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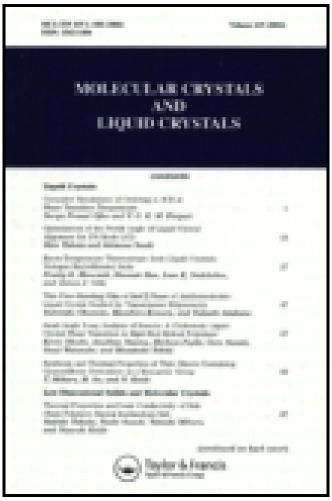

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Induction of Smectic A Phases and Cubic Phases in Binary Systems of New Hexacatenar Substances

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INDUCTION OF SMECTIC A PHASES AND CUBIC PHASES IN BINARY SYSTEMS OF NEW HEXACATENAR SUBSTANCES

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Abstract It is shown that in binary systems of hexacatenar (phasmidic) compounds with relatively short rod-shaped compounds smectic A phases can be induced provided that the rod-like component acts as an electron acceptor and the hexacatenar compound is a weak electron donator.
According to X-ray investigations the stabilization of the smectic layer structure is due to the incorporation of the short rod-like molecules within the gaps between the terminal branches of the phasmidic molecules. In two binary systems the phase region of the induced smectic A phase and the region of the columnar phase is separated by an induced cubic phase.

INTRODUCTION

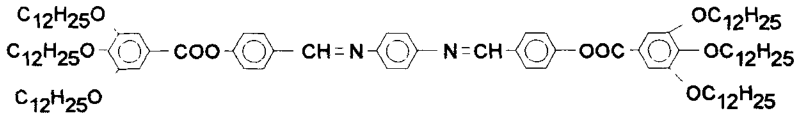
Bi-swallow-tailed compounds are polycatenar compounds where the terminal branches are fixed at terminal groups like -CH=C(COOR)$_2$ [1]. These compounds generally form nematic phases and smectic C phases. Derivatives with six benzene rings in the core show, in addition, also rectangular columnar phases [2].
If sufficiently short rod-like molecules are admixed to the bi-swallow-tailed molecules smectic A phases are induced, which are designated as "filled smectic A phases" because the rod-like molecules are considered to occupy the gaps between the aromatic cores of the double swallow-tailed mesogens.
Up to now such a behaviour could not be detected for biforked or phasmidic polycatenar substances in which the terminal branches are directly substituted at the terminal benzene rings [5, 6]. The reason can be that the molecular shape much more deviates from the rod-like shape than that of the bi-swallow-tailed molecules. It can be explained by a higher repulsive interaction at the ends of the molecules in comparison with the attractive forces between the aromatic moities, so that the gaps in the middle part of the

orthogonally arranged molecules in the smectic layers are too large. The question arises if filled smectic A phases can be induced by an additional lateral interaction, e.g. electron-donator-acceptor (EDA) interaction. Therefore as mixing components of the phasmidic compounds rod-like electron acceptor compounds were selected.

2. MATERIALS

As polycatenar component we used a five-ring (1) and six-ring hexacatenar compound (2)

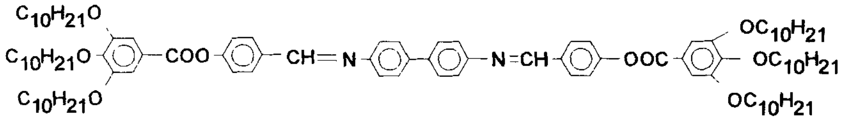
1



$$C \xrightarrow[99{,}0\ \mathrm{kJmol^{-1}}]{108\ ^{\circ}C} I^{7}$$

L*: 62.4 Å

2



$$C \xrightarrow[57{,}3\ \mathrm{kJmol^{-1}}]{82\ ^{\circ}C} D_{ob} \xleftrightarrow[3{,}4\ \mathrm{kJmol^{-1}}]{148^{\circ}C} I^{7}$$

L*: 62.4 Å

The transition temperatures were determined by polarizing microscopy as well as by calorimetric measurements (DSC 7, Perkin-Elmer).

Synthetic route:

Compounds 1 and 2 were prepared starting with the alkylation of methyl 3,4,5-trihydroxybenzoate (I) followed by saponification with potassium hydroxide.

Esterfication of 4-hydroxybenzaldehyde with the substituted benzoic acids (III) yielded the 4-(3,4,5-trialkyloxybenzoyloxy)benzadehydes (IV). The polycatenar substances 1 and 2 were synthesized by condensation of (IV) with 1,4-diaminobenzene or 4,4'-diaminobiphenyl, respectively.

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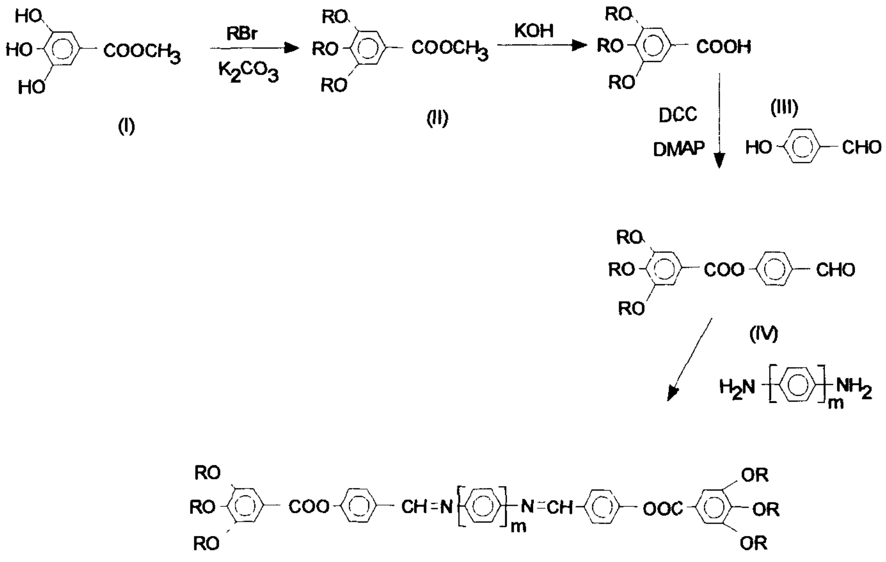
*L = molecular length of the most stretched conformation



1,2

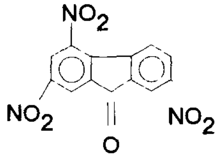
m = 1 R = $-C_{12}H_{25}$ (1)

m = 2 R = $-C_{10}H_{21}$ (2)

It is seen from the transition scheme that the five-ring compound does not exhibit a liquid-crystalline phase whereas the six-ring compound forms a columnar phase.

As rod-like mixing components acting as electron acceptors we used trinitrofluorenone (3) (TNF) and 4-n-butyloxyphenyl 4'-nitrocinnamate (4).

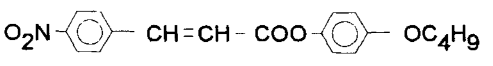
3



L:14,8 Å

$$C \xrightarrow{175\,°C} I$$

4



$O_2N-C_6H_4-CH=CH-COO-C_6H_4-OC_4H_9$

L: 22.4 Å

$$\begin{tikzcd}
C \arrow[rr, "128\,°C"] & & I\;[8] \arrow[dl, "124\,°C"] \\
& N \arrow[ul] &
\end{tikzcd}$$

Contrary to TNF 4-n-butyloxyphenyl 4'-nitrocinnamate exhibit a metastable nematic phase.

3. EXPERIMENTAL

The isobaric phase diagrams were studied using a polarizing microscope by means of the contact method [9] and by determination of the transition temperatures of mixtures with known concentration. For some selected mixtures the phase transition temperatures were measured by differential scanning calorimetry (DSC 7, Perkin Elmer). X-ray investigations have been performed with a Guinier camera or a Guinier-Goniometer.

4. RESULTS

In Figure 1 the phase diagram of the non-mesogenic polycatenar compound 1 with the electron-acceptor compound 3 (TNF) is presented. Although both components of the mixture do not exhibit liquid crystalline phases, in the mixed phase region liquid crystalline phases are induced. At middle concentration a columnar phase appears in the supercooled state.

The structure of this phase could not be identified because this monotropic phase crystallizes immediately after formation from the isotropic liquid. At high concentration of TNF an induced smectic A phase occurs which is metastable with respect to the solid state. It follows from X-ray investigations that the d-value of this metastable smectic A phase is clearly higher than the average molecular length L which can be calculated by

$$L = x_A L_A + x_B L_B$$

x_A, x_B: molar fractions of the components A and B, respectively

L_A, L_B: molecular lengths of the components A and B, respectively

For concentrations $x_{TNF} = 0.87$ and 0.83 the ratio d/L was found to be 1.98 and 1.96, respectively.

It is seen from the phase diagram that the smectic A phase disappears at 161 °C in a three-phase equilibrium reaction whereby two liquid phases are formed. This demixing in the isotropic liquid state is visible in the contact preparation as well as in samples of singular concentration. It is surprising that in a concentration region in which a demixing of the isotropic liquid occurs, there is no mixing gap in the S_A phase region.

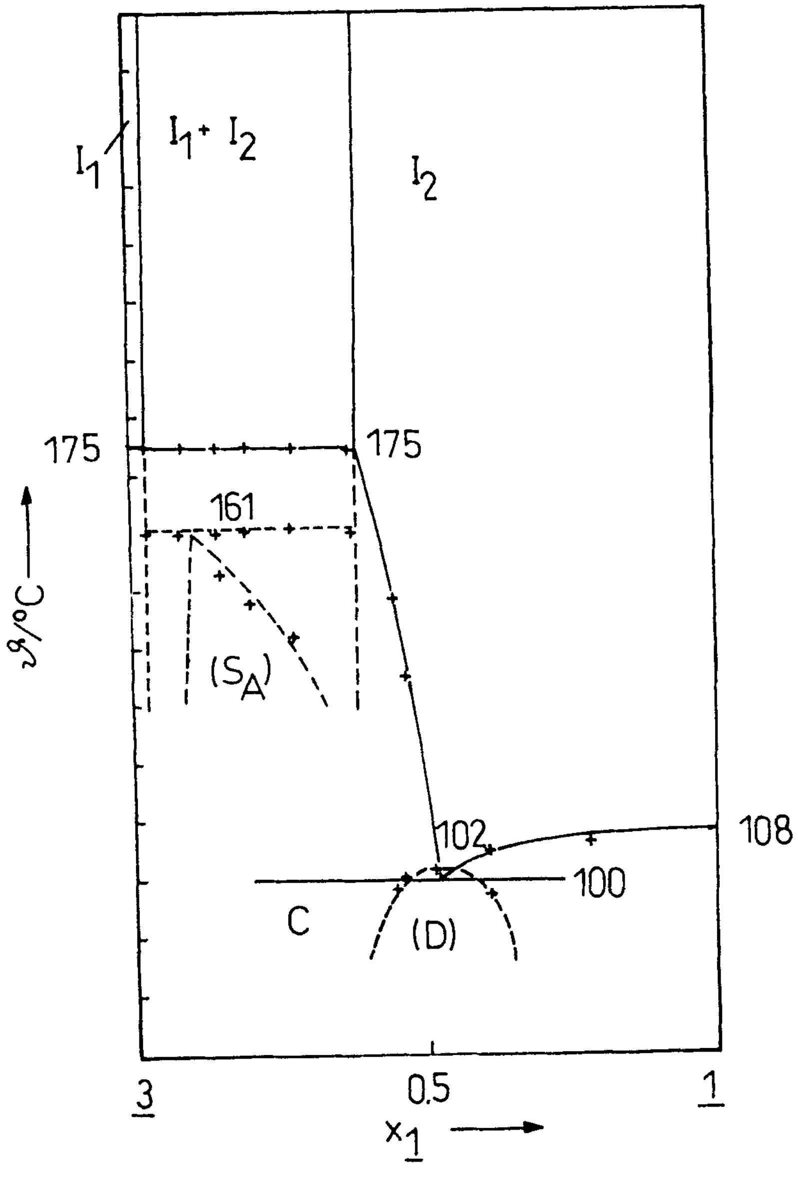


FIGURE 1 The isobaric phase diagram of the binary system of components 3/1 (x = molar fraction); dotted lines correspond to transitions in the supercooled state

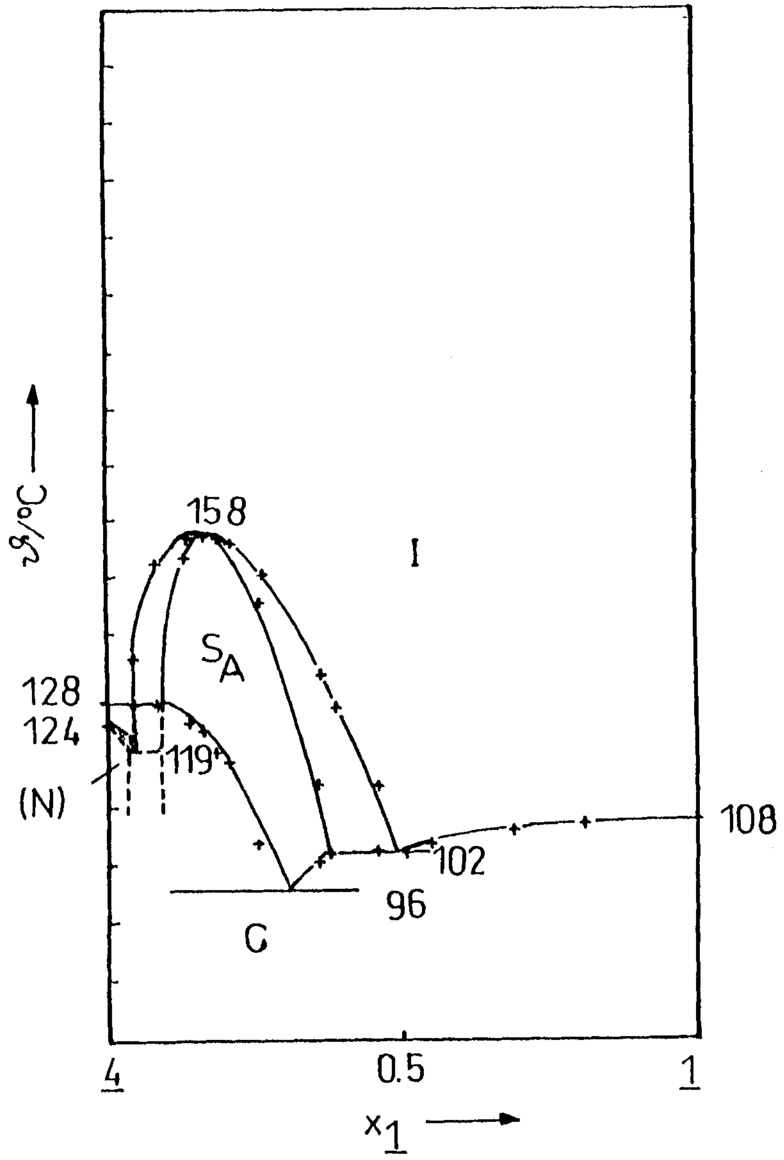


FIGURE 2 The isobaric phase diagram of the binary system of components 4/1

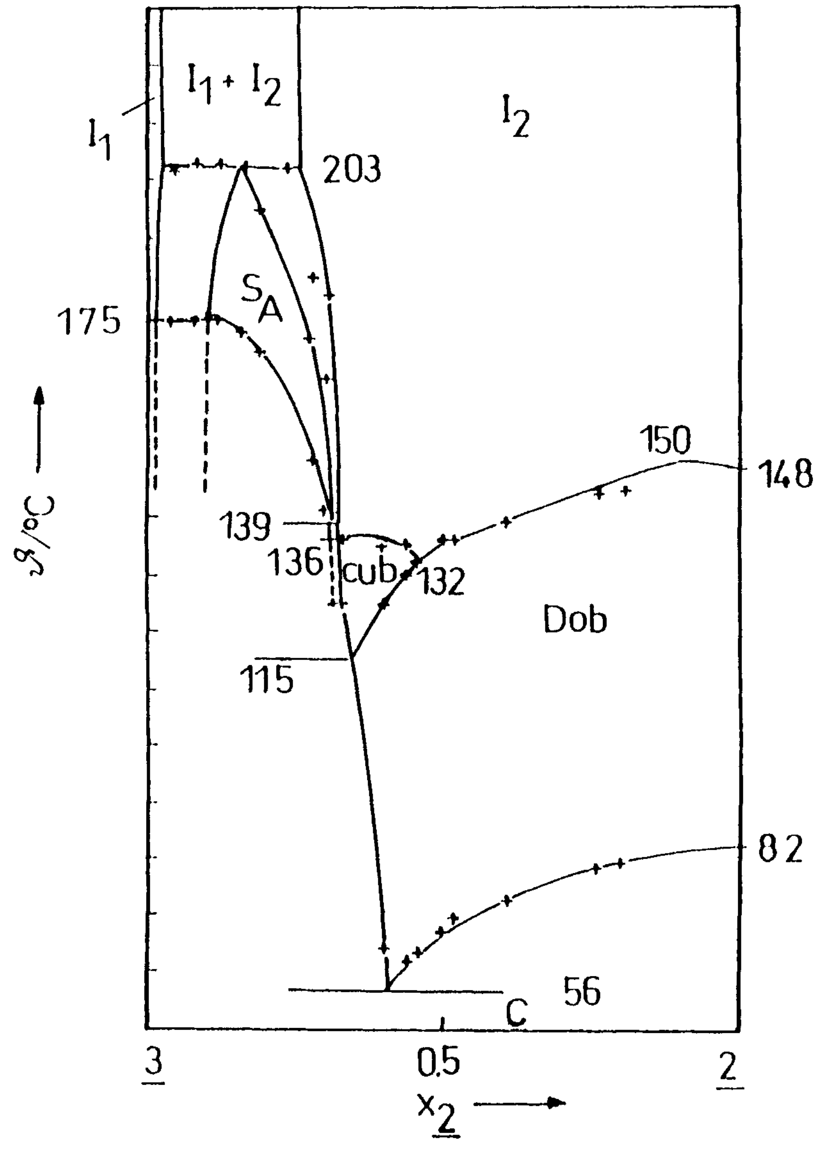


FIGURE 3 The isobaric phase diagram of the binary system of components 3/2

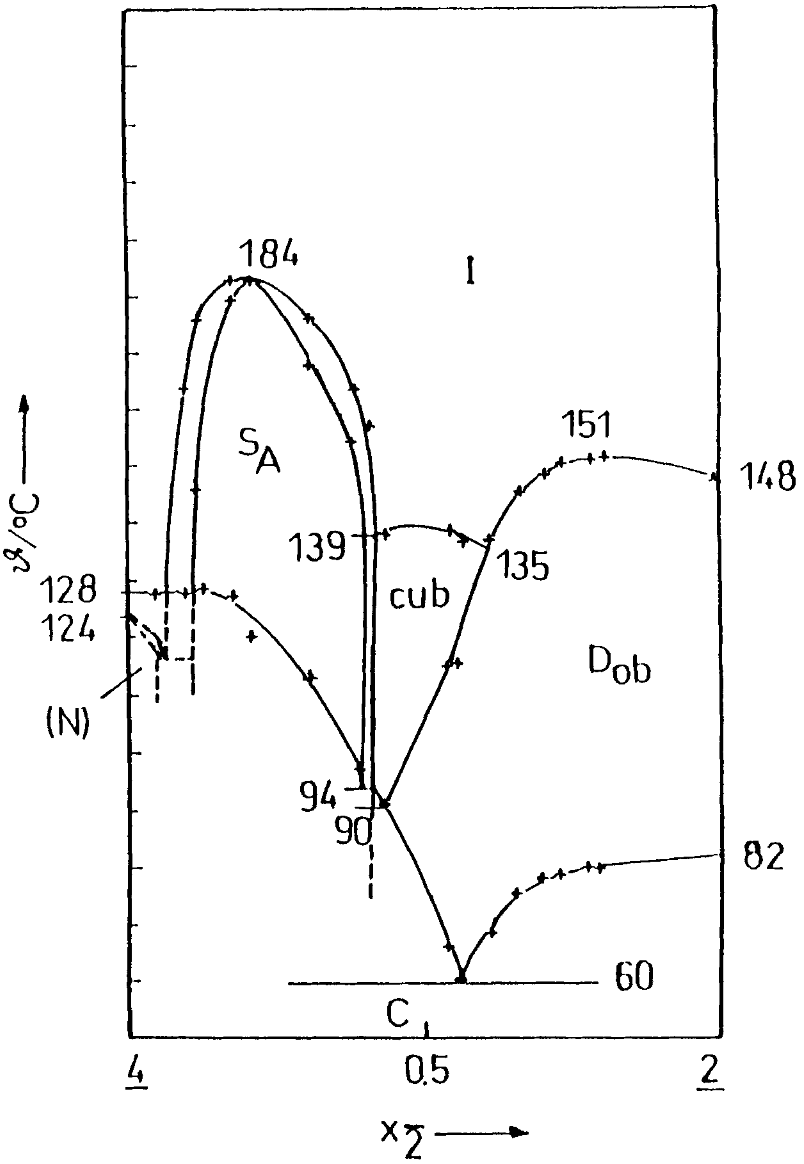


FIGURE 4 The isobaric phase diagram of the binary system of components 4/2

In the binary system of Figure 2 TNF is replaced by the other electron acceptor compound 4 which is characterized by a more elongated molecular shape. Contrary to the system 3/1 (Figure 1) an induced columnar phase could not be observed, furthermore, there is no mixing gap in the isotropic liquid state. Similar to the system 3/1 also in the system 4/1 a smectic A phase is induced between about 90 and 65 mole % acceptor compound. This induced smectic A phase is stable, the maximum of the smectic A-isotropic transition curve (at about 80 mole % of compound 4)) lies at 158 °C. The ratio d/L for $x(4) = 0.81$ is found to be 1.47.

Figures 3 and 4 present the phase diagrams of the six-ring hexacatenar compound 2 with the electron acceptor compounds 3 and 4, respectively.

It should be noted that the hexacatenar compound 2 possesses a columnar phase. The identification of the columnar phase was performed by X-ray investigations. The X-ray diffraction pattern (95 °C) obtained by a Guinier goniometer exhibits a diffuse scattering in the wide angle region and four sharp reflexes in the small angle region (see Figure 5). These four reflections could be undoubtless detected also by means of film methods.

The X-ray data can be described by an oblique columnar structure (D_{ob}).

The comparison of the phase diagrams in Figures 3 and 4 shows that the topology of both diagrams is quite similar. In both systems the oblique columnar phase of the hexacatenar compound is extended over a relatively great concentration range. The other common feature of the diagrams is the pronounced stabilization of the smectic A phase at higher concentrations of the electron acceptor compound. For the system 4/2 a maximum in the smectic A-isotropic transition curve (at about 80 mole % of compound 4) is found, but for the system 3/2 the smectic A phase is transformed at a three-phase equilibrium at 203° C into two isotropic liquid phases - similar to the finding in the system 3/1.

A further characteristic of both phase diagrams is that the phase regions of the smectic A phase and the columnar D_{ob} phase are separated by a cubic phase. The transition between the cubic mesophase and the isotropic liquid phase can be detected by microscopical as well as calorimetric investigations. The phase transition enthalpy is in the order of 1 $kJmol^{-1}$.

Similar to the smectic A phases in the systems 3/1 and 4/1 also in the systems 3/2 and 4/2 the d-value is clearly higher than the average molecular length L. For the system 4/2 the d/L ratio was found to be 1.59 for $x(4) = 0.81$. For the system 3/2 Table 1 shows the d/L ratio in dependence of the concentration. According to Table 1 at high concentration of TNF d/L is nearly 2 and decreases with decreasing concentration of TNF.

It should be noted that the d-values in the smectic A phase are nearly independent on the temperature.

reflections	$\Theta_{meas.}$ (deg.)	d-value (nm)	$\Theta_{calc.}$ (deg.)	indexing
A	1,07	4,12	/	(10)
B	1,74	2,54	/	(11)
C	1,86	2,37	/	(01)
D	2,15	2,05	2,15	(20)
E	9,92	0,45	/	d_{Alkyl}

lattice parameters : a = 4,49 nm; b = 2,58 nm; γ = 66,7°

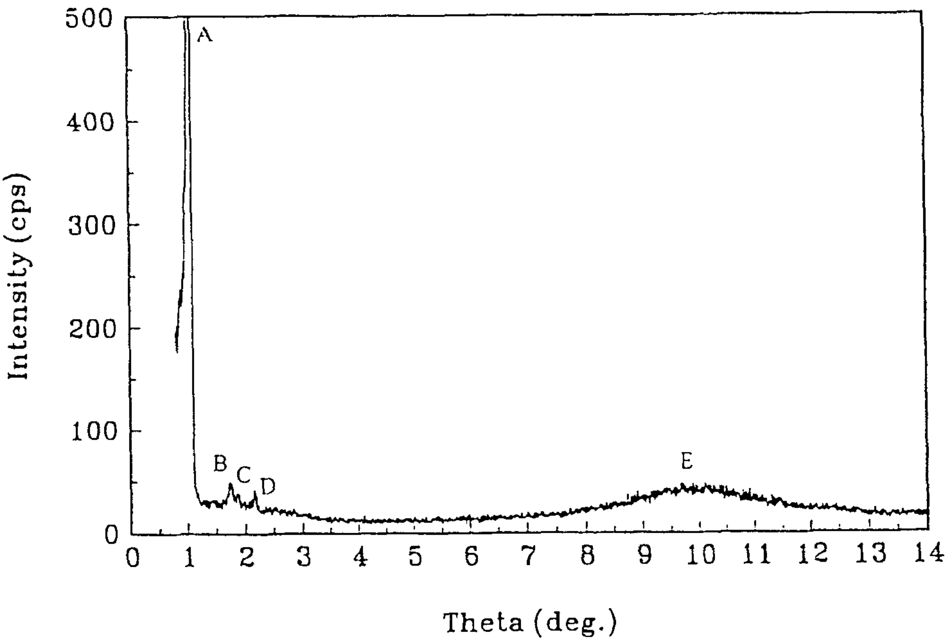


FIGURE 5 X-ray diffraction pattern of the columnar mesophase of compound 2 (95 °C)

TABLE 1 Ratio d/L in dependence of the molar fraction of TNF

x (TNF)	d/L
0.83	1.98
0.81	2.05
0.72	1.74
0.67	1.49

5. DISCUSSION

In general, in smectic A mixed phases the layer spacing d is nearly the average of the molecular lengths of the components even if their lengths are quite different [10].

In most cases the experimental d-value is somewhat lower than the molecular length because the terminal alkyl chains of the molecules do not exist in the most stretched conformation. Exceptions from the additivity rule were found if the components of the mixture possess structural features, such as terminal dipole moments [11] or a special molecular shape [12].

In the case of the smectic A mixed phases presented here the $d > L$ is obviously the result of the special steric situation within the smectic layers. The d-values are in the same order of magnitude although the length of the mixing components are quite different. The short molecules (3, 4) are preferably incorparated into the gaps between the aromatic cores of the phasmidic molecules A. By this incorporation the number of the "independent" rod-like molecules within the smectic layer are reduced, so that the effective molar fraction of both components representing different translational periods is changed: the molar fraction of the short molecules should decrease whereas the molar fraction of the phasmidic molecules should increase. Considering the additivity equation, the d-value should become greater than the averaged molecular length L. The unusual high d/L ratio for the systems 3/1 and 3/2 can be explained by the fact that probably two TNF molecules fit in each gaps between the aromatic cores because the length of the gaps (25 Å and 29 Å for the compounds 1 and 2, respectively) is about twice the length of a TNF molecule[4].

It is obvious, that the proposed packing model is a rough static model which cannot completely reflect the reality. Nevertheless, the results of the X-ray investigations indicate that also in the case of hexacatenar substances the induction of lamellar smectic A phases is possible if the steric interaction is supported by an additional lateral attraction. This is plausible because the phasmidic molecules (1, 2) much more deviates from the rod-like shape than the bi-swallow-tailed molecules. This additional cohesion is achieved by EDA interaction between the rod-like acceptor molecules and the phasmidic molecules acting as weak electron donors. It should be emphasized that an induction of S_A phases could not be detected if the phasmidic molecules do not exhibit an azomethine group and if the incorporated rod-like molecules do not possess pronounced electron acceptor properties. The EDA interaction is indicated by a dark-red colour of the mixed phases whereas the single compounds are nearly colourless and yellow, respectively. This colour change is much more pronounced in the binary systems of TNF (3/1, 3/2) pointing to a stronger EDA interaction.

It is not clear why the phase regions of the smectic A phase and of the D_{ob} phase have not a common borderline but are separated by a cubic mesophase (Figure 3 and 4). To our knowledge, up to now for hexacatenar substances never a transition between a smectic A and a columnar phase was found. But, otherwise, in phase diagrams of lyotropic systems the phase regions of the lamellar L_α phase and the columnar phases are often separated by a region of a cubic phase [13].

It is not unusual that mixtures of strongly and weakly polar liquids show partial demixing. In the phenomenological thermodynamic this demixing can be described by the characteristic behaviour of the free excess enthalpy in dependence of the concentration. But for definite systems it is difficult to interprete the macroscopic properties on the base of molecular interaction.

It is a striking feature of the binary systems 3/1 and 3/2 that in the isotropic liquid state a partial demixing occurs whereas in the smectic phase at the same concentrations no demixing is observed. Obviously the transition from the isotropic liquid into the smectic A phase is accompanied by a significant increase of molecular interaction - steric interaction as well as EDA interaction. This can be the reason why in the smectic state demixing does not occur contrary to the isotropic liquid.

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REFERENCES

1. W.Weissflog, A.Wiegeleben, S.Diele and D.Demus, Cryst. Res. Technol, 19, 983(1984)
2. S.Diele, K.Ziebarth, G.Pelzl, and D.Demus, Liq. Crystals, 8, 211(1990)
3. S.Diele, G.Pelzl, W.Weissflog, and D.Demus Liq. Crystals, 3, 1047(1988)
4. G.Pelzl, S.Diele, K.Ziebarth, W.Weissflog, and D.Demus Liq. Crystals, 8, 765 (1990)
5. J.Malthete, A.M.Levelut, and H.T.Nguyen J.Phys.Lett. (Paris), 46, L-875 (1985)
6. J.Malthete, H.T.Nguyen, and A.M.Levelut, J.Chem.Soc., Chem.Commun., 1549(1986)
7. I.Letko, U.Nütz, W.Weissflog, S.Diele, and G.Pelzl Proceedings of the Freiburger Arbeitstagung Flüssigkristalle, P38(1994)
8. F.Kuschel, and D.Demus Z.Chem., 15, 350(1975)
9. H.Sackmann, and D.Demus, Z. phys. Chem., 222, 143(1963)
10. S.Diele, and H.Sackmann Ber.Bunsenges. Phys. Chem., 93, 467(1989)
11. J.E.Lydon, and C.J.Coakley J.Phys. (Paris), C1-36, 45(1975)
12. S.Diele, A.Maedicke, K.Knauft, I.Neutzler, W.Weissflog, and D.Demus Liq. Crystals, 10, 47(1991)
13. J.Charvolin, Mol.Cryst.Liq.Cryst. 198,145(1991)