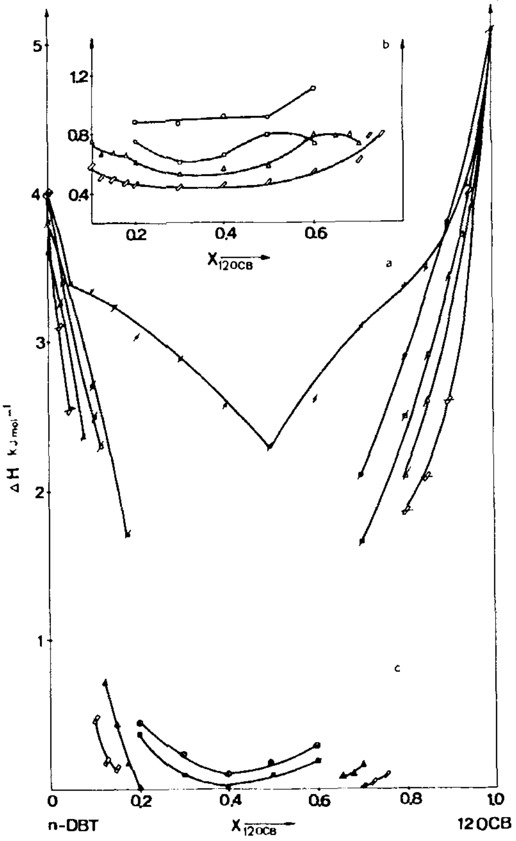

FIGURE 8 Effect of the smectic layer spacing ratio (r) on the enthalpies of phase transitions for the binary mixture composed of one member of the n-DBT homologous series and 12OCB (4-n′-dodecyloxy-4′-cyanobiphenyl): (a) S→I transition, (b) N→I transition, (c) S→N transition. ●—12DBT, ○—9DBT, □—8DBT, △—7DBT, □—4DBT, I→S(/), I→N (empty mark), N→S (crosses).

mixtures composed of polar smectics A which indicates that the incomeasurabilities of the dimensions of molecules in the smectic layers produce the decay of the forces bonding the molecules in the smectic layer and are the main cause of the virtual nematic properties of the compounds being revealed.[27]

In the case of nematic mixtures in which the induction of the smectic phase is observed the values of the S→N and S→I phase transition enthalpies assume maximal values in the central part of the mixture concentration range.[26]

5.2. Molar mixing volumes

The molar mixing volumes, V^S, were measured for the 4DBT-8OCB binary system by the dilatometric method.[16] The mixing of these compounds produces an increase of V^S concentrations from $X_{8OCB} = 0$ to $X_{8OCB} = 0.95$. The greatest expansion of volume observed is shifted from the concentration corresponding to the central part of the nematic gap in the direction of the 4DBT excess to the mole fraction $X_{4DBT} \approx 0.8$ (in this concentration range $\Delta H_{S \to N} \to 0$). The molar mixing volume V^S in the isotropic phase is approximately equal to that in the smectic phase for $X_{4DBT} = 0.825$, $V^S = 3.2$ cm^3/mole at 82°C—mixture and both components in isotropic phase, and $V^S = 4.09$ cm^3/mole at 63°C—both components in smectic phase and mixture in nematic phase). This makes us think that the forces acting in both phases between the molecules decrease in a similar manner as a result of mixing. In mixtures of nematic compounds in which the smectic phase is induced we observe after mixing a decrease of the volume of the system (V^S is negative).[28] In this case V^S has a maximal absolute value for the approximately equimolar composition. For instance, the creation of a smectic mixture from the nematic compounds: 4-ethyl-4′-pentylazoxybenzene and PCB produces a decrease of volume by 2.6 cm^3/mole. If we take into account that the N→S phase transition is accompanied in such a mixture by a volume contraction of ca. 1 cm^3/mole, the effect of mixing in this some phase provides for the change of volume of ca. -1.6 cm^3/mole. The latter effect as regards its absolute value is lower than of V^S observed for the mixing of compounds 4DBT-8OCB of similar polarity. May be, however, that this is related to the individual properties of the tested compounds and cannot be considered to be a general rule.

5.3. Changes in the internal structure of the mixtures

The X-ray scattering patterns for the 8DBT-12OCB mixture (see phase diagram in Figure 2) indicate that the characteristic molecular dimensions in these mixtures change neither monotonically nor additively (Figure 9). On the side of the 12OCB excess the spacing of the smectic layer *d* decreases at a smaller rate than that resulting from the weighted mean of the n-DBT molecule and 12OCB dimer lengths. It is only from the concentration $X_{4DBT} \geqslant 0.5$ that a rapid decrease of *d* takes place to a value close to the mean length of the single molecules. This indicates that the dimeric structure of 12OCB is preserved in wide concentration range in the mixture with the other polar compound having a monomeric structure. The decay of the

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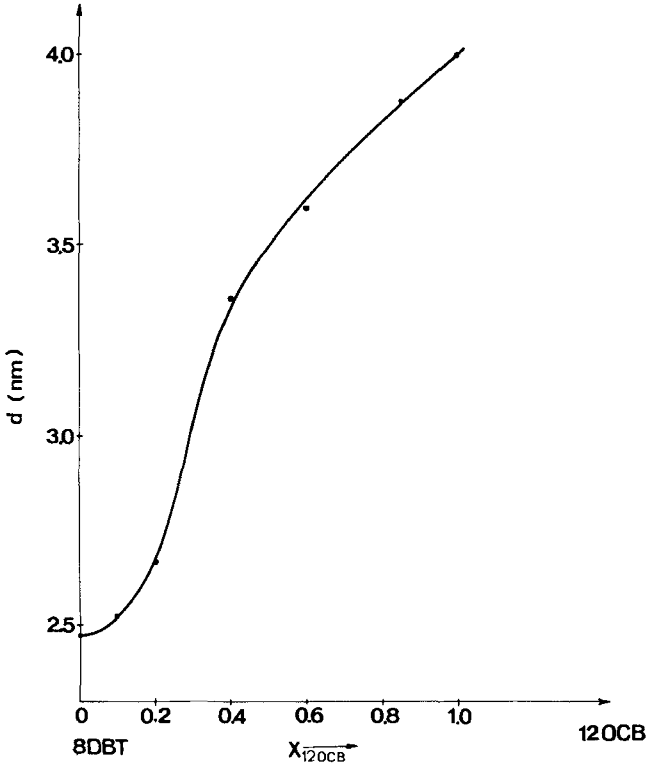

FIGURE 9 Smectic layer spacings (*d*) in 8DBT-12OCB mixtures (for phase diagrams see Figure 2) as determined by X-ray diffraction (inner reflection).

dimers proceeds rapidly only after the excess concentration of the monomeric component is exceeded. This behavior is distinctly different from that observed for mixtures of non-polar smectic A_1 and polar smectic A_d wherein the smectic phase is induced.[29] In the latter case the smectic layer spacing varies more rapidly from the side of excess of the compound with the A_d smectic phase than it could be expected from the mean length of the molecule of the non-polar compound and the dimer of the polar compound.

In this case the non-polar component destroys as it is added the dimeric structure of the polar component of the mixture and this process is completed before the equimolar composition is achieved.

5.4. Viscosity of the mixtures in the nematic gap

The viscosity of the nematics created from smectic compounds varies with temperatures in a way typical for normal nematics (Figure 10).

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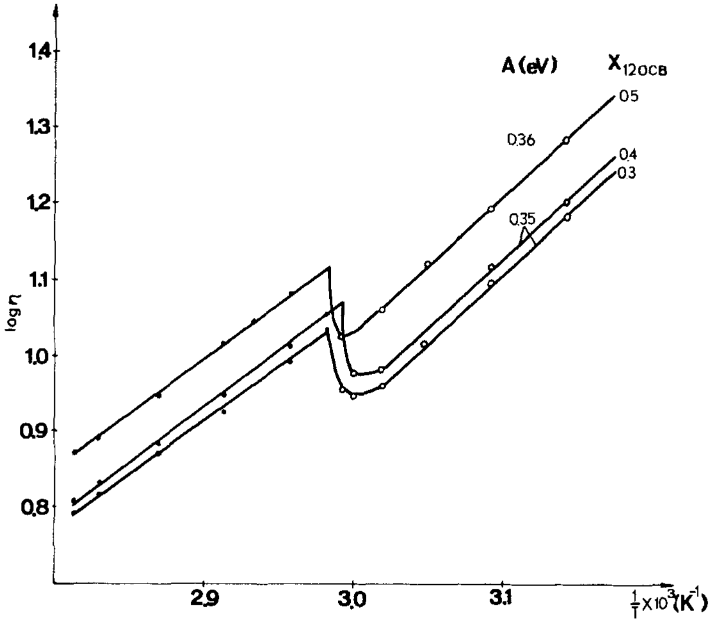

FIGURE 10 Variation of viscosity with temperature for 4DBT-12OCB mixtures of different composition.

This relationship is exponential ($\eta = \eta_0 \exp A/kT$) and a characteristic stepwise decrease of viscosity is observed on transition from the isotropic to the nematic phase; the value of the viscosity activation energy A is some smaller than 0.4 eV. The mixtures composed of 4DBT and 12OCB reveal a lowest viscosity in the central part of the nematic gap; a similar behavior was observed for mixture of 4DBT and 8OCB.[16]

VI. CONCLUSIONS

The compounds that are smectics A in binary and multicomponent mixtures may manifest their virtual nematic properties. It is possible to obtain solely from compounds with the smectic A phase nematic mixtures with properties characteristic of normal nematic (e.g. with low viscosity, diffused spots of the X-ray pattern). The nematic phase is created as a result of the weakening of the intermolecular attraction forces in the disturbed smectic layer. To make possible the observation of the enhancement of the nematic phase at the cost of the smectic one in a mixture consisting of compounds with the smectic A and nematic phases or the induction of the nematic phase in a

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mixture prepared from smectic A compounds only one should select the components in such a way that:

1. Their polarity and electron affinity be similar (for instance both components are electron acceptors). Strongly polar compounds should be mixed with strongly polar ones or weakly polar with weakly polar ones.
2. Their smectic layers be different. The smectic layers of the pure components should have different spacings. Besides, it is advantageous if they differ as regards the arrangement of the molecules in the smectic layers, e.g. one component of the mixture is a smectic A_d and the other a smectic A_1.
3. The orientation of the dipole moment of the terminal polar group in the mesogene molecule be coincident with the remaining polar groups in the molecules.

The nematic phase is induced in the mixtures the easier and the nematic gap between the two smectic regions is the wider when the greater is the smectic layer spacing ratio of the mixture components and the smaller is the enthalpy $\Delta H_{S\rightarrow N}$ or $\Delta H_{S\rightarrow I}$ or the smaller is the ratio $T_{S\rightarrow N}/T_{N\rightarrow I}$ for these components.

In mixtures made up of molecules with polar groups whose dipole moments are opposite no nematic gap was observed between the smectic regions and it was found that in mixtures composed of the compound with smectic phase A_1 and a compound with smectic phase A_d these phases mix in a limited interval of concentrations and temperatures. This fact confirms the conclusion that the nematic gap observed in mixtures composed of compounds with the same orientation of the dipole moments is not due to the lack of miscibility of the smectic phases of the components differing as regards the spacing of the smectic layers, but is the result of the weakening of the intermolecular forces in the layers. At present it is difficult to ascertain whether the weakening of the intermolecular forces in the smectic layers is due only to the disturbing of the smectic lattice by placing in it elements of different length or whether it results also from a change of some other properties of the system.

Premises exist that allow us to expect the creation of the nematic phase not only in mixtures composed of smectics A but also of other kinds of smectics. The nematic phase should be created particularly easily in mixtures of smectics A and C, especially if the smectic layers differ as regards their tilt. The above discussed phenomenon of induction of the nematic phase may find practical application. For displays with thermal recording and cancelling of information in smec-

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tic layer, we require smectics with a nematic phase existing directly before the clearing point, since then it is easy to obtain a uniformly oriented smectic layer. Such smectics in the form of mixture can be obtained from compounds with different smectic layer spacings and concordant orientation of the dipole moments of the polar groups. It is also possible to prevent the creation at low temperatures of smectic phases in nematic mixtures used in displays by taking account of the above formulated principles of smectic phase destabilization when selecting the mixture components.

Acknowledgment

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