Comparing X-ray studies of smectic A phases formed by laterally branched molecules

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Comparing X-ray studies of smectic A phases formed by laterally branched molecules

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By observation of optical and miscibility studies the liquid-crystalline phases of compounds with the general formula

$$R_1: \quad -COO-CH_2-\langle\bigcirc\rangle-NO_2$$

$$R_{2,3}: \quad -COO(CH_2)_mO-\langle\bigcirc\rangle-NO_2 \qquad m=4,8$$

$$R_4: \quad -COO(CH_2)_2O-\langle\bigcirc\rangle-COC_2H_5$$

$$R_5: \quad -COO(CH_2)_2-O-\langle\bigcirc\rangle-CH=C$$
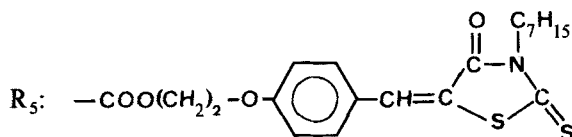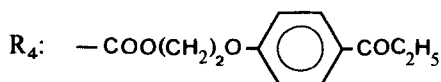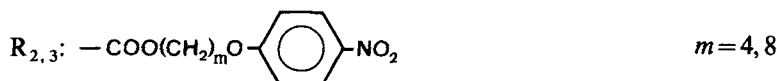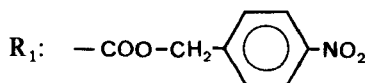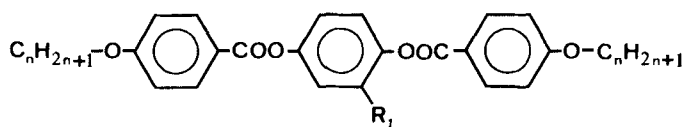
Notation-code: nR_1

have been classified. The structures of the S_A phases of the pure compounds as well as of mixtures with rod-like molecules have been studied.

1. Introduction

In several previous papers [1–3] the influence of lateral branches on liquid-crystalline properties has been discussed. Compounds with laterally attached alkyl chains prefer to form nematic phases. However, smectic phases have been observed, if

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the lateral branches contain aromatic moieties [4]. The former investigations [1, 2, 5, 6] have shown that the lateral branches are aligned parallel to the long axis of the basic molecule. The molecule is therefore, characterized by two parts with different cross-sections. The packing of such molecules into smectic layers of the S_A type leads to some peculiarities which have been reported in a preliminary paper [5]. In order to prove the postulated model for the S_A phase the compounds investigated have been varied systematically. At first the chain length of the basis molecule has been changed. Then the lateral substituents have been altered and finally the S_A structure has been studied in binary mixtures.

2. Experimental

The compounds under discussion have been characterized by microscopic observations in polarized light (Jena Pol D equipped with a heating stage). The phase diagrams of the binary mixtures were constructed by determination of the transition temperatures of selected mixtures with a known concentration. The X-ray studies have been performed using a small angle camera and, for oriented samples, using a flat film method. The orientation of the samples has been achieved with a magnetic field of about 1·5 T. The thickness, d^A, of the smectic layers in the S_A phases has been measured with the small angle camera as a function of temperature and of concentration. The lengths L of the molecules have been determined by the help of CPK models. The error in the determination of d^A and L is within the limits of $\pm 0·05$ nm.

3. Results

3.1. *Molecular shape*

To obtain a better understanding the molecular shape of compound 8 R_1 has been calculated by a program which uses standard bond lengths, bond angles, torsion angles and the assumption that the phenyl rings I, III and IV are co-planar and perpendicular to ring II (see figure 1). The program allows us to calculate the length L of the molecule projected onto an axis of inertia as well as the greatest distance b of an atom from this axis. Figure 1 shows the result with respect to the middle part of the molecule. The calculation proves that the rings III and IV are neighbours and that the end of the lateral branch nearly coincides with the end of the aromatic part of the basis molecule.
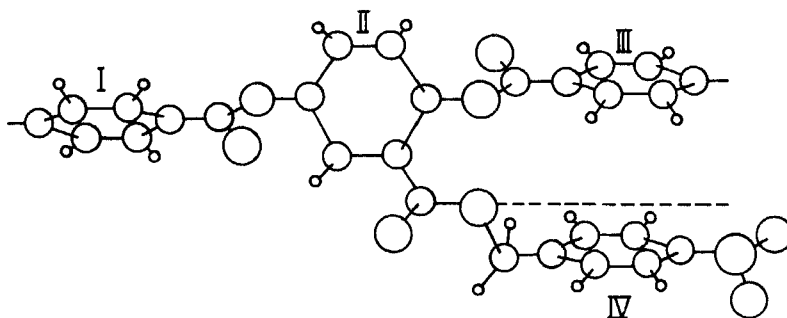

Figure 1.   Calculated molecular shape of the middle part of compound 8 R_1.

For the octyl homologue ($8 R_1$) the values $L = 4.04$ nm and $b = 0.528$ nm have been obtained. The length L is in agreement with the value measured from CPK models.

3.2. *Variation of the basis molecule*

At first the influence of the lengths of the alkyl chains on the layer thickness was studied in the homologous series nR_1

n: 5, 6, 7, 8, 9, 10

R_1: —COO—CH$_2$—⟨◯⟩—NO$_2$
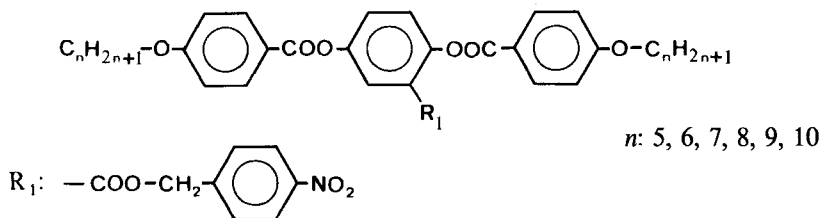
As shown in figure 2 the existence range of the S_A phase is enhanced with increasing chain length. The temperature dependence of d^A is small (< 0.1 nm) and is neglected in the following discussions. Figure 3 shows d^A together with measured length L of the molecules as a function of the chain length. The unusual high differences Δ between L and d^A, especially for the pentyl and hexyl homologues, indicate peculiarities of the structure.

Well oriented samples have been obtained, the X-ray patterns of which exclude any tilt of the molecules as well as great fluctuations of the molecular long axis around a preferred direction.
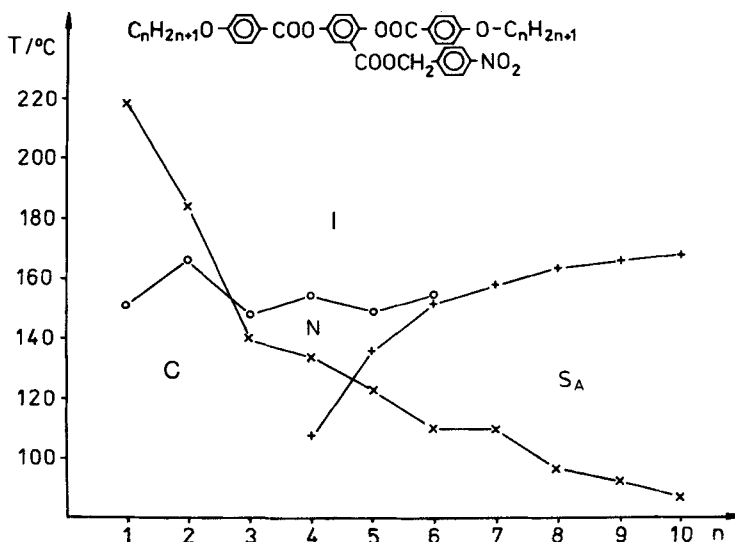

Figure 2.   Transition temperatures of the homologous series.
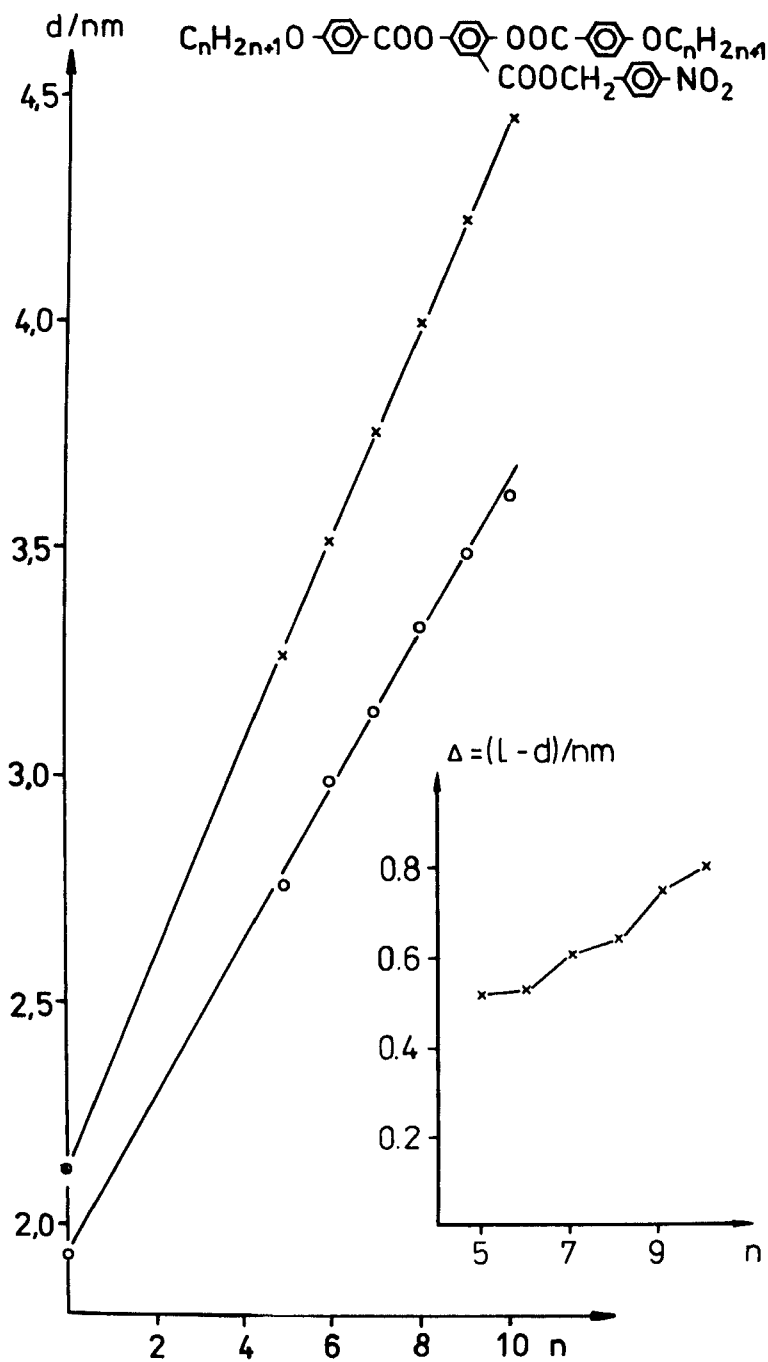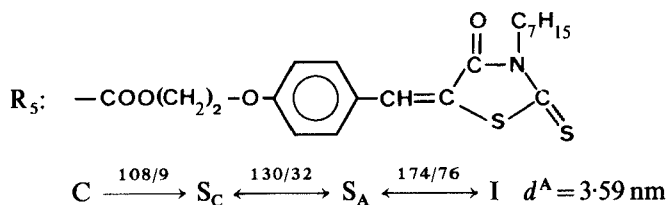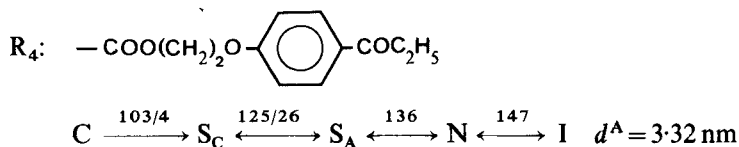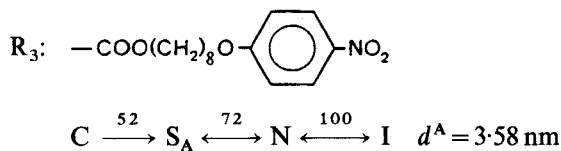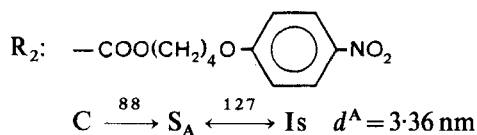
Figure 3.   The length (×) of the molecules according to CPK models and layer thickness (○) as
a function of the number of carbon atoms in the chains.

3.3. *Variation of the lateral branch*

The octyl homologue of series nR has been linked with branches of different length:

R_2: $\quad$ —$COO(CH_2)_4O$—⟨◯⟩—NO_2

$$C \xrightarrow{88} S_A \xleftrightarrow{127} Is \quad d^A = 3\cdot36\,nm$$

R_3: $\quad$ —$COO(CH_2)_8O$—⟨◯⟩—NO_2

$$C \xrightarrow{52} S_A \xleftrightarrow{72} N \xleftrightarrow{100} I \quad d^A = 3\cdot58\,nm$$

R_4: $\quad$ —$COO(CH_2)_2O$—⟨◯⟩—COC_2H_5

$$C \xrightarrow{103/4} S_C \xleftrightarrow{125/26} S_A \xleftrightarrow{136} N \xleftrightarrow{147} I \quad d^A = 3\cdot32\,nm$$

R_5: $\quad$ —$COO(CH_2)_2$—O—⟨◯⟩—$CH=C$⟨ structure ⟩

$$C \xrightarrow{108/9} S_C \xleftrightarrow{130/32} S_A \xleftrightarrow{174/76} I \quad d^A = 3\cdot59\,nm$$

The lengthening of the lateral branch by introducing the additional spacer groups (R_2, R_3) causes an unexpected small increase of d^A ($< 0\cdot2\,nm$ instead of $0\cdot5\,nm$). Also the variation of the chemical nature of the branch (R_4, R_5) does not yield an essential alteration in d^A. These last examples prove that the kind of the smectic structure is not basically connected with the presence of a terminal NO_2 group in the branch.

3.4. *Binary systems*

To obtain more information about a possible packing of the molecules d^A has been determined in binary systems. Three systems have been selected in which the compound 8 R_1 is mixed with compounds whose molecular length is equal (system I), greater (system II) or essentially shorter (system III) than d^A_A of the pure laterally branched compound. The miscibility studies (see figures 4, 5 and 6) show a complete miscibility of the S_A phase in systems I and II whereas in system III the S_A phase region is interrupted by a nematic. The complete miscibility of the phase under discussion with conventional S_A phases of rod-like molecules justified the designation.

Diffraction pattern of oriented samples taken in the S_A phases of the mixtures exhibit well-known features (see figures 7 (a), (b) and (c)): that is spot like interferences and their second order reflections on the meridian of the patterns and perpendicular to this the diffuse, crescent-like outer scattering. The sharpness of the spots indicates that the long range order character of the smectic layer structure is not disturbed by the mixing process, a result which has also been observed in other systems, [7]. The outer scattering is concentrated in a small region around the equator of the pattern. It indicates that large deviations from the preferred direction do not occur.
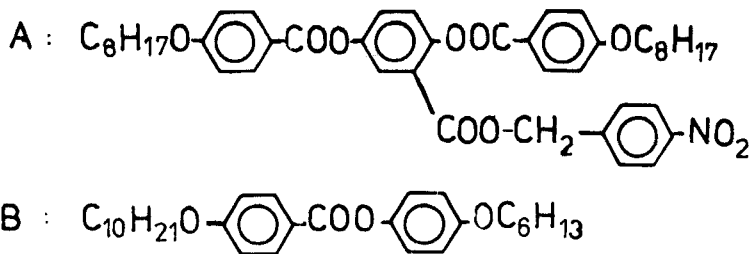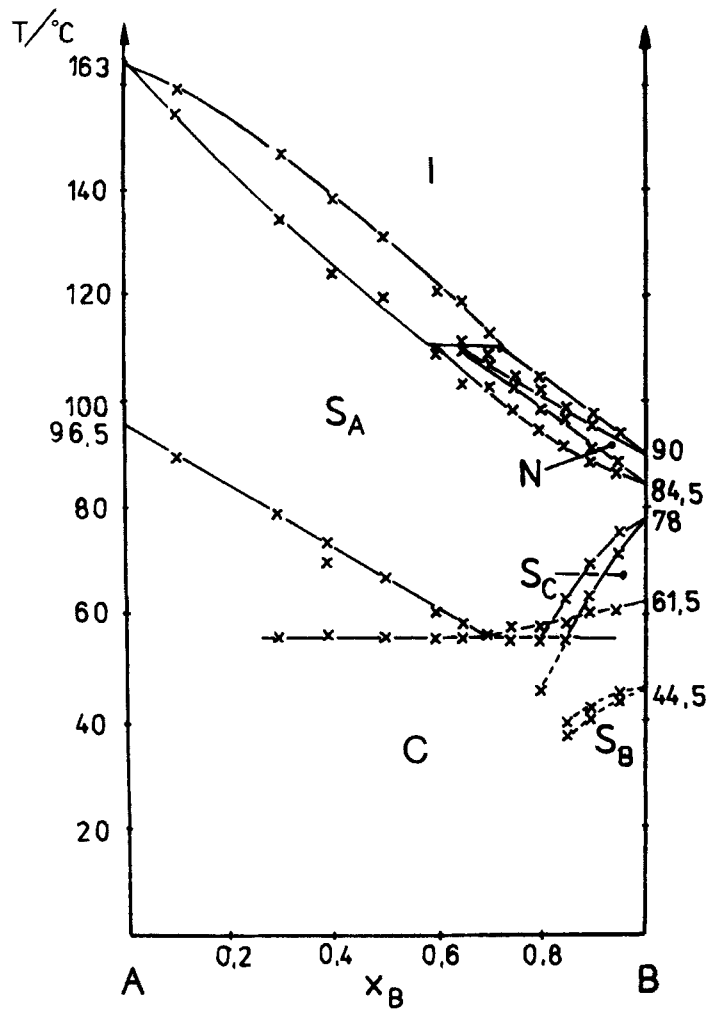
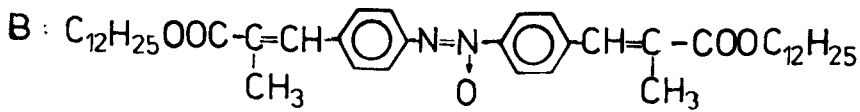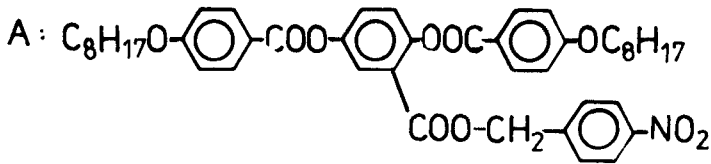Figure 4.   The phase diagram for binary system I.
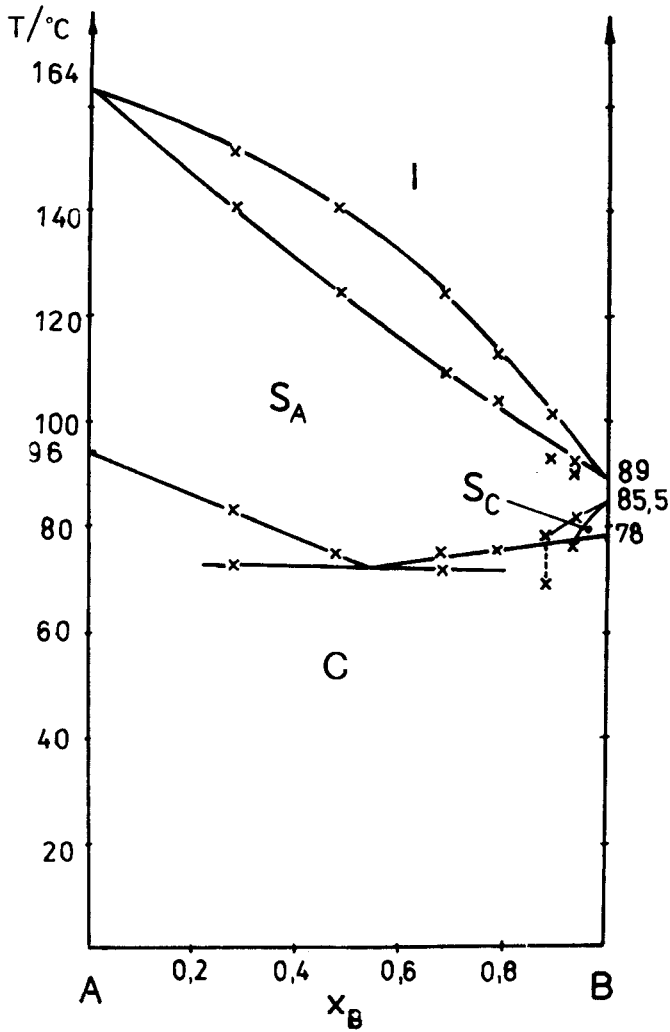
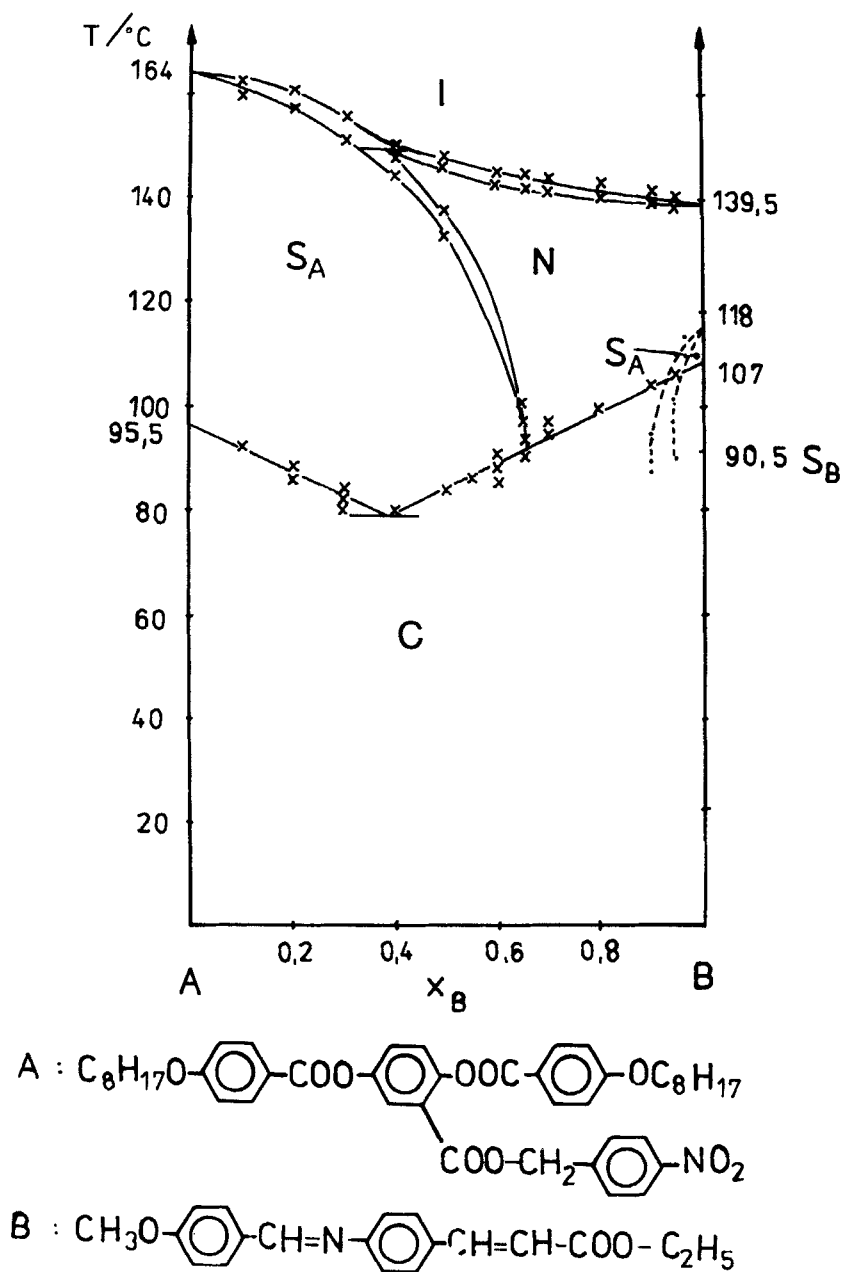Figure 5.   The phase diagram for binary system II.
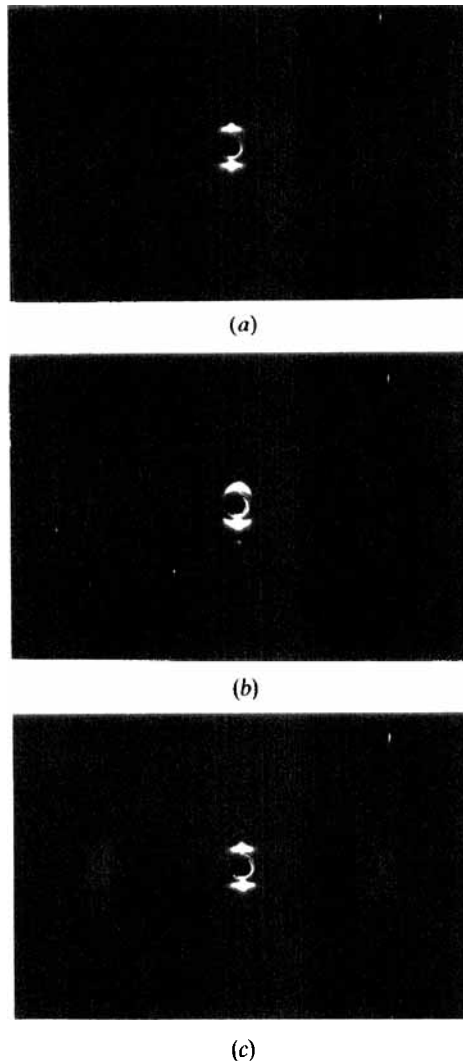
Figure 6.   The phase diagram for binary system III.

(a)

(b)

(c)

Figure 7. X-ray patterns of oriented samples in the S_A phase of system I. (a) $x_B = 0.1$; $T = 145°C$, (b) $x_B = 0.5$; $T = 11°C$, (c) $x_B = 0.9$; $T = 78°C$.

Figure 8 shows d^A for system I. The value of the left hand compound (d_A^A) is essentially smaller than the length of the basic molecule and is explained by the model. The value d_B^A of the right hand component corresponds to the length of the molecule. The values of the mixtures behave additively, that is

$$d^A = x_A d_A^A + x_B d_B^A \tag{1}$$

where $x_{A,B}$ is the mole fractions. This indicates that the nature of the layer structure of component A is maintained in the mixture. The additive behaviour of the d values is the same as that found in mixtures of rod-like molecules [7].

In the second system the length of the admixed compound is essentially greater than d_A^A of the branched compound. The great difference d_B^A and the length of the molecule of
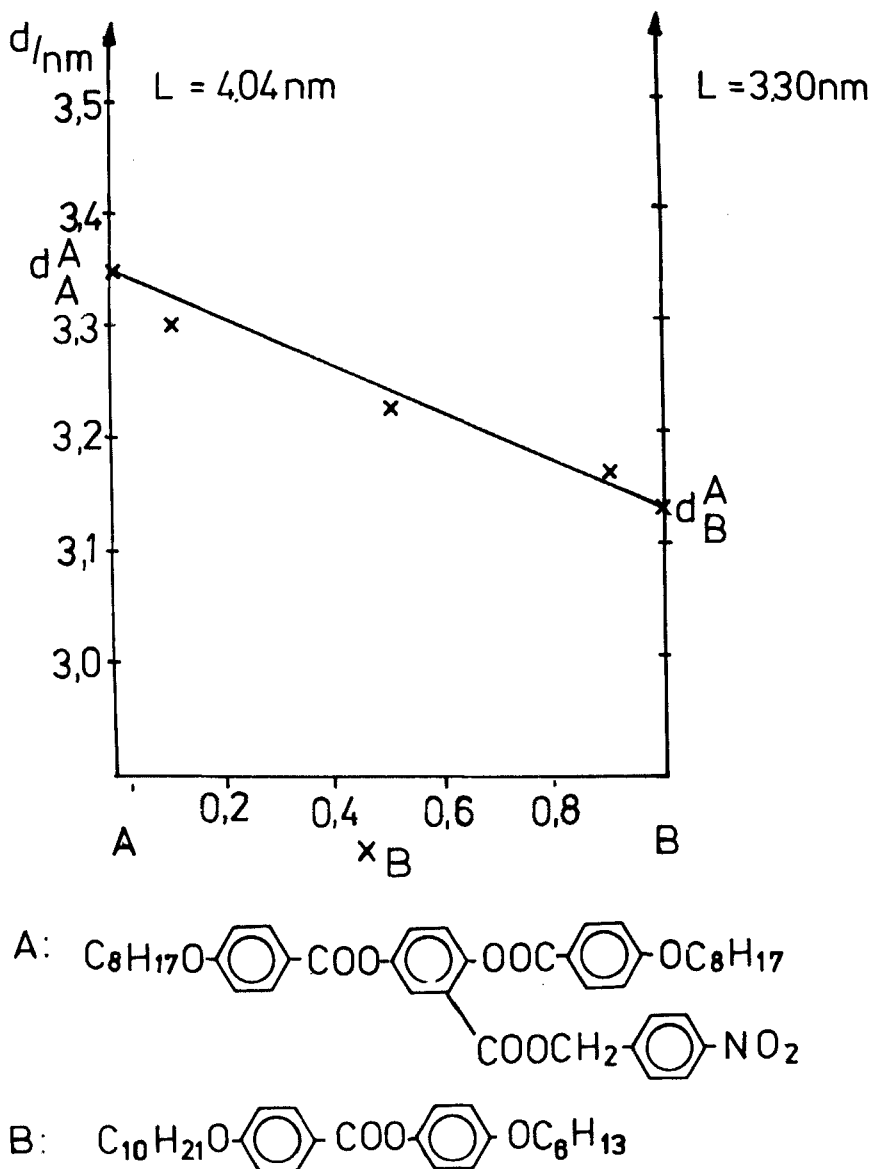
Figure 8.   *d*-values for system I as a function of composition.

the second component is attributed to the deviation of the chain from the all-trans conformation, leading to an apparent length d_B^A (see figure 9) for long chain compounds. However, this d_B^A value nearly agrees with the calculated length L of the basic molecule of the left hand compound. None the less the d^A value of the mixtures can be described again by equation (1). It means that the length L of the basic molecule does not act as the fundamental length.

Finally, in the third system the length of the admixed compound is essentially shorter than d_A^A (see figure 10). Surprisingly d^A for the mixtures does not behave additively. The incorporation of the short molecules does not alter the layer period of the host structure in a wide concentration region. The patterns of the oriented samples
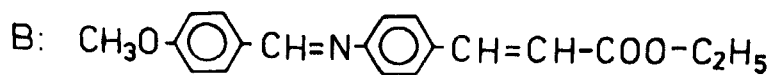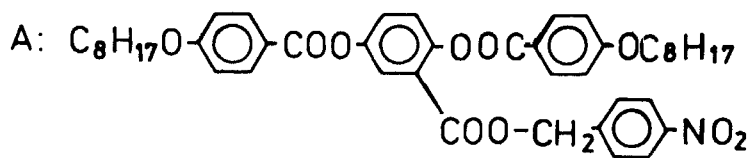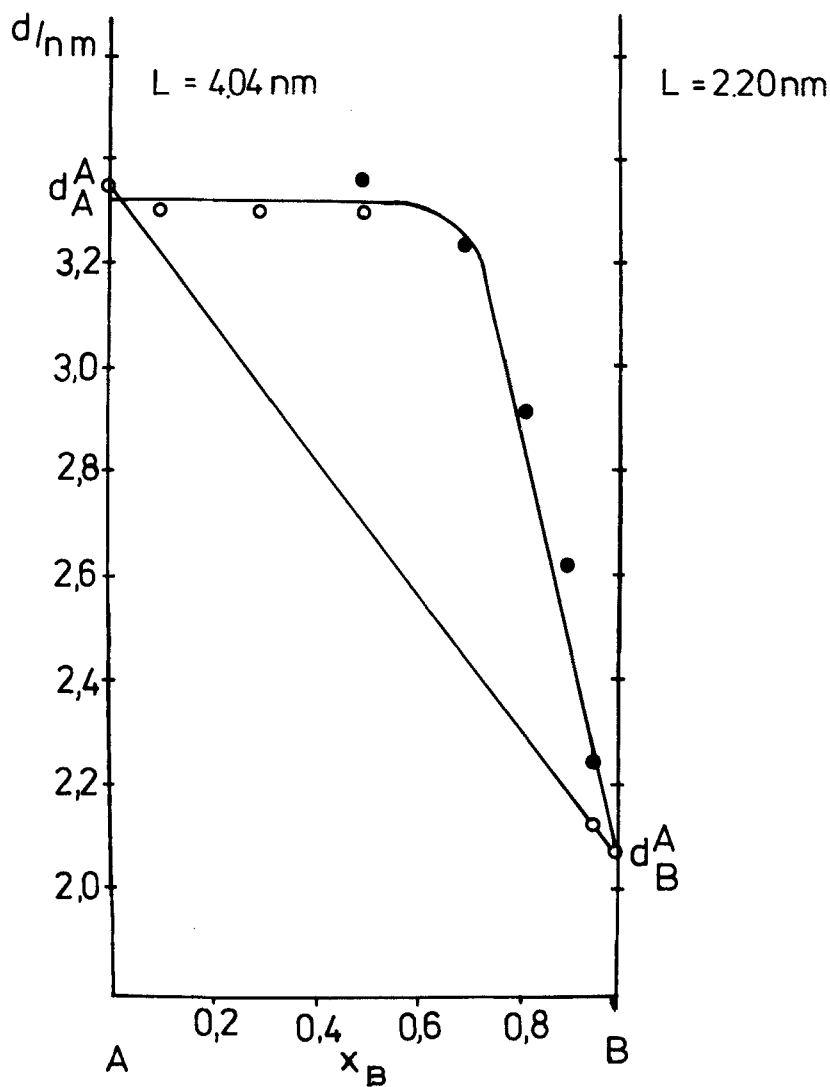
Figure 9. *d*-values for system II as a function of composition.

Figure 10.   *d*-values for system III as a function of composition; (○) smectic A phase (●) nematic phase.

(*a*)

(*b*)
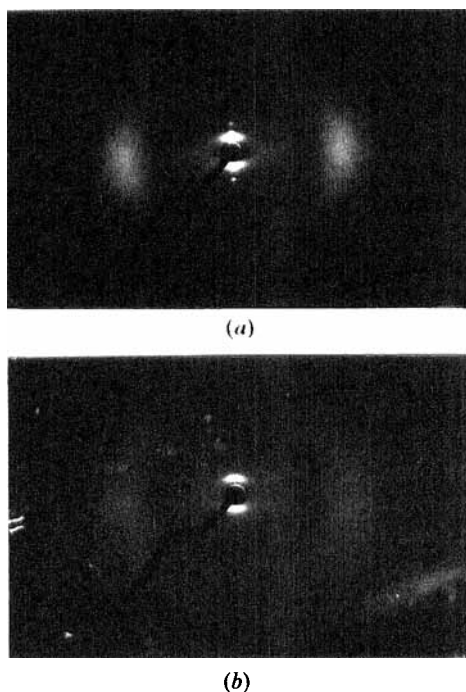
Figure 11.   X-ray patterns of oriented samples at $x_B = 0.5$ in system III (*a*) S_A phase; $T = 115°C$, (*b*) N phase; $T = 140°C$.

again prove the well-ordered layer structure of an S_A type (see figure 11 (*a*)) and its transition into the N phase (see figure 11 (*b*)).

Using the period of the density fluctuations in the nematic phase the diagram in figure 10 can be completed for mixtures with $x_B > 0.5$. It can be seen that the d values start to decrease in a concentration region in which the smectic phase disappears in the phase diagram. Extrapolation of the values yields for $x_B = 1$ again the d^A value of the right hand compound (d_B^A value).

4.   Discussion

The starting point in the discussion of a structural model is the fact that different parts of the molecule require different cross sections. This necessarily leads to difficulties if a dense layer packing of S_A type is to be generated with molecules of such kind. Additional assumptions are necessary to prevent a great number of holes in the layers. For compounds containing polar groups an irregular up-to-down alignment of the molecules must be assumed to prevent ferroelectric properties which have not been observed in this case [8].

The most remarkable experimental result is the great difference between the length of the molecules and the measured layer thickness d^A. Especially for the lower members of the series $n R_1$ ($n = 5, n = 6$) have unexpected high differences been observed. Therefore a model is postulated, shown in figure 12, in which the alkyl chains are interdigitated. The molecular shape used in figure 12 is taken from the envelope of a CPK model of $8 R_1$. By the interdigitation the difference $\Delta (\equiv L - d^A)$ can be explained.
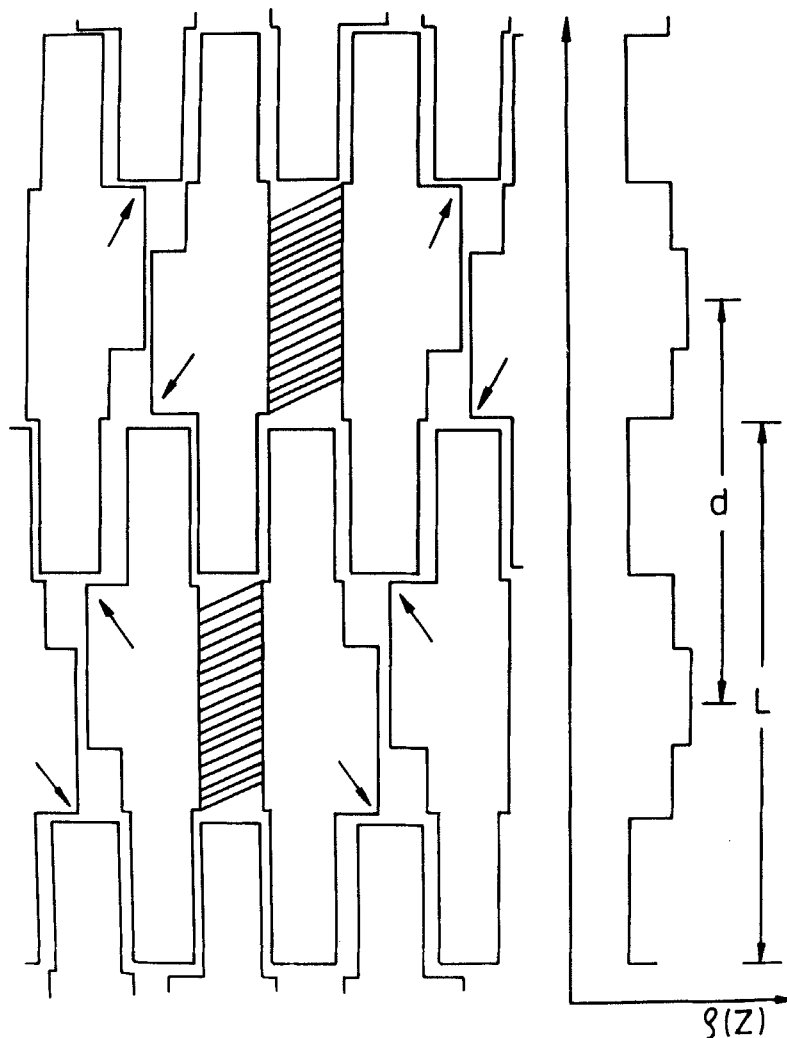
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Figure 12. Proposed structural model together with a sketch of the electron density distribution, $\rho(z)$.

However, an analysis of the d^A values as a function of the chain length points at the incompleteness of the proposed model. The increase of d^A is 0·174 nm for two methylene groups instead of 0·125 nm expected for fully interdigitated chains. Considering only this result a model based on completely disordered chains could be assumed to explain the difference between L and d. However, the patterns of oriented samples suggest an order parameter similar to that found in conventional S_A phases. That is in agreement with results of NMR measurements [6] according to which the observed order parameter is not exceptionally small. Therefore a model with interdigitated chains is prefered to explain the observed results.

Furthermore the model is supported by the result found for binary systems. The host structure of the laterally branched compound contains, according to our model, a certain number of holes (dashed regions in figure 12). As far as the length of the admixed

molecules is greater than the remaining holes the d^A values of the mixtures behave additively with concentration. Both sorts of molecules are incorporated into the same layers and the d^A values of both components are the fundamental lengths leading to equation (1). If the length of the admixed compound is comparable with the length of the holes the latter are filled by guest molecules and, in consequence, the d^A values of the host structure are kept constant over a great concentration region. The results under discussion are similar to recently published investigations in which by filling gaps between bi-swallow-tailed compounds S_A phases are induced in binary systems [9, 10]. A non-linear behaviour of the apparent length on the concentration has also been observed in nematic mixed phases of biforked and rod-like molecules [11].

References

[1] DEMUS, D., DIELE, S., HAUSER, H., LATIF, I., SELBMANN, Ch., and WEISSFLOG, W., 1985, *Cryst. Res. Technol.*, **20**, 1547.
[2] DIELE, S., ROTH, K., and DEMUS, D., 1986, *Cryst. Res. Technol.*, **21**, 97.
[3] WEISSFLOG, W., and DEMUS, D., 1985, *Molec. Crystals liq. Crystals*, **129**, 235.
[4] WEISSFLOG, W., and DEMUS, D., 1989, *Liq. Crystals*, **5**, 111.
[5] DIELE, S., WEISSFLOG, W., PELZL, G., MAHNKE, H., and DEMUS, D., 1986, *Liq. Crystals*, **1**, 101.
[6] GRANDE, S., (private communication). SINGH, H. K., 1987, Dissertation (Leipzig).
[7] DIELE, S., and SACKMANN, H., 1989, *Ber. Bunsenges. phys. Chem.*, **93**, 467.
[8] KRESSE, H., and WEISSFLOG, W., 1988, *Phys. Stat. Sol. (a)*, **106**, K 89.
[9] DIELE, S., PELZL, G., WEISSFLOG, W., and DEMUS, D., 1989, *Liq. Crystals*, **3**, 1047.
[10] PELZL, G., HUMKE, A., DIELE, S., DEMUS, D., and WEISSFLOG, W., 1990, *Liq. Crystals*, **8**, 765.
[11] LEVELUT, A. M., FANG, Y., and DESTRADE, C., 1989, *Liq. Crystals*, **4**, 441.