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A NEMATIC GAP IN BINARY SMECTIC MIXTURES OF COMPOUNDS WITHOUT A STRONG POLAR GROUP

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Abstract Phase diagrams are determined of binary mixtures composed of azo- and azoxyarylethanes with smectic A and C phases. 1,2-bis butylbenzenoyloxy-azobenzene-4 ethane compound 1 revealing the smectic C phase yields mixtures characterized by a wide nematic gap separating the smectic phases of the pure components. It has been found by X-ray diffraction that the smectic C phase in compound 1 reveals a two-dimensional ordering similar to that observes in compounds with the antiphase $\tilde{C}$. It is suggested that the observed destabilization of the smectic C phase in the mixtures of the tested compound is due to the difference in the ordering of the smectic C phase of the mixture components.

INTRODUCTION

Mixtures of smectic compounds with suitably selected structure may reveal nematic properties. Such a behaviour was observed by us in binary mixtures of smectics A possessing strongly polar molecules in which the dipole moments of the terminal groups NO_2, CN or NCS are concordant with the dipole moments of the remaining

mesogenic groups of the molecule and besides the components of the mixture are selected in such a manner that they show different spacing of the smectic layer [1-4]. The induction of the nematic phase, also in compounds without polar terminal groups, was observed by other authors [5-12], however, in a limited range of concentrations and temperatures.

In one of our earlier works [13] concerned with the synthesis of multiring liquidcrystalline ethane derivatives and their application as stationary phases in gas chromatography we observed that compound 1 shows a smectic phase that is strongly destibilized in mixtures whose second component is a structuraly similar compound; these mixtures reveal in a wide concentration range the nematic phase only.

1 $\left(C_4H_9\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}CH_2\right)_2$

2 $\left(C_4H_9\text{-}O\text{-}C_6H_4\text{-}N(\rightarrow O){=}N\text{-}C_6H_4\text{-}CH_2\right)_2$

3 $\left(C_4H_9\text{-}O\text{-}C_6H_3(Cl)\text{-}N(\rightarrow O){=}N\text{-}C_6H_4\text{-}CH_2\right)_2$

4 $\left(C_4H_9\text{-}COO\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}CH_2\right)_2$

In order to explain this behaviour we studied more accurately in the present work the structure of the smectic phase of compound 1 and the properties of its mixtures with compounds 2, 3, 4.

RESULTS

Phase diagrams and miscibility studies

In Figure 1 and 2 phase diagrams are presented of binary mixtures of compounds: 1+2, 1+3, 1+4 and 3+4, respectively. The smectic phases of compounds 1 and 2,

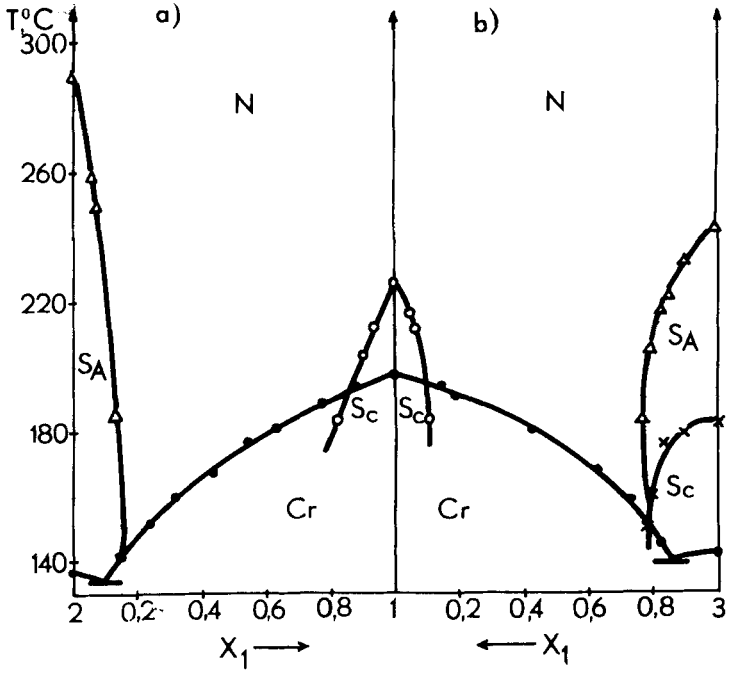

FIGURE 1. Fragments of the phase diagrams of binary mixtures including compounds 1 showing a nematic gap between smectic regions, Phase transitions • -Cr - mesophase, o - $S_C \rightarrow N$, Δ - $S_A \rightarrow N$, x - $S_C \rightarrow S_A$.

and 3 are separated by a wide nematic gap. Besides, the smectic phase of compound 1 does not mix in the whole concentration range with the smectic phase of 4,4'-diheptylazoxybenzene which shows the following phase sequence: $Cr \rightarrow S_C \rightarrow N \rightarrow I$.

The smectic phase of compound 1 mixes in the whole concentration range with the smectic C phase of compound 4. In the concentration range corresponding to the

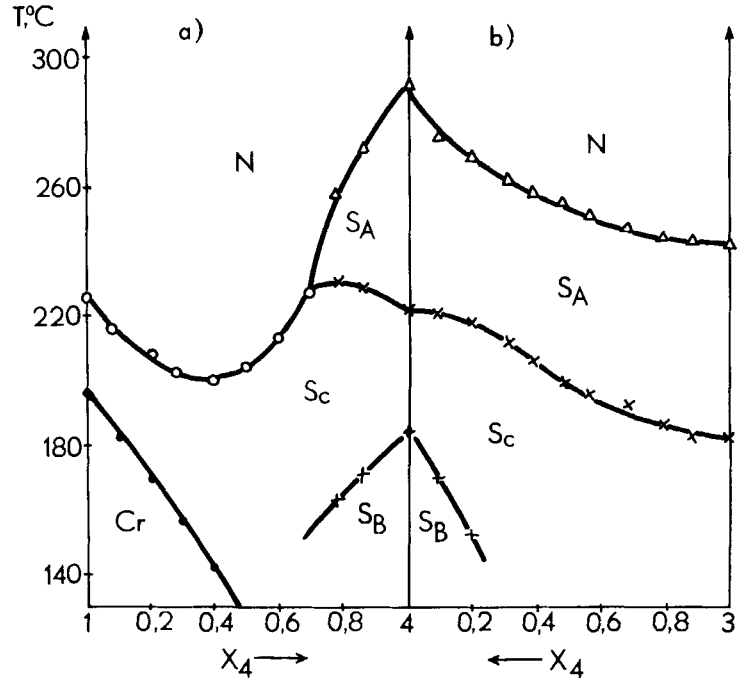

FIGURE 2. Fragments of the phase diagrams of binary mixtures showing complete miscibility of the smectic C phases of the components.

excess of compound 4 we even observe an enhancement of

the S_C phase, but in the concentration range corresponding to the excess of compound 1 we observe a decrease of stability of the smectic phase.

The smectic C phase of compound 3 mixes in the whole concentration range with the smectic C phase of compound 4 ; it also combines in the whole concentration range with the smectic C phase of 4,4'-diheptyloxyazoxybenzene.

Phase transitions and smectic phase textures

The phase transitions of compounds 1 to 4 have been repeatedly tested by the thermooptical method and DSC.

Compound 1: Cr 197°C S_C 226°C N 360°C I.

In the nematic and smectic phases of this compound we only observed a marble texture. At the S→N phase transition point rapid changes of the texture are observed due to the appearance of transition bars. The texture of compound 1 observed in polarized light is very similar to that presented by Demus[4] for octyloxybenzoic acid having smectic C and nematic phase . Long heat treatment of the smectic phase of compound 1 in the vicinity of the S→N phase transition point allows us to obtain a texture similar to the focal-conic fan shaped one.

Compound 2: Cr 137°C S_A 290°C N 330°C I shows a typical for smectics A focal-conic fan or homeotropic texture.

Compound 3: Cr 143°C S_C 183°C S_A 243°C N 262°C I.

The S_A phase of compound 3 was observed in the form of

focal-conic fan or homeotropic texture, and the S_C phase in the form of broken focal-conic fan or schlieren texture. The latter texture is formed during the cooling of the S_A phase ordered homeotropically.

Compound 4:

Cr 103,5 S_E 168 S_B 184°C S_C 222°C S_A 292°C N 303°C I

In ref. [13] compound 4 was assigned erroneously the phase sequence: Cr 165°C S_A 184°C N 303°C I, wherein the schlieren texture of phase S_C was attributed to the nematic phase. The cooling of the nematic phase of compound 4 manifests itself by the appearance of the S_A phase with focal-conic fan texture which converts to the broken focal-conic fan texture in phase C. The $S_C \rightarrow S_B$ phase transition is accompanied by the formation of transition bars. Above 222°C a homeotropic texture is formed when the microscope slides are shifting, this texture converts below 222°C S_C phase to the schlieren one and subseqvently, below 184°C phase S_B assumes again the homeotropic texture.

X-Ray studies

Compound 1

The X-ray pattern of compound 1 shows in the temperature range 190-220°C four diffraction maxima in the form of spots along the direction perpendicular to the magnetic field B lines and four very weak reflexes in the form hyperbole sections (Figure 3). Figure 3 has been drawn

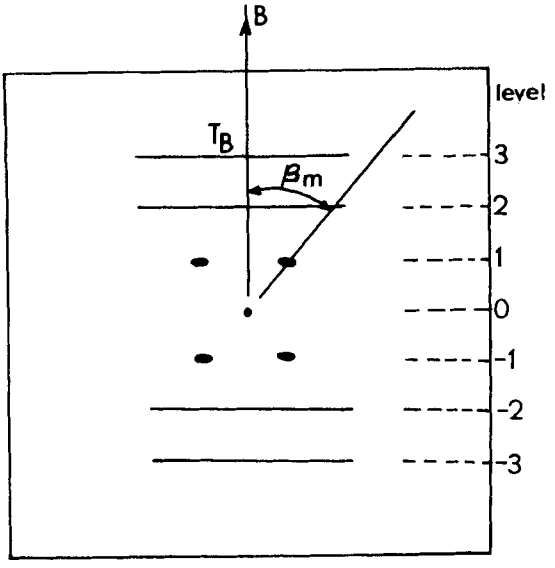

Figure 3. Schematic representation of the X-ray pattern of compounds 1.

on the basic of the X-ray photograph, since direct photographic reproduction does not ensure mapping of the well visible by the naked eye higher order reflexes. As the temperature increases, the earlier separated spots become more diffused along the direction of the magnetic field, but no changes in the distances between maxima of the spots.

The X-ray pattern of compound 1 is similar to that of a substance with axial texture, and thus is similar in some extent to the X-ray pattern of a rotated crystal.

In view of this similarity we used for calculating the idendity period T_B the formula:

$$T_B = \frac{n\lambda}{\sin\mu_n}$$

where $\sin\mu_n = \frac{y}{Z_o^2 + x^2}$, n is the number of the level λ- wavelength, μ_n - angle between the oth level and nth level, Z_o - distance of the sample from the film, x - coordinate of the reflex in the direction perpendicular to the magnetic field, y - coordinate of the reflex parallel to the magnetic field.

In Figure 4 the procedure for calculating the identity period T_B from the X-ray pattern is illustrated in grater detail. Table 1 lists the calculated values of identity periods: T_B - in the direction of the magnetic field, d - in the direction perpendicular to the smectic layers (spacing of the smectic layer) found from the formula $n\lambda = 2d \sin\theta$, and the tilt angle β_c found from the formula:

$$\cos\beta_c = \frac{d}{T_B}$$

The angle β_m (measured as shown in Figure 3) is the angle between the direction of the magnetic field B and the line passing the reflex maxima and the trace of the direct beam (Figure 4). It is equal the smectic C tilt [14,15].

The identity period T_B determined as described above is in very good agreement with the length of the molecule calculated independently on the basis of the assumed mo-

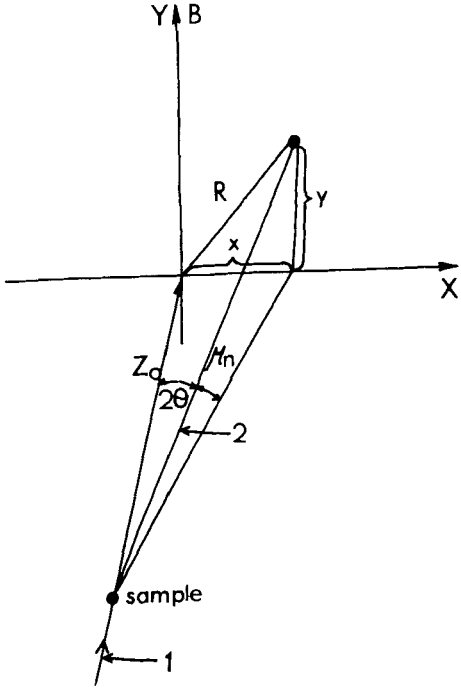

Figure 4. Relationship between film coordinates x, y and angle μ_n.
1 - direct beam, 2 - diffracted beam, Z_o - sample-film distance, R - direct - diffracted beam distance.

lecule geometry and the known lengths of the bounds ($l_1 \approx T_B$). The same value of l_1 was obtained by direct measurement of the angle β_m on X-ray photograph and d_1.

TABLE 1

Experimental values obtained from X-ray pattern for compound 1 and its binary mixtures at 190°C.

Level	x mm	y mm	R mm	d Å	T_B Å	β_c grade	β_m grade	Z_o mm
				Compound 1				
1	3.5	3.5	4.9	34.8	48.9	44.6	45	74.6
2	0	7.0			49.0			
3	0	10.5			49.2			
				94 mole % 1 + 6 mole % 3				
1				32.7	47.2	46	45	
				50 mole % 1 + 50 mole % 4				
1	2.4	3.8	4.5	37.7	44.7	32.3	32.4	74.1

Calculated lengths of the molecules: l_1 = 48.2 to 49.1 Å, l_2 = 38.0 to 38.7 Å, l_3 = 38.0 to 38.7 Å, l_4 = 40.2 to 41.1 Å.

The mixture of compounds 1 + 3 containing 94 mole % of 1 and 6 mole % of 3 ($S_C \rightarrow N$ phase transition at about 214°C, Figure 1) gives a X-ray diffraction pattern similar to that of pure compound 1 with the only difference that the reflexes of the second order in the form of continous line is very weak, and refluxes of the third order is not seen at all. The smectic C layer tilt angle is preserved. At temperatures above 210°C the intensity of the reflexes decreases but their geometry remains the same (d, T_B and y = const.).

The mixture of compounds 1 + 4 (the smectic phases of these compounds mix, Fig. 2) in an equimilar ratio yields an X-ray diffraction pattern similar to that of compound 1 (four spots) but different from the pattern of compound 4. In the temperature range 180-210°C the geometry of the X-ray pattern does not change, however, in the vicinity of this temperature the reflexes are more diffused what is related to that the mixture is a nematic at this temperature (Figure 2a).

The obtained identity period $T_B \approx \frac{l_1 + l_4}{2}$, and the tilt angle β is smaller than that observed in pure compound 1 (see Table 1).

Compound 2

Compound 2 reveals only one pair of diffused reflexes and it is weakly ordered under the action of the magnetic field $d_2 = 38.5$ Å.

Compound 3

The variation of the smectic layer spacing with temperature is shown in Figure 5. In the temperature range 140-180°C the smectic C layer spacing d_3 increases from 31.2 Å to 38.0 Å; the tilt angle β changes from 30° to 0°.

The compounds 3 shows in phase C a weak ordering, one pair of diffused weak reflexes which become stronger nearby phase A. For phase A the observed intensity of reflexes is the greatest. The mixture composed of 85 mole % of 3 and 15 mole % of 1 (Figure 4) reveals very weak reflexes of the smectic layer, d=33.8 Å at 140°C

and 38.8 Å at 180°C.

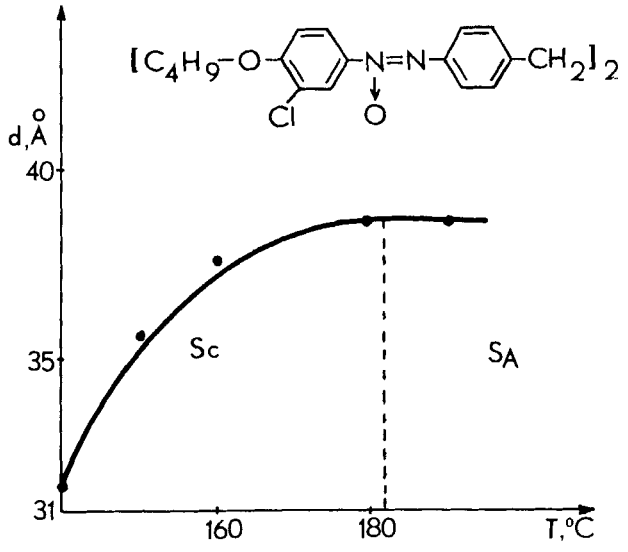

Figure 5. Dependence of the smectic C layer spacing on temperature for compounds 3.

Compound 4

In the temperature range 190-210°C the compound shows one pair of reflexes of constant geometry which corresponds to the smectic layer spacing $d_4 \approx 38.6$ Å, and the tilt angle is $\beta = 21.5°$. At 230°C phase A the smectic layer spacing is $d_4 \approx 41.7$ Å $(d_4 \approx l_4)$. We observe reflexes characteristic of smectic B phase below 184°C and of smectic E phase below 168°C.

DISCUSSION

The X-ray diffraction and miscibility studies have confirmed the thermooptical observations regarding the sequence and character of smectic phases of compounds 1 to 4 .

The main problem requiring discussion is still the character of phase C in compound 1. Is it a normal smectic C phase or an antiphase $\tilde{C}$? The X-ray diffraction pattern indicates that in this compound the phase C has a two-dimensional oblique lattice; the X-ray pattern is, in principle, similar to that observed in the antiphase $\tilde{C}$ of the polar mesogen DB_9ONO_2 [17].

So far the antiphase $\tilde{C}$ was always observed as an intermediate phase between A_1 and A_2 or A_d and A_2 [18,19,20]. In our case it appears directly before the phase N. The phase C of compound 1 observed by us has a marble texture and differs distinctly from those of antiphases $\tilde{C}$ observed in 4-n-alkoxybiphenyl-4'-cyanobenzoates which reveal broken focal-conic or discotic textures [20].

An analogous texture to that observed by us in compound 1 was described by Demus [16] for alkoxybenzoic acids which has the smectic C phase. Chistyakov et al. [21] have studied by X-ray diffraction nonyloxybenzoic acid ordered by the electric field . The X-ray pattern obtained by them in the nematic phase reminds the one obtained by us for compound 1 in the smectic phase, however, it does not have

reflexes of higher orders. May be, if the smectic C phase in alkoxybenzoic acids was studied once more, a two-dimensional ordering would be found to exist, since the presence of hydrogen bonds in carboxylic acid may favour such an ordering. The smectic C phase of compound 1 is characterized by a high value of the tilt angle which varies but slightly with temperature and two-dimensional ordering.

The smectic phase of compound 3 is characterized by a smaller degree of ordering what is confirmed by the strong dependence of the smectic tilt angle on temperature. The degree of ordering of the smectic layer in compounds 1, 3 and 4 varies in the order: $1 \rangle 4 \rangle 3$. The smectic C phases of compounds 1 and 3 are immiscible. Compound 4 with intermediate ordering mixes both with compound 1 and compound 3. On this basis it can be assumed that the big difference in the structure of the smectic C layers of compounds 1 and 3 is responsible for the lack of miscibility of these phases and the strong destabilization of the smectic phase in the mixture what converts, in consequence, the system into a nematic. The chemical similarity of compound 1 and 3, and 1 and 2 results in that their molecules behave in the nematic phase in a way close to ideal. The separation of the smectic phases of such a nematic mixture during cooling is hindered, and since, in view of the structural differences, a common smectic lattice cannot be formed, the nematic

features of the system stabilize.

EXPERIMENTAL

Compounds 1 to 4 were obtained according to the procedures described in ref. 13 . The phase transition points were determined by the thermooptical method. The hot stage VEB Analitic Dresden microscope was used.

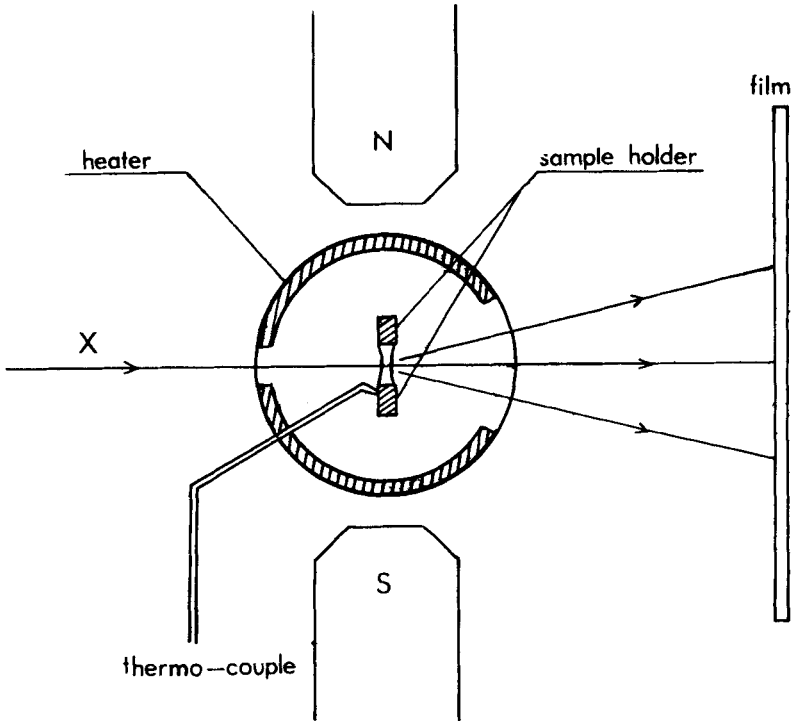

Figure 6. X-ray experimental geometry.

The phase diagrams were determined by the single concentration method. The X-ray patterns were obtained in way similar to the Laue transmission method. The X-ray were passed through the freely hanging sample in a circular aperture 2 mm in diametre. The X-rays did not enter into contact with any wall of the container what made possible the registration of weak reflexes. The radiation used was: $Cr_{K\alpha}$, $\lambda = 2.29$ Å. The sample was heated with an electric heater and thermostated up to $\pm 0.03^{\circ}C$. For sample ordering a magnetic field of 1.6 T was applied. The experimental set-up is shown schematically in Figure 6. The ordering of the sample was achieved by heating it to $240^{\circ}C$ when it is in the N or S_A phase and subsequent cooling to the lowest temperature used in the measurements. The X-ray reflexes were registered at fixed temperature in the heating cycle. Long heating at a temperature above $220^{\circ}C$ produced degradation of the sample.

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REFERENCES

1. R. Dąbrowski and J. Szulc, J. Physique 45, 1213 (1984)
2. K. Czupryński, R. Dąbrowski, J. Baran and J. Przedmojski, J. Physique 47, 1577 (1986).

3. R.Dąbrowski, B.Ważyńska and B.Sosnowska, Liq. Cryst., 1 , 415 (1986).
4. R.Dąbrowski, J.Baran, B.Sosnowska and. J.Przedmojski, Z. Naturforsch., 42a , 35 (1987).
5. G.Pelzl, U.Bättger and D.Demus, Mol.Cryst.Liq. Cryst.Lett., 64, 283 (1981).
6. D. Demus, K.H. Katz and H. Sackmann, Z.Phys. Chem., 249, 217 (1972).
7. D.Demus, G. Kunicke, G. Pelzl, B.Roblıng, B.Sackmann and R. Salffner, Z.Phys., 254, 373 (1973).
8. D. Demus, L.Richter, C.E. Rümp, H. Sackmann and H.Schubert, J.Physique, 36, C1 349 (1975).
9. G.Pelzl, G.Diele, L.Latif, D.Demus, W.Schäffer and H.Zaschke,Mol.Cryst.Liq.Cryst.Lett., 1, 39 (1985).
10. H.Arnold and H. Sackmann, Z.Elektrochem.Ber.Bunsenges, 63, 1171 (1959).
11. H. Ziemnicka, A.de Vries, J.W. Doane and S.L.Arora, Mol.Cryst Liq.Cryst., 132, 289 (1986).
12. M.E.Neubert, K.Leung and W.A.Saupe, Mol.Cryst. Liq. Cryst., 135, 283 (1986).
13. A.Ziółek, R. Dąbrowski and Z.Witkiewicz, Mol.Cryst. Liq.Cryst., 109, 107 (1984).
14. A.de Vries, Mol.Cryst.Liq.Cryst.,10, 219 (1970).
15. A.J. Leadbetter, The Molecular Physics of Liquid Crystals, ed. G.R. Luckhurst and G.W. Gray (Academic Press,London-New York- San Francisco 1979), p 305.

16. D. Demus and L. Richter, Textures of Liquid Crystals, (VEB Deutscher Verlag für Grundstoff Industrie, Leipzig 1978), p. 136.

17. E. Fontes, P.A. Heineg, J.L. Haseltine and A.B. Smith, J. Physique, 47, 1533 (1986).

18. F. Hardouin, M.F. Achard, C. Destrade and Nguyen Huu Tinh, J. Physique, 45, 765 (1984).

19. F. Hardouin, A.M. Levelut, M.F. Achard and G. Sigaud, J. Chim. Physique, 80, 53 (1983).

20. J.W. Goodby and C.R. Walton, Mol. Cryst. Liq. Cryst., 122, 219 (1985).

21. I.G. Chistyakov, L.S. Schabischev, R.J. Jarenov and L.A. Gusakova, Mol. Cryst. Liq. Cryst., 7, 279 (1969).