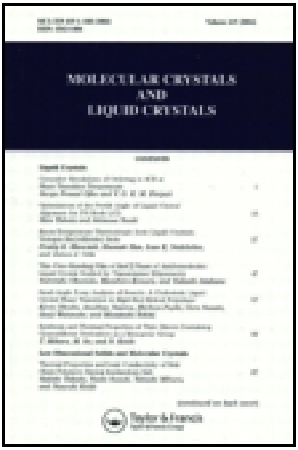

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EDA Complexes in Liquid Crystalline Mixed Phases

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EDA Complexes in Liquid Crystalline Mixed Phases

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The diagrams of state of 11 binary systems are presented which form EDA complexes in the liquid crystalline state. The influence of the molecular length and the complex stability on the formation of enhanced smectic A phases have been studied.

1 INTRODUCTION

The occurrence of electron donor acceptor (EDA) interaction in liquid crystalline mixed phases was presumed by some authors, but could not be detected with certainty.[1–4] Clear evidence of EDA interaction was provided by the homologous series of 4,4′-bis-(alkylamino)-biphenyls,[5] which possess excellent electron donor properties. These compounds form, with a number of liquid crystalline compounds which act as electron acceptors, colored EDA complexes in the solid, liquid crystalline, and isotropic states.[6] Recently, Araya and Matsunaga[7] have found induced nematic and smectic phases in mixtures of potentially-liquid crystalline donors and acceptors.

According to Sharma *et al.*[6] the charge transfer (CT) bands in the visible region show negative dichroism, i.e., the electron transition moments responsible for the absorption are oriented perpendicular to the molecular long axis. It is characteristic of liquid crystalline EDA systems that smectic A phases often occur in the middle concentration range even when the pure compounds do not possess any smectic A phase.

In the following account we examine the influence of molecular length and complex stability on the formation of such smectic A phases.

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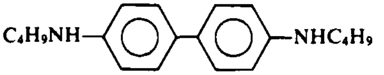
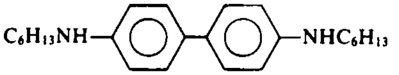
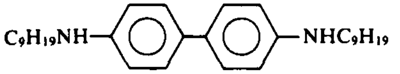
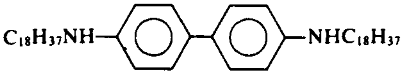
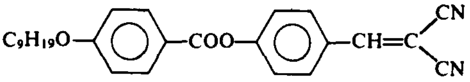
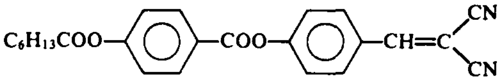
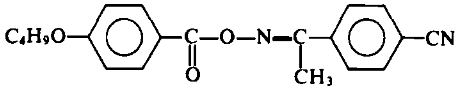
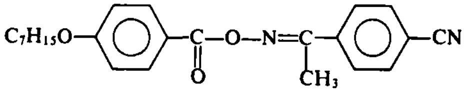
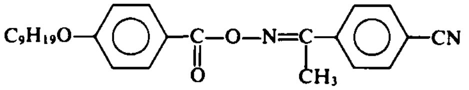
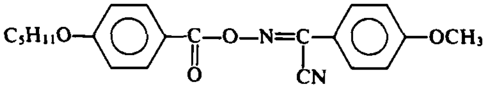
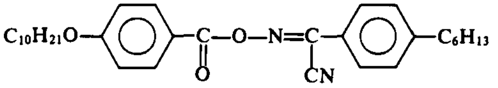
2 SUBSTANCES

The experiments were performed with the substances shown below in Table I.

3 EXPERIMENTAL

The diagrams of state for binary systems formed from 4,4'-bis-(alkylamino)-biphenyls and some liquid crystalline electron acceptors were studied by the contact method[8] and by the investigation of mixtures with known concentrations.

TABLE I

	Cr 345.4 N 369.7 Is[5]
	Cr 366.8 N 376.2 Is[5]
	Cr 372.5 S_C 383.2 N 383.6 Is[5]
	Cr 378.4 S_I 387.8 Is[5]
	Cr 353 S_A 362.2 N 368.4 Is[9]
	Cr 358.7 N 375.5 Is[9]
	Cr 389.2 N 415.2 Is[10]
	Cr 373.2 N 400.2 Is[10]
	Cr 363.2 S_A 386.2 N 399.2 Is[10]
	Cr 376.2 N 391.5 Is[11]
	Cr 346.2 N 354.2 Is[11]

Cr: solid crystal
N: nematic
S_A, S_C, S_I: smectic A, C, I
Is: isotropic liquid
The numbers between the phase symbols are the transition temperatures (K)

4 EXPERIMENTAL RESULTS

4-(2′,2′-Dicyanoethenyl)phenyl 4-*n*-nonyloxybenzoate forms with the 4,4′-bis-(alkylamino)-biphenyls stable EDA complexes, which are violet in the solid state and red in the liquid crystalline and isotropic states. The maximum of the CT band in the liquid crystalline and isotropic state was found to be at about 500 nm.

Figures 1–4 show the diagrams of state obtained with the dicyanoethenyl compound and the C_4, C_6, C_9, and C_{18} homologues of the 4,4′-bis-(alkylamino)-biphenyls. Complete miscibility in the nematic state is observed with the C_4 compound (Figure 1). The induced S_A phase is separated from the S_A phase of the acceptor compound by a nematic region. In the diagram for the C_6 homologue, both S_A regions are connected, but the nematic regions are separated from each other (Figure 2), because the S_A/Is transition curve shows a pronounced maximum. Also in the diagrams for the C_9 and C_{18} compounds, large S_A regions with a maximum in the S_A/Is curve are observed, whereas the region of the nematic phase and the regions of the tilted smectic phases (S_C, S_I) are limited to small concentration ranges (see Figures 3 and 4).

Similarly to 4-(2′,2′-dicyanoethenyl)phenyl 4-*n*-nonyloxybenzoate, 4-(2′,2′-dicyanoethenyl)phenyl 4-*n*-heptanoyloxybenzoate also forms stable red-

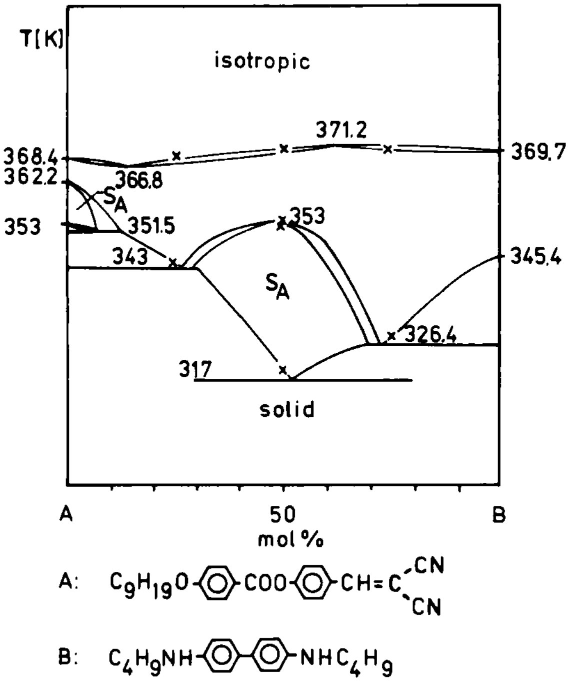


FIGURE 1

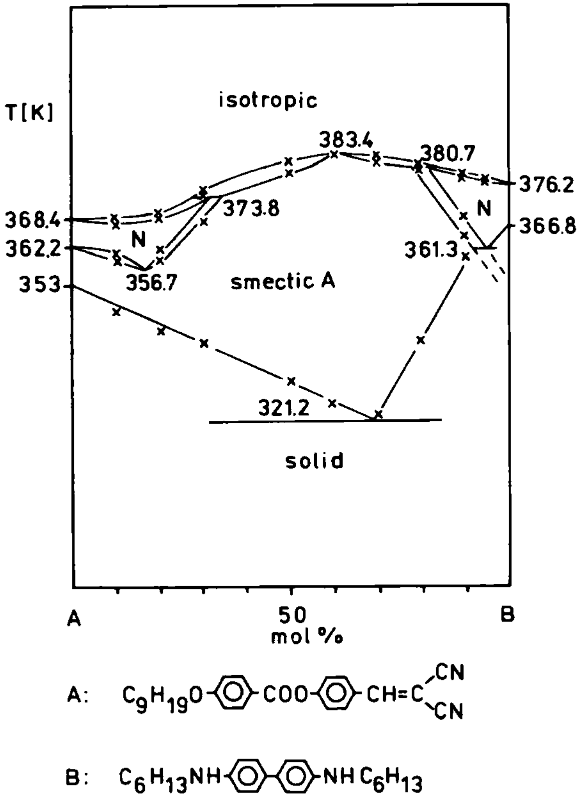


FIGURE 2

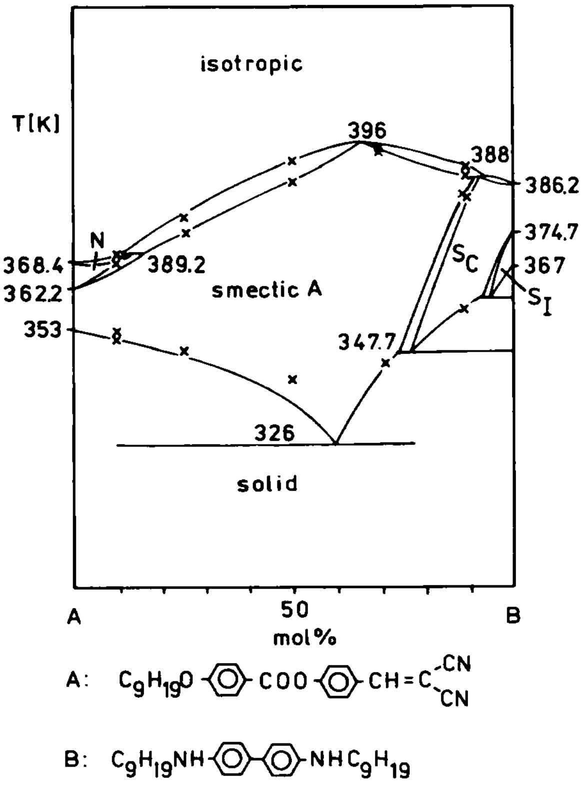


FIGURE 3

colored EDA-complexes with the 4,4'-bis-(alkylamino)-biphenyls ($\lambda_{CT} = 500$ nm). As seen from Figure 5, analogous types of diagram were obtained.

In the diagrams shown in Figures 6–8, the donor compound (4,4'-bis-(hexylamino)-biphenyl) was combined with some homologous 4-cyanocetophenonoxime 4'-*n*-alkyloxybenzoates (C_4, C_7, C_9), acting as electron acceptor compounds. The CT band of the yellow-colored complexes lies at about 410 nm. Generally speaking, in analogous series of complexes, the wavelength of the CT band rises with increasing formation constant of the complex. Therefore, the EDA complexes of the oxime benzoates ($\lambda_{CT} = 410$ nm) should be less stable than those of the dicyanoethenyl compounds ($\lambda_{CT} = 500$ nm).

As seen from Figures 6 and 7, induced S_A phases with maxima in the S_A-N curves occur in the diagrams of state for the C_4 and C_7 compounds. The magnitude of the S_A region increases with increasing alkyl chain length of the acceptor compound. Compared with the diagrams in Figures 1–5, the S_A regions are smaller; furthermore, the maxima in the S_A transition curves are less pronounced. No S_A maximum has been observed for the binary system of the C_9 compound (Figure 8).

When in Figure 6, the 4,4'-bis-(hexylamino)-biphenyl is replaced by the corresponding butyl homologue, an induced S_A phase was not detectable, but complex formation in the solid state occurs (Figure 9).

In Figures 10 and 11, two further examples of liquid crystalline EDA systems are presented which exhibit only a nematic phase. The CT band of these yellow colored complexes lies at 415 nm. Similarly to the diagrams in Figures 6 and 7, the clearing curves show minima.

5 DISCUSSION

The analysis of the diagrams of state shows that the EDA interaction favors the formation of S_A phases. Obviously by the EDA interaction the movement of the molecules is additionally hindered. Comparing Figures 1–4 on the one hand, and Figures 6–8 on the other, we can conclude that the tendency to form smectic A phases clearly increases with increasing strength of EDA interaction.

Increase in the magnitude of the S_A regions is also observed within the complex series, although the CT band, and therefore the strength of the EDA interaction, is not noticeably changed with the chain length of the complex components. This finding may be reduced to the fact that generally, on ascending homologous series of liquid crystals, the tendency for formation of smectic phases increases.[13] For this reason, for example, the exchange of the C_6 compound for the C_4 homologue in Figure 6 gives rise to the disappearance of the induced S_A phase. It seems that induced S_A phases are not observed when the smectogenic nature of the complex components and the EDA interaction are relatively weak (see Figures 9–11).

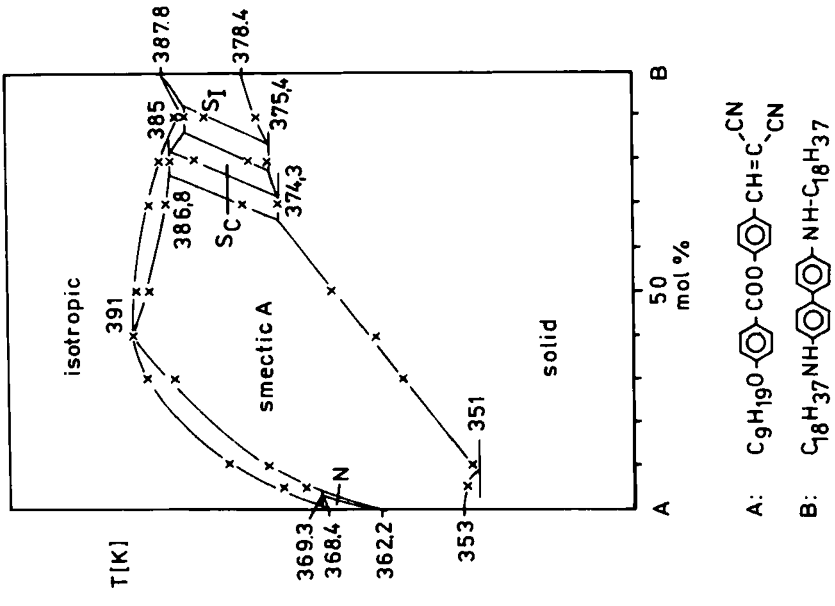


FIGURE 4

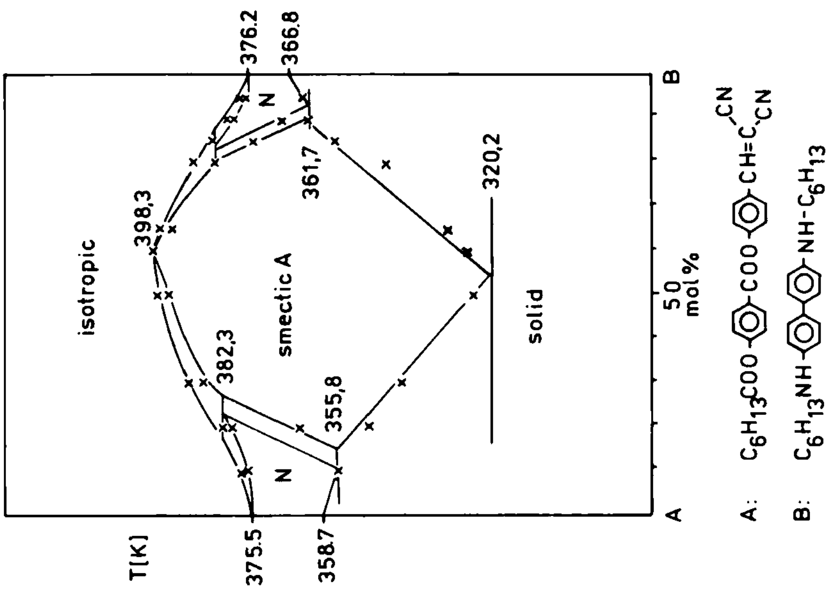


FIGURE 5

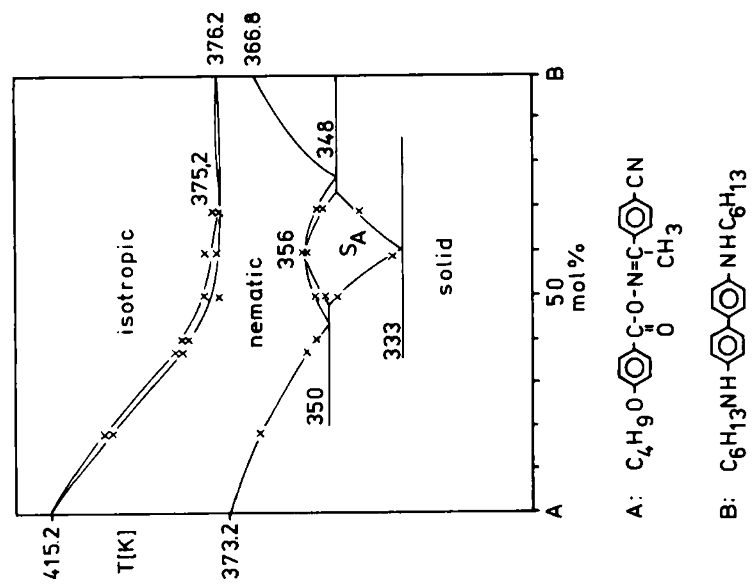


FIGURE 6

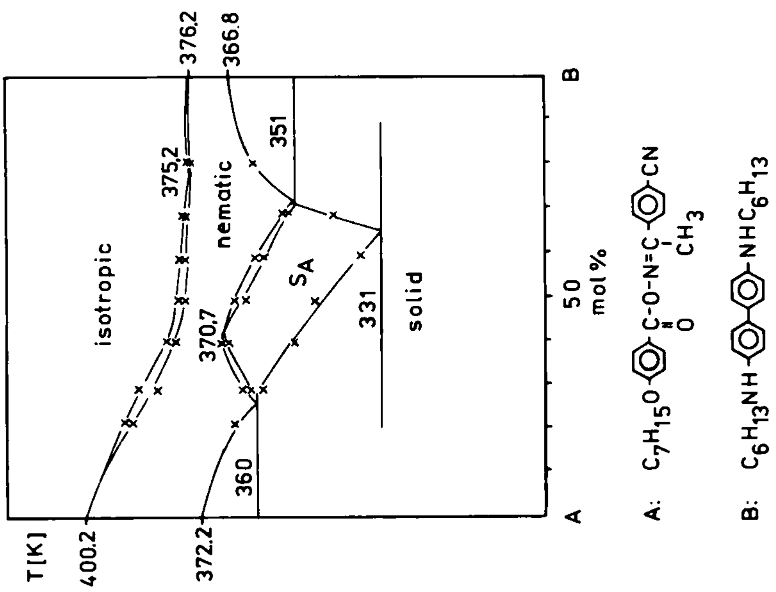


FIGURE 7

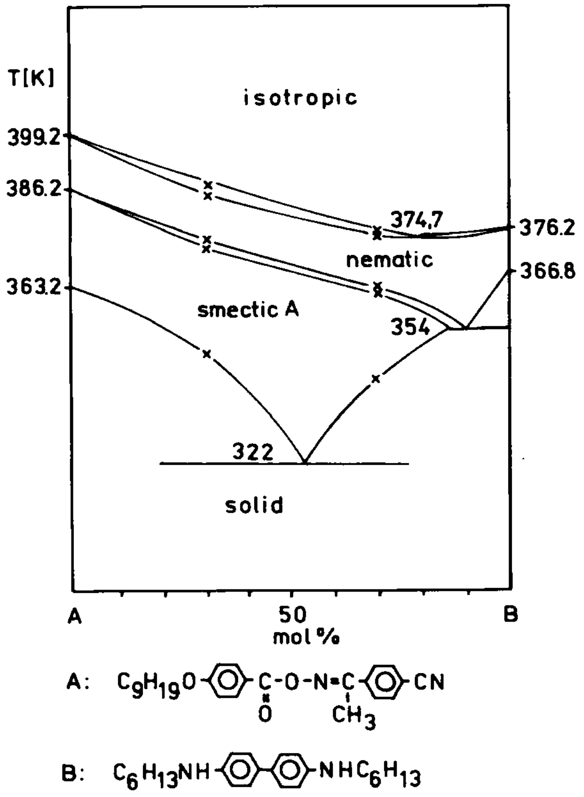


FIGURE 8

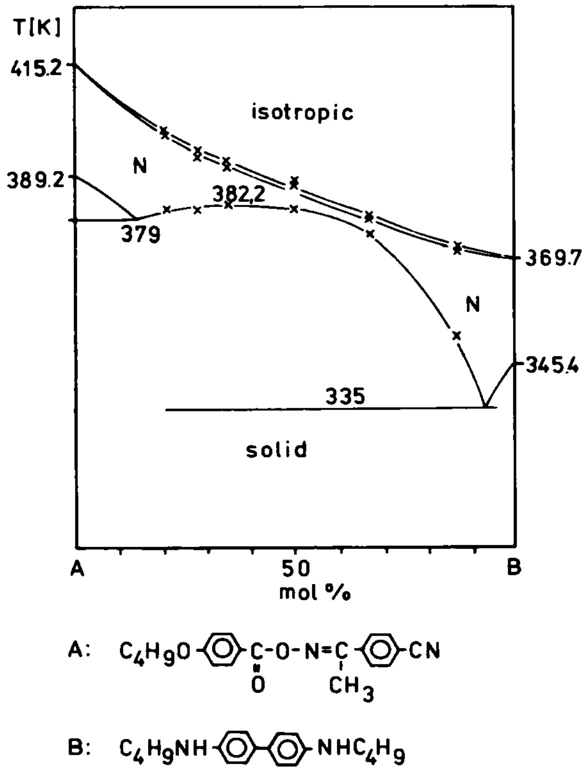


FIGURE 9

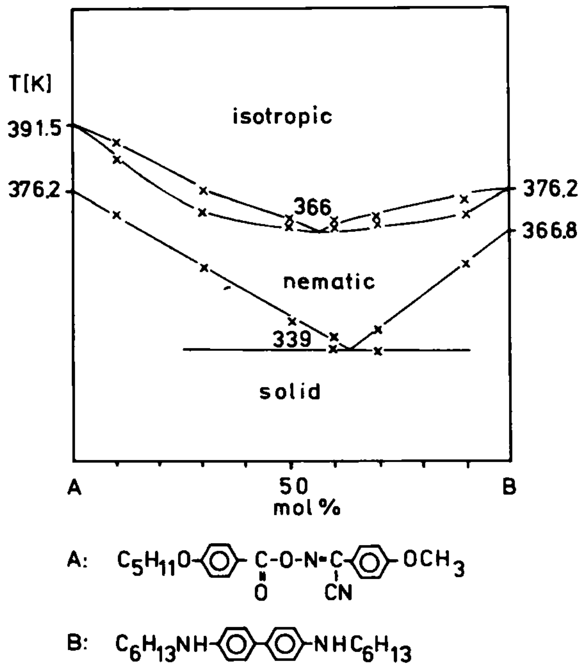


FIGURE 10

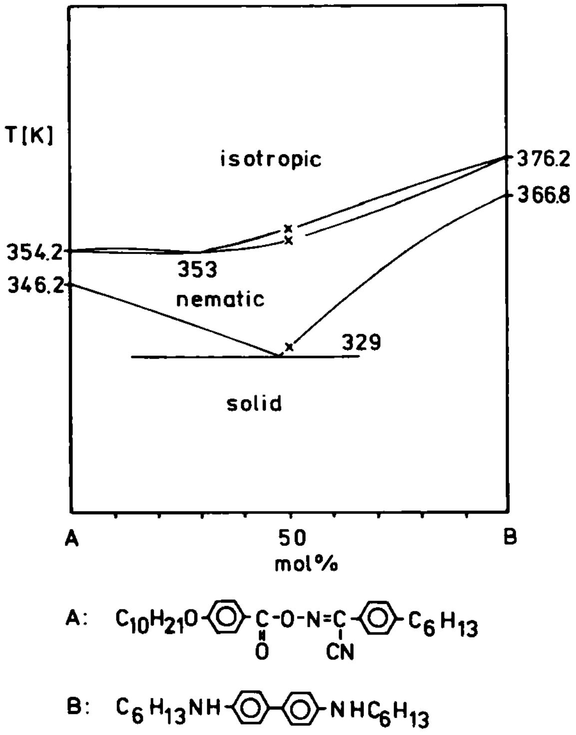


FIGURE 11

The diagrams of state show that the complex formation enhances remarkably the temperatures of the transition S_A/N, but not the N/Is temperatures. This fact may be interpreted by the slightly modified theory of McMillan[14,15] derived for N and S_A phases.

The one particle potential is given by

$$V_1(z, \cos\theta) = -V_0[\eta + \sigma\cdot\alpha \cos(2\pi z/d)](\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})$$

where

$\eta = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle$ (orientational order parameter)
$\sigma = \langle \cos(2\pi z/d)(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\rangle$(translational order parameter)
$d =$ layer thickness
$z =$ z-coordinate
$\theta =$ angle between the director and the molecular long axis
$V_0 =$ potential amplitude, which determines the N/Is transition temperature
$\alpha = 2e^{-(\pi r_0/d)^2}$ (interaction strength for the S_A phase)
$r_0 =$ length of the rigid section of the molecule

Obviously, by the complex formation, V_0 is not affected to a remarkable extent, but the smectic interaction strength α is dramatically changed. In the original McMillan theory α depends only on the ratio r_0/d, which gives an explanation for the usual trend to smectic phases on enlargement of the alkyl chains in homologous series. This consideration, for example, explains the enlargement of the smectic regions in our binary phase diagrams.

The increased temperature of the transition S_A/N caused by complex formation could be interpreted by the enhancement of α. This part of the smectic interaction strength α was not taken into account by McMillan. Since we do not have an explicit equation for this additional interaction we only want to consider its physical origin. In many cases, the formation of EDA complexes leads to stable dimers, with static relative orientations of both the molecules. In other cases the association is very incomplete; thermal motion prevents the formation of static stable dimers and the association may be considered as a dynamic phenomenon caused by "contact potentials."[12]

We assume that the latter is true in the case of our EDA systems. These contact potentials may be assumed to lie in the rigid centers of the molecules, and therefore they can be interpreted without difficulty as a part of the "smectic interaction strength" α.

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