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

Filled smectic A phases in binary liquid-crystalline systems of terminal-nonpolar compounds. V. Smectic A phases with unusually high ratio of the layer spacing and the average molecular length

G. Pelzl[a]; S. Diele[a]; K. Ziebarth[a]; W. Weissflog[a]; D. Demus[a]
[a] Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, G.D.R. VEB Laborchemie Apolda, Leipzig, G.D.R

To cite this Article Pelzl, G. , Diele, S. , Ziebarth, K. , Weissflog, W. and Demus, D.(1990) 'Filled smectic A phases in binary liquid-crystalline systems of terminal-nonpolar compounds. V. Smectic A phases with unusually high ratio of the layer spacing and the average molecular length', Liquid Crystals, 8: 6, 765 — 773

To link to this Article: DOI: 10.1080/02678299008047387

URL: http://dx.doi.org/10.1080/02678299008047387

LIQUID CRYSTALS, 1990, VOL. 8, NO. 6, 765–773

Filled smectic A phases in binary liquid-crystalline systems of terminal-nonpolar compounds

V. Smectic A phases with unusually high ratio of the layer spacing and the average molecular length

by G. PELZL, S. DIELE, K. ZIEBARTH, W. WEISSFLOG† and D. DEMUS
Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, G.D.R.
† VEB Laborchemie Apolda, Betriebsteil Spezialchemie Leipzig, G.D.R.

(*Received 24 November 1989; accepted 7 June 1990*)

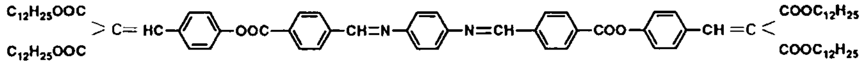
The phase diagrams of four binary systems are presented in which one component is a bi-swallow tailed compound and the second is a nematogenic rod-like compound. In all of the phase diagrams studied an induced smectic A phase occurs. According to X-ray measurements the layer spacing d of the smectic A phase is considerably higher than the average molecular length $\bar{L}$. Depending on the binary system and the concentration $d/\bar{L}$ ratios between 1·17 and 2·13 were found. We propose an interpretation of the results on the basis of a simple packing model.

1. Introduction

In binary systems of bi-swallow tailed compounds we have found induced S_A phases if the second component has a relatively short molecular length or possessed a bulky middle part [1–4]. The occurrence of such induced phases can be interpreted by a model in which the gaps between the terminal branches of the bi-swallow tailed compounds are filled with the whole molecule of the second component or with only the bulky middle part of a relatively long molecule. Therefore we have called this new kind of induced S_A phase a filled S_A phase. In this paper we present new examples of this topic where the influence of the filling component is studied for four representative compounds.

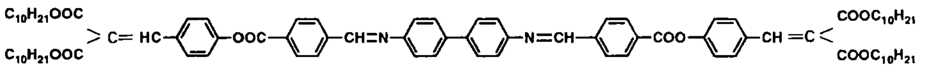
2. Materials

As bi-swallow tailed component we have used two new compounds which possess five and six aromatic rings; both compounds exhibit nematic as well as S_C phases. The six-ring bi-swallow tailed compound (B) forms a third liquid-crystalline phase on cooling the S_C phase. According to preliminary X-ray investigations this liquid-crystalline phase is a rectangular columnar phase [8].



(A)

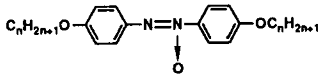
C 155°C S_C 163°C N 186·5°C I (L = 6·88 nm where L is the molecular length obtained from space filling models).



(B)

C 160°C rectangular columnar 210°C S_C 240°C N 268°C I (L = 6·83 nm).

The mixing components for the bi-swallow tailed compounds are members of the homologous 4,4′-bis-alkyloxyazoxybenzenes:



	n	C		S_C		N		I	L/nm
C1	1	●	118·5°C	–	–	●	135°C	●	1·76
C6	6	●	81°C	–	–	●	129°C	●	2·92
C12	12	●	81·7°C	●	122°C	–	–	●	4·44

3. The phase diagrams

The phase diagrams of binary mixtures were studied using a hot stage polarizing microscope by means of the contact method [5] and by determination of the transition temperatures of selected mixtures with known concentrations. In figures 1–3 the phase diagrams of such binary systems are presented in which the five-ring bi-swallow tailed compound (A) is mixed with three members of the homologous 4,4′-bis-alkyloxy-azoxybenzenes (C1, C6, C12). The characteristic feature of all of the diagrams is the occurrence of an induced S_A phase. For the methoxy compound (C1) the S_A phase region is restricted to a concentration interval of about 30 mole %, the maximum of the transition curve $S_A \rightarrow$ N lies at 25 mole % A (see figure 1).

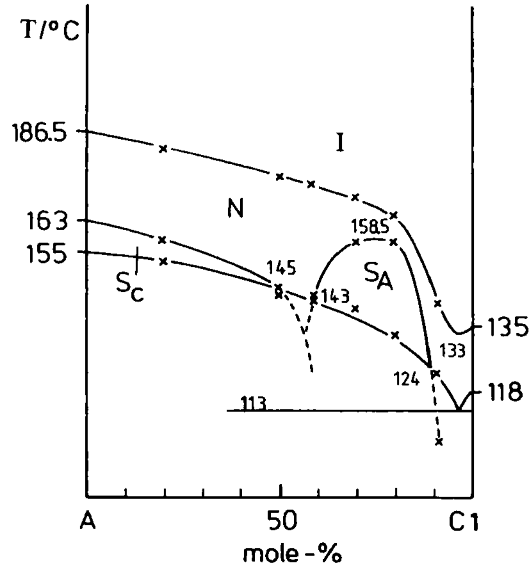


Figure 1. The composition–temperature phase diagram for the binary mixture with components A and C1. (Dotted lines indicate transitions in the supercooled state.)

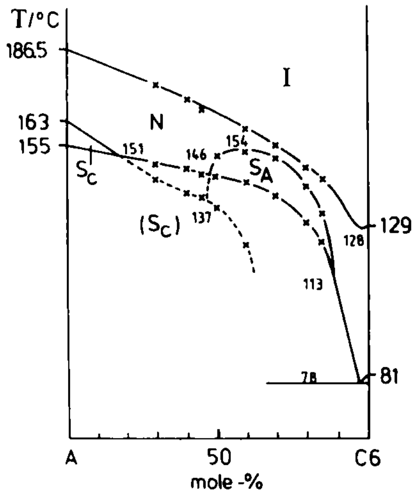


Figure 2. The composition–temperature phase diagram for the binary mixture with components A and C6. (Dotted lines indicate transitions in the supercooled state.)

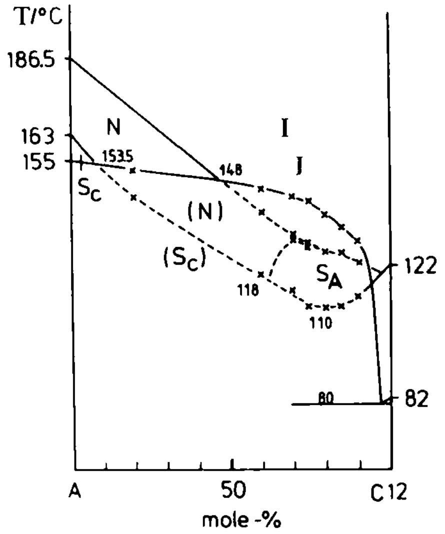


Figure 3. The composition–temperature phase diagram for the binary mixture with components A and C12. (Dotted lines indicate transitions in the supercooled state.)

For the hexyloxy compound (C6) the maximum is shifted to a higher concentration of component A (about 45 mole % A), but the extension on the concentration scale is about the same as for the system A/C1 (see figure 2). In the phase diagrams for the long chain homologue (C12) the induced S_A phase can be detected in the supercooled state. Its concentration interval, to a first approximation, agrees with that of the other systems. The S_C phases of both components are completely miscible. Over nearly the whole concentration range this S_C phase is metastable. The transition curve $S_C \rightarrow S_A$ shows a minimum at 20 mole % A. The maximum of the transition curve $S_A \rightarrow N$ is at about 30 mole % A. If in the binary system of figure 1 A/C1 the five-ring bi-swallow tailed component (A) is replaced by the corresponding six-ring compound

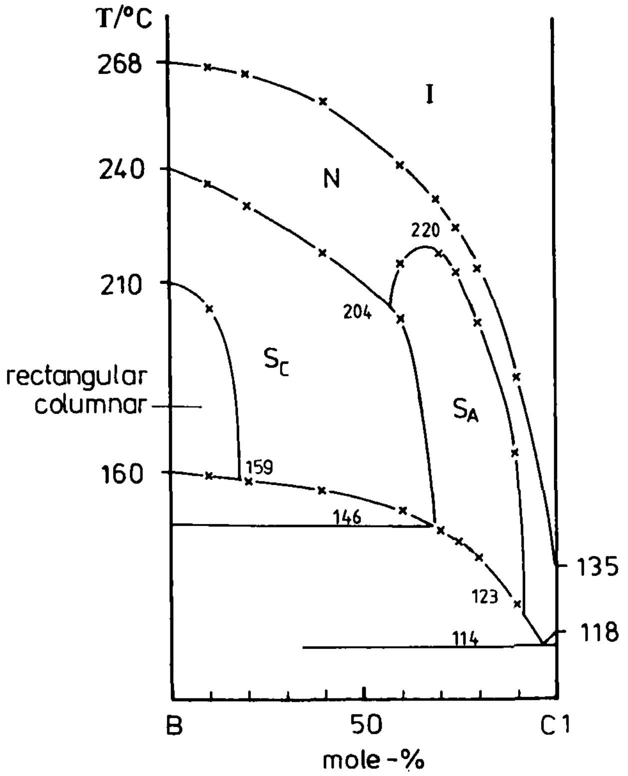


Figure 4. The transition-temperature phase diagram for the binary mixture with components B and C1.

(B) the type of diagram is not essentially changed (see figure 4). Also in this case a smectic A phase is induced in a concentration range between 57 and 92 mole % C1. Compared with the system A/C1 in the system B/C1 the maximum of the S_A phase region (~33 mole % A) is clearly enhanced. The columnar rectangular phase exists only at high concentrations of compound (B).

4. X-ray measurements

For some selected samples of the binary systems A/C1 and A/C6 the layer spacing, *d*, of the S_A phase was determined by X-ray investigations using small angle equipment. Unfortunately such measurements were impossible in the system A/C12 because the S_A phase exists only in the supercooled state.

For a mixture of 30 mole % A and 70 mole % C1 *d* was found to be 5·7 nm. The average molecule length $\bar{L}$ of the mixtures can be calculated according to

$$\bar{L} = x_A L_A + x_C L_C, \qquad (1)$$

x_A, x_C are the mole fractions, L_A, L_c are the molecular lengths of components (A) and (C) respectively. We found that $\bar{L}$ = 3·29 nm which is clearly smaller than the experimental smectic layer spacing so that an unusually high ratio $d/\bar{L}$ = 1·73 results. In addition for the binary systems A/C6 we found that *d* for the S_A phase is greater than $\bar{L}$ but the ratios are smaller than those for the system A/C1:

	d/nm	$\bar{L}$/nm	$d/\bar{L}$
46 mole % A	5·56	4·74	1·17
20 mole % A	5·23	3·71	1·41

It is seen that with an increasing amount of component C6 the ratio $d/\bar{L}$ clearly increases.

Also for two selected mixtures of the binary system B/C1 the layer spacing d was determined which is unexpectedly about twice the average molecular length:

	d/nm	$\bar{L}$	$d/\bar{L}$
30 mole % B	5·88	3·28	1·83
20 mole % B	6·00	2·70	2.13

5. Discussion

The following main experimental results have to be discussed and explained:

the induction of the S_A phases,

the non-additivity of the d values in the binary systems with partly unusually high $d/\bar{L}$ ratios

the concentrations of the maxima of the S_A phase regions in the different systems.

The induction of smectic phases in binary systems may be caused by several physical reasons, for example electron donor–acceptor interactions [9–11] and dipole–dipole interactions [12]. It should be emphasized that in the binary systems studied there is no indication of electron donor–acceptor or strong dipole–dipole interactions because the molecules of the components do not possess strongly polar substituents. Therefore we have to look for an alternative explanation for the non-additivity of the d values in the binary systems.

As already discussed in [1–4] the induction of the smectic A phase in the binary mixtures with bi-swallow tailed compounds is mainly due to a steric packing effect. The host structure of the swallow tailed molecules acts as a cage for the short rod-like molecules, which fill out the gaps between the bulky ends of the host molecules. Therefore these induced phases are called filled phases. It has been found that for a number of smectic A mixed phases the layer spacing is nearly the average of the molecular lengths of the components even if their lengths are quite different [6]

$$d = \bar{L}. \tag{2}$$

In many cases, the experimental layer spacing is somewhat lower than $\bar{L}$ because the terminal alkyl chains of the molecules do not exist in the most stretched (all-trans) conformation. Exceptions from this additivity rule were found for special systems, e.g. systems with terminal polar compounds. Because of the dimerization of the polar molecules the ratio $d/\bar{L}$ may have values from 1·1 to 2 [7]. In the binary systems under discussion ratios $d/\bar{L}$ have been found, which are significantly greater than unity (systems A/C1 or B/C1: 1·7 to 2·13; system A/C6: 1·17 to 1·4). It should be emphasized that the results of our X-ray investigations prove the homogeneous

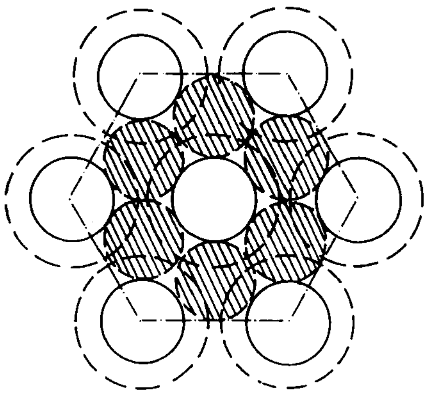


Figure 5. Schematic representation of the gaps in a smectic layer with two dimensional quasi-hexagonal packing. The cross sections of the different parts of the molecules (full lines = aromatic cores; dashed lines = swallow tails) are indicated by circles because of the rotational disorder on average around the molecular long axes. The hatched circles indicate the gaps.

character of the filled smectic A phases. Furthermore it has been proved by the outer diffuse scattering maximum that the lateral distances are caused by a statistical distribution, which is well known for smectic A phases. On the basis of the proposed packing model according to which the short molecules are incorporated in the free space between the swallow tailed molecules the result can be explained by a reduction of the single free C molecules within the layers. By this incorporation the effective mole fraction of both components representing different translation periods is changed: x_C should decrease to x'_C and x_A should increse to x'_A. Introducing these effective mole fractions x'_A and x'_C we can write

$$d = x'_A L_A + x'_C L_C. \tag{3}$$

This equation is able to explain the enlarged experimental d values.

In figure 5 the two dimensional packing of nearest neighbours is sketched. Because of the rotational disorder around the long molecular axes the bi-swallow tailed molecules are assumed to exhibit cylindrical symmetry on average. Without rotation it would lead to a biaxial structure, which has never been observed. Therefore a quasi-hexagonal packing of the host molecules can be assumed. Looking for gaps in this packing (see figure 5) it can easily be seen that three molecules (only one third of the molecules of the corner belong to the cell) create six gaps on average which can be filled by the shorter rod-like molecules. If only one short molecule fits in each gap (see system A/C6, figure 6) and all C molecules are incorporated into the gaps of the smectic A layer d should be expected to remain constant ($d = L_A$) up to the concentration $x'_C = 0{\cdot}66$ because up to this concentration $x'_C = 0$ and $x'_A = 1$. For this concentration which corresponds to a molar ratio A : C6 = 1 : 2 all free gaps between the A molecules are occupied by C molecules. For $x_C > 0{\cdot}66$ all additional C molecules cannot be incorporated and exist as simple independent molecules within the smectic layers causing a decrease of d corresponding to the concentration x'_C. In the binary system A/C1 the gap between the swallow tailed ends of the A molecule is long enough that even two molecules can be incorporated (figure 7).

Provided that in each case all C molecules fill the gaps of the layer structure up to $x_C = 0{\cdot}8$, a constant $d = L_A$ should be expected. This concentration corresponds

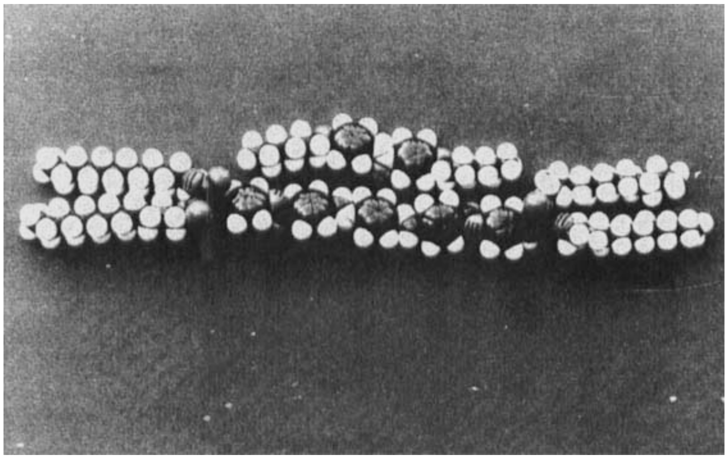


Figure 6. Space-filling models showing the incorporation of a molecule of component C6 into the free space between the bulky swallow tailed ends of a molecule of component A.

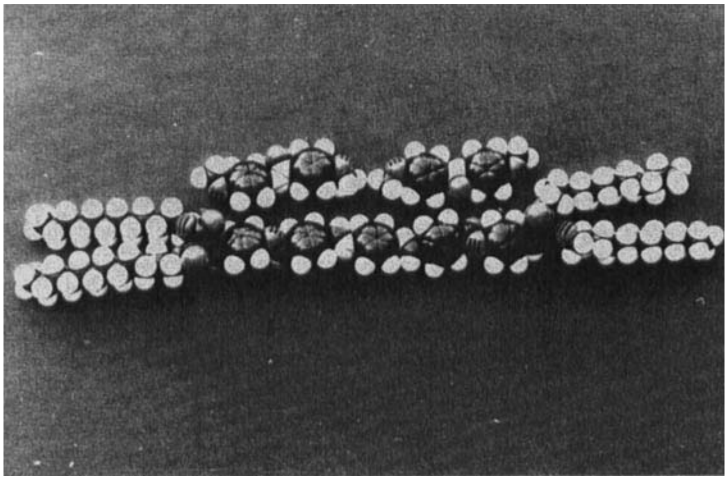


Figure 7. Space filling models showing the incorporation of two molecules of component C1 into the free space between the bulky swallow tailed ends of a molecule of component A.

to a mole ratio A : C1 of 1 : 4. It means that at a given concentration x_C the effective mole fraction x'_C is smaller in the system A/C1 than compared with that of the system A/C6 and the ratio $d/\bar{L}$ is clearly higher, in agreement with the experimental results. Additionally the maximum of the smectic A–nematic phase transition curve is shifted from about $x_C = 0{\cdot}6$ (system A/C6) to $x_C = 0{\cdot}8$ (system A/C1). It is an indication that around these concentrations the smectic A phase is structurally stabilized. This interpretation must be considered as a rough approximation. The static character of the model under discussion cannot reflect fully the reality. Nevertheless the experimental results can be explained essentially by the model which is based on steric interactions.

In order to obtain more information about the relative amount of the incorporated C molecules we used our model for a semi-quantitative consideration. If n_0

is the total number of molecules, n_A and n_C are the numbers of molecules A and C, respectively, the mole fractions

$$x_A = n_A/n_0; \quad x_C = n_C/n_0. \tag{4}$$

In this case the incorporation of the short molecules is not considered. By the incorporation effect the number of A molecules remains unchanged whereas the effective number of n_C is reduced to n'_C. From this it follows that for the effective molar fractions of A and C

$$x'_A = n_A/(n_A + n'_C), \tag{5a}$$

$$x'_C = n'_C/(n_A + n'_C). \tag{5b}$$

Using equation (3) x'_A and x'_C can be expressed in terms of the molecular lengths L_A and L_C and the experimental value of d

$$x'_A = \frac{d - L_C}{L_A - L_C}, \tag{6a}$$

$$x'_C = \frac{d - L_A}{L_C - L_A}. \tag{6b}$$

Combinations of equations (5*b*) and (4*b*) yield

$$n'_C = \left(\frac{1}{x'_A} - 1\right) n_A = \left(\frac{L_A - L_C}{d - L_C} - 1\right) x_A n_0, \tag{7}$$

which can be used to calculate the number n'_C of single molecules C. The difference of the original number of C molecules (n_C) and the remaining number n'_C of single C molecules after the incorporation effect is the number of incorporated molecules which can be determined from

$$\begin{aligned} n_C - n'_C &= n_0 x_C - \left(\frac{1}{x'_A} - 1\right) n_0 x_A \\ &= n_0\left[x_C - \left(\frac{1}{x'_A} - 1\right) x_A\right]. \end{aligned} \tag{8}$$

From this number we can calculate the ratio of incorporated C molecules and bi-swallow tailed molecules

$$\begin{aligned} (n_c - n'_c)/n_A &= \frac{x_C}{x_A} - \left(\frac{L_A - L_C}{d - L_C} - 1\right) \\ &= \frac{x_C}{x_A} - \frac{L_A - d}{d - L_C}. \end{aligned} \tag{9}$$

Using equations (3), (6), (7), (8) and (9) we have estimated the effective mole fractions x'_A and x'_C together with n'_C; the number of incorporated molecules $n_C - n'_C$ and the ratio $(n_C - n'_C)/n_A$ for the binary systems A/C6, A/C1 and B/C1. The results are summarized in the table. It follows from these results that a relatively greater portion of C molecules is incorporated in the available gaps of the layer structure. This portion obviously increases with increasing x_C. With the exception of the mixture A/C6 (x_A = 0·46) more than 80 per cent of all C molecules must be incorporated if we want to explain the high $d/\bar{L}$ ratio by our model.

The effective concentrations for three mixtures.

System	$x_{A,B}$	x_C	d/nm	$x'_{A,B}$	x'_C	n_C/n_0	n'_C/n_0	$(n_C - n'_C)/n_0$	$n_C - n'_C/n_{A,B}$
A/C6	0·46	0·54	5·56	0·67	0·33	0·54	0·23	0·31	0·67
	0·20	0·80	5·23	0·58	0·42	0·80	0·14	0·66	3.3
A/C1	0·30	0·70	5·70	0·77	0·23	0·70	0·09	0·61	2·0
B/C1	0·30	0·70	6·00	0·84	0·16	0·70	0·13	0·57	1·9
	0·20	0·80	5·88	0·81	0·19	0·80	0·05	0·75	3·7

x, mole fraction; x', effective mole fraction taking into consideration the incorporation effect; n_A; n_B; n_C, number of A, B or C molecules; n_0, total number of molecules; n_C, number of single molecules C which are not incorporated; $n_C - n'_C$, number of incorporated molecules.

In the mixture A/C6 ($x_A = 0{\cdot}2$) there are more C molecules than available free gaps. In this case the calculated ratio $n_C - n'_C/n_A$ of 3·3 is higher than the maximum ratio for a two dimensional quasi-hexagonal arrangement of molecules at $x_C = 0{\cdot}66$ (2·0). It is not easy to give a plausible explanation. Probably the quasi-hexagonal arrangement is too strong a simplification. It seems that the real smectic layer has more gaps than predicted by our simple static model.

In conclusion further experimental investigations are necessary, above all a detailed measurement of the smectic layer spacing and its dependence on the concentration and temperature over the whole region of the smectic A phase and if possible, also for the cybotactic smectic groups in the nematic region.

References

[1] Diele, S., Pelzl, G., Weissflog, W., and Demus, D., 1988, *Liq. Crystals*, **3**, 1047.

[2] Pelzl, G., Humke, A., Diele, S., Demus, D., and Weissflog, W., 1990, *Liq. Crystals*, **7**, 115.

[3] Pelzl, G., Humke, A., Diele, D., Ziebarth, K., Weissflog, W., and Demus, D., 1990, *Cryst. Res. Technol.*, **25**, 587.

[4] Pelzl, G., Humke, A., Demus, D., and Weissflog, W., 1990, *Cryst. Res. Technol.*, **25**, 597.

[5] Sackmann, H., and Demus, D., 1963, *Z. phys. Chem.*, **222**, 143.

[6] Diele, S., and Sackmann, H., 1989, *Ber. Bunsenges. phys. Chem.*, **93**, 467.

[7] Hardouin, F., Levelut, A. M., Achard. M. F., and Sigaud, G., 1983, *J. Chim. phys.*, **80**, 53.

[8] Diele, S., Ziebarth, K., Pelzl, G., Demus, D., and Weissflog, W., 1990, *Liq. Crystals*, **8**, 211.

[9] Sharma, N. K., Pelzl, G., Demus, D., and Weissflog, W., 1980, *Z. phys. Chem.*, **261**, 579.

[10] Schneider, F., and Sharma, N. K., 1989, *Z. Naturf.* (*a*), **36**, 1086.

[11] Araya, K., and Matsunaga, Y., 1981, *Molec. Crystals liq. Crystals*, **67**, 153.

[12] Dave, J. S., Patel, P. R., and Vasanth, K. L., 1966, *Ind. J. Chem.*, **4**, 505; 1969, *Molec. Crystals liq. Crystals*, **8**, 93.