Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Diele, S. , Pelzl, G. , Weissflog, W. and Demus, D.(1988) 'A filled smectic A phase A novel kind of induced smectic A phase observed for binary mixtures', Liquid Crystals, 3: 8, 1047 — 1053
To link to this Article: DOI: 10.1080/02678298808086561
URL: http://dx.doi.org/10.1080/02678298808086561

LIQUID CRYSTALS, 1988, VOL. 3, NO. 8, 1047–1053

A filled smectic A phase

A novel kind of induced smectic A phase observed for binary mixtures

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(*Received 4 January 1988; accepted 5 March 1988*)

We present the phase diagram of a binary system of two nematogenic terminal, non-polar compounds in which an induced smectic A phase appears over a large concentration–temperature range. X-ray measurements give evidence that the layer spacing, d, of this induced smectic A phase is clearly larger than the average molecular length, L (d/L: 1·12 . . . 1·23). The unusual experimental results are interpreted on the basis of a pronounced steric interaction by which gaps between the large double swallow-tailed compounds are filled with small molecules. We propose the term *filled smectic A phase* for this new type of induced phase.

1. Introduction

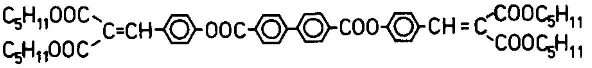
Liquid-crystalline swallow-tailed compounds are substances with long-chain substituents branched outside the ring system [1, 2]. In our experiments, we used a member of the homologous series, the 4,4-bis[di-*n*-alkyl 4-carbonyloxybenzylidenemalonate]-biphenyls [2]; these four-ring compounds possess four terminal alkyl chains. The early members of this series exhibit nematic behaviour only; the higher homologues (pentyl and above) have additional metastable smectic C phases. The clearing temperatures of this series show the usual decreasing trend with increasing chain length; this is obviously due to the increasing number of gauche conformers as the alkyl chains are increased in length [2]. The members with long alkyl chains exhibit liquid-crystalline behaviour at relatively low temperatures which are comparable with those of certain two- or three-ring compounds. In consequence, such swallow-tailed compounds may be used to study the influence of steric factors on the packing of molecules in smectic layers of binary mixtures.

In preliminary investigations we have found that binary mixtures of the intermediate members of this series with two- or three-ring compounds of quite different chemical structure exhibit stable induced smectic A phases. Here we present one representative example of such a binary system. In order to obtain structural information on the system, we have performed X-ray investigations on the individual components as well as on selected mixtures.

2. Materials

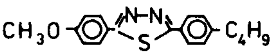
The structures and transition temperatures of the compounds, A and B, which we have used are

A:



C 95°C (S_C 61°C) N 151°C I [2]

B:



C 96°C N 196°C I [3]

3. Experimental

The phase diagram was established using polarizing microscopy by means of the contact method [4] and the determination of transition temperatures of selected mixtures of known concentrations. The layer spacings (*d* values) of the smectic phases were measured by X-ray diffraction using small-angle equipment as well as a Guinier camera. Patterns of oriented samples were obtained by cooling the sample in a magnetic field of about 1·2 T.

4. Experimental results

4.1. *The single components*

The X-ray diffraction pattern of the nematic phase of component A shows several orders of diffuse scattering maxima on the meridian as well as an outer, crescent shaped scattering on the equator; the intensity of the third order reflection is remarkably enhanced. Cooling the sample to temperatures below 90°C, the pattern shows the appearance of cybotactic groups (see figure 1 (*a*)). From the positions of the four diffuse maxima, the thickness (*d*) of a cybotactic group is estimated to be 3·9 nm. The normal of the group is inclined at an angle of about 28° to the director. Using these values, the length of the building units of the cybotactic group is calculated to be 4·4 nm which is in agreement with the length of the molecule (L = 4·3 nm). It should be emphasized that the period *d* of 3·8 nm resulting from the scattering vector of the diffuse scattering on the meridian is incommensurable with the molecular length. This can be explained, however, by the existence of strings of molecules which are shifted with respect to each other by the length of one swallow tail part; this structure is sketched in figure 2. Such a structure explains both the formation of cybotactic groups and the observation of metastable S_C phases; it may be stabilized by the greater packing efficiency of the molecules.

The X-ray diffraction pattern of compound B (see figure 1 (*e*)) also clearly indicates the existence of skewed cybotactic groups in the nematic phase; although, this compound does not exhibit a smectic C phase. The four diffuse maxima permit only an approximate estimate of the structural parameters. The thickness of the cybotactic groups is estimated to be 1·9 nm; the tilt angle of the normal of the groups with respect to the field direction is approximately 37°. The length of the building unit calculated using these values is (2·3 ± 0·1 nm) and this is in satisfactory agreement with the length of B (L_B = 2·18 nm).

4.2. *The binary system*

Figure 3 shows the phase diagram of the binary system; although both components form only stable nematic phases, a very pronounced smectic A phase region is induced over a relatively large concentration–temperature region. For example, in

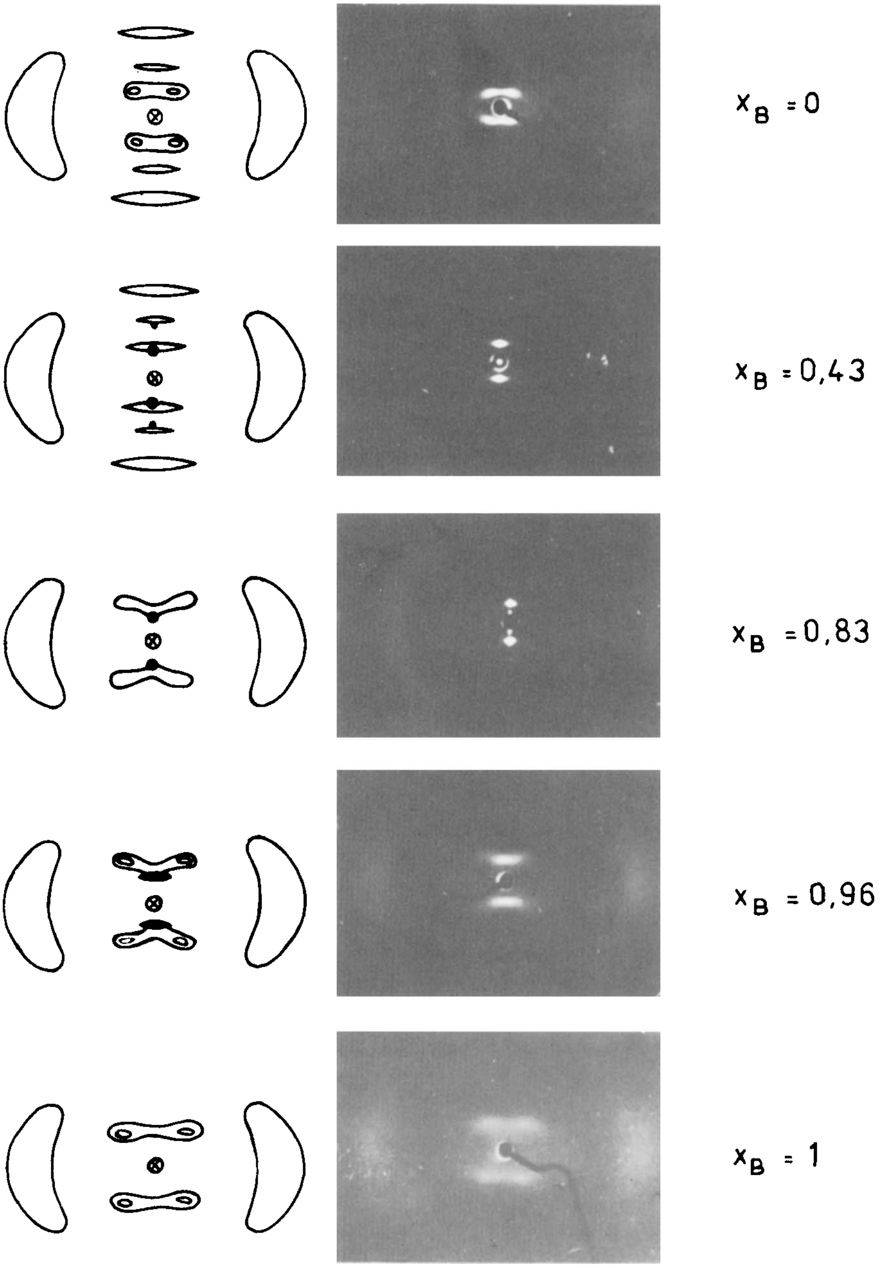


Figure 1. X-ray diffraction patterns of oriented samples together with their schematic drawings: (*a*) nematic phase, $\vartheta = 95°C$; (*b*) smectic A phase, $\vartheta = 95°C$; (*c*) smectic A phase, $\vartheta = 95°C$; (*d*) nematic phase, $\vartheta = 115°C$; (*e*) nematic phase, $\vartheta = 98°C$. The magnetic field is parallel to the meridian (vertical direction).

the mixture containing 65 mol % B a stable smectic A phase exists between 48°C and 183°C. The metastable smectic C phase of component A generates a smectic C mixed phase region with an increasing smectic C–nematic transition curve. At intermediate concentrations the smectic C phase lies in the stable region.

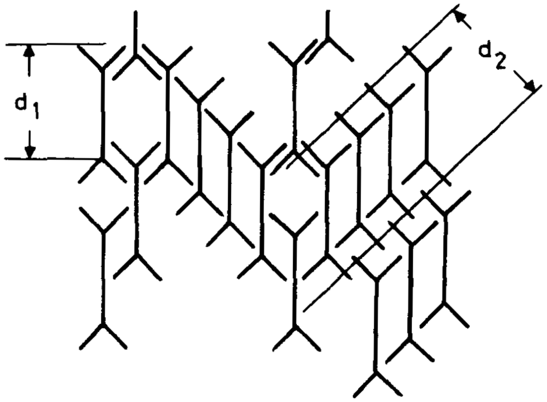


Figure 2. Schematic representation of cybotactic groups in the nematic phase of component A which explain the different density waves. It is not drawn to scale.

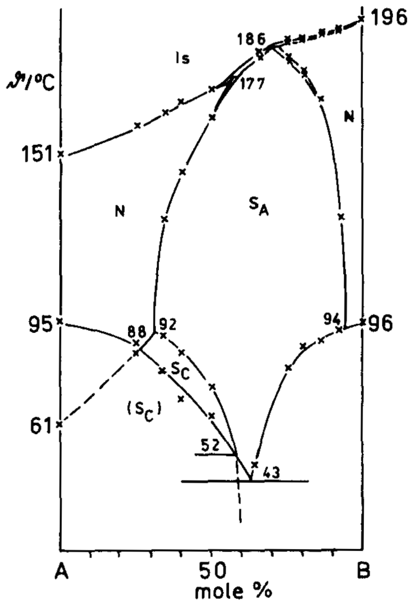


Figure 3. The composition-temperature phase diagram for the binary system of the components shown.

X-ray diffraction studies have been performed on mixtures with the mole fractions of component B equal to: 0·4; 0·43; 0·65; 0·75; 0·8; 0·83; and 0·96. The patterns of oriented samples (see figures 1 (*b*)–1 (*d*)) exhibit the characteristic features of the smectic A phase: a strong Bragg spot and its second order indicating the layer structure, together with the diffuse outer scattering maxima in a plane perpendicular to the Bragg spots. However, additional diffuse scattering maxima have been detected, the position of which changes with increasing concentration of the second component. Comparing the schematic drawings of the patterns $x_B = 0{\cdot}43$ (see figure 1 (*b*)) and $x_B = 0{\cdot}83$ (see figure 1 (*c*)) with those of the patterns for $x_B = 0$ (see figure 1 (*a*)) and for $x_B = 1$ (see figure 1 (*e*)) respectively, reveals similarities with the pure compounds. For example, the density wave along the preferred direction, as discussed for component A, can be observed in the pattern of the mixture, $x_B = 0{\cdot}43$, and this has approximately the same period of 3·5 nm. In addition, the intensity of the third order reflection is very pronounced; this was also observed in the X-ray diffraction pattern of the mixture $x_B = 0$. The pattern of the mixture $x_B = 0{\cdot}83$ exhibits, in addition to the Bragg spots, four very weak diffuse maxima; their connection line forms an angle with the meridian of about 46°. These experimental findings are supported by the pattern of the mixture with $x_B = 0{\cdot}96$ which forms only a nematic phase; the pattern shows an enhanced diffuse inner scattering maximum as well as four diffuse maxima (see figure 1 (*d*)) which prove the connection between the scattering phenomena of the mixture, $x_B = 0{\cdot}83$, with that of component B (see figure 1 (*e*)).

The enhancement of the inner diffuse scattering maximum can be explained by the close proximity of the smectic region in the phase diagram; this effect has been found in other binary systems [5]. Figure 4 compares the thickness of the smectic layers, *d*, as a function of the concentration. The *d* values decrease nearly linearly with increasing concentration of component B. However, in contradiction to many other binary systems, the *d* values cannot be calculated from the molecular lengths, L_A and L_B, of the pure components using the simple additivity rule [6–9]

$$d = \bar{L} = x_A L_A + x_B L_B.$$

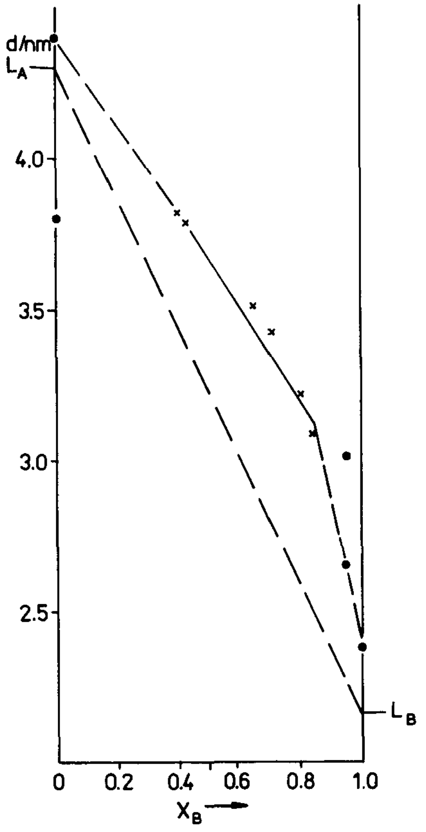


Figure 4. The dependence of the layer spacings upon the mol fraction of compound B. The crosses indicate the *d* values in the smectic A phase and the full circles correspond to the period of the density wave in the nematic phase. The values have been measured at $\vartheta = 100°C$ but they are nearly independent of temperature.

The ratio $d/\bar{L}$ ranges from values of 1·12 up to 1·23. This result must be caused by special steric interactions of the compounds under discussion.

5. Discussion

To our knowledge, only for one class of terminal non-polar compounds has a d/L ratio greater than unity been measured and for this particular case d/L was about 1·05 [10]. In the binary system presented here, the values of d/L greater than unity appear to result from the special molecular shape of the swallow-tailed compound. The swallow-tailed compounds with only one branched terminal chain exhibit both nematic and smectic A phases whereas the compounds with two terminal branched chains form nematic phases and the long chain homologues, in addition, show metastable smectic C phases [2]. This differing behaviour must result from the differing packing considerations of the molecules. If the molecules having two terminal branched chains are arranged so that the director is perpendicular to the smectic layer plane, shown in Figure 5 (*a*), then this results in unfavourable packing whereas the tilted alignment, sketched in figure 5 (*b*) allows a far greater packing efficiency of the molecules. However, the incorporation of shorter molecules into the free space between the bulky swallow-tailed ends of the molecules, in a certain concentration–temperature range, promotes the formation of smectic A phases with respect to the nematic phase. In such an arrangement the lateral interactions between the aromatic cores are enhanced. It is conceivable that in smectic layers stabilized by the incorporation of shorter molecules into the space between the swallow-tailed ends, the d value of the smectic A phase can be greater than the average molecule length $\bar{L}$.

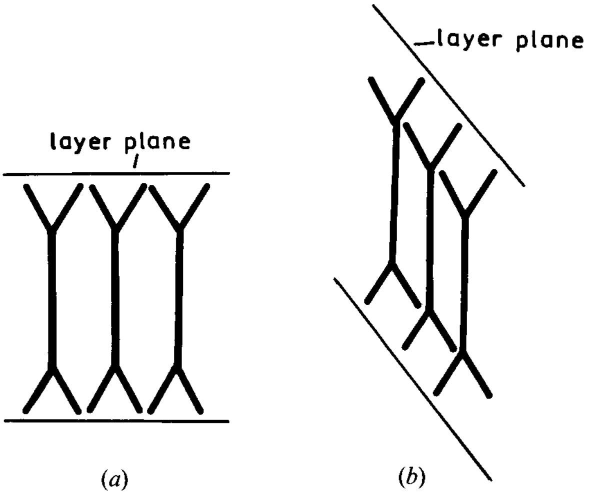


Figure 5. Schematic model of a smectic layer: (*a*) with a perpendicular arrangement; (*b*) with a tilted arrangement of the swallow-tailed molecules.

It is, however, very difficult to interpret the $d/\bar{L}$ ratios of greater than one quantitatively on the basis of a convincing structural model. The smectic layers are probably formed by three molecular units: swallow-tailed molecules with incorporated short molecules (as shown in figure 6), and single molecules of the components A and B.

Figure 6. Space-filling models showing the incorporation of a molecule of component B into the free space between the bulky swallow-tailed ends of the molecule of component A.

These experimental results are an impressive example of the strong influence of steric factors on the formation of smectic layer structures [11]. In future, it will be interesting to study in detail the connection between the size and shape of the incorporated short molecules and the smectic induction in similar binary systems.

We thank Professor Dr. H. Zaschke for providing compound B.

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