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Preliminary communication

Helical superstructures in a novel smectic mesophase formed by achiral banana-shaped molecules

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A new smectic type mesophase without in-plane order is presented which is formed by nitro substituted banana-shaped compounds. The structure of this phase is not yet known in detail. The growth of germs and also the textures point to a helicoidal structure. The helical structure is obviously the result of the chirality of the smectic layers which is caused by the tilt of the molecules together with the polar arrangement of the angled molecules.

In liquid crystals helical superstructures can occur which are due to the chirality of the molecules. In the case of cholesteric or smectic C* phases, the molecular chirality leads to a spiralling of the mean orientation of the molecules with respect to the helix axis which is manifested as circular dichroism, optical activity or as special features of the textures. Recently a helical superstructure could be detected in a solid-like phase, the so-called 'blue crystalline phase' or B_4 phase formed by achiral banana-shaped molecules. The helical arrangement is indicated by the circular dichroism and by optical activity, but also directly by atomic force microscopy [1, 2].

In this paper we present a new smectic type phase also formed by banana-shaped molecules. This phase shows optical textures which clearly point to a helical superstructure. Probably this helical structure is the result of a chirality of the smectic layers similarly to the B_4 phase. The chirality of smectic layers constituted by banana-shaped molecules was first detected by Link *et al.* [3] for the antiferroelectric B_2 phase. Also for this phase a helical structure is discussed [4], but according to [3] the birefringence in the fan-shaped texture can be interpreted as domains with oppositely tilted directors, but not by a helical twist.

The materials studied are members—see the table—of a new homologous series of banana-shaped compounds [5]. In comparison to the banana-shaped compounds which were first presented by Niori *et al.* [6], the central core is substituted in the 2-position by a nitro group. All homologues exhibit the same mesophase, previously designated, as B_7. This phase symbol follows the recommendation made at the International Workshop on Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules organized by the Technical University in Berlin in December 1997. This nomenclature has a preliminary character until the phase structure and the structural relations to the smectic phases of calamitic compounds are known in more detail.

The transition temperatures and the transition enthalpies for the new materials are listed in the table. It is remarkable that the clearing enthalpies are relatively high and clearly higher than the melting enthalpies. The B_7 phase is not miscible with other B phases or with any known smectic phase of calamitic compounds.

The synthesis of 2-nitro-1,3-phenylene bis[4-(4-*n*-alkyloxyphenyliminomethyl)benzoates] was achieved by esterification of 2-nitroresorcinol with 4-(4-*n*-alkyloxyphenyliminomethyl)benzoic acids using dicyclohexylcarbodiimide in the presence of dimethylaminopyridine in dichloromethane according to Steglich and Neises [7]. The raw materials have to be recrystallized several times and purified by flash column chromatography on aluminium oxide to obtain final products pure enough for further investigation. The precursor substituted benzoic acids prepared by condensation of 4-*n*-alkyloxyanilines with 4-formylbenzoic acid are themselves liquid crystalline [8].

2-Nitroresorcinol (2.0 mmol) and the appropriate 4-(4-*n*-alkyloxyphenyliminomethyl)benzoic acid (4.0 mmol)

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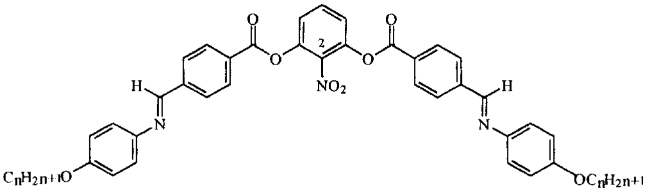
Table. Phase transition temperatures (°C) and transition enthalpies [kJ mol^{-1}] of homologous 2-nitro-1,3-phenylene bis[4-(4-*n*-alkyloxyphenyliminomethyl)benzoates].



n	Cr		B$_7$		I
6	•	107 [17.65]	•	177 [29.28]	•
7	•	85 [17.66]	•	176 [29.85]	•
8	•	116 [6.59]	•	177 [30.17]	•
9	•	a	•	174 [30.20]	•
12	•	85 [13.92]	•	173 [28.41]	•

[a] The melting point could not be determined either by calorimetry or by polarizing microscopy.

were dissolved in dichloromethane (100 ml). After the addition of dicyclohexylcarbodiimide (5.0 mmol) and a catalytic amount of dimethylaminopyridine, the mixture was stirred at room temperature for 48 h. The dicyclohexylurea precipitated was filtered off and the solvent evaporated. The product was recrystallized twice from ethanol/dimethylformamide. Then, the substance dissolved in chloroform was purified by flash chromatography on neutral aluminium oxide. Finally, the product was recrystallized several times from ethanol/dimethylformamide or toluene/heptane. Yields after purification: 21–31%. Analytical data are given for the dodecyloxy derivative, ($n = 12$).

Elemental analysis: $C_{58}H_{71}N_3O_8$ (M_m: 938.22); calc: C= 74.25, H= 7.63, N= 4.48; found: C= 74.22, H= 7.45, N= 4.46%. ^{1}H NMR (200 MHz, CDCl$_3$): δ= 8.59 (s, 2H, CH=N), 8.25 (d, 4H, Ar–H, J = 8.4 Hz), 8.04 (d, 4H, Ar–H, J = 8.2 Hz), 7.58 (m, 1H, Ar–H), 7.31 (d, 4H, Ar–H, J = 8.8 Hz), 7.25 (m, 2H, Ar–H), 6.96 (d, 4H, Ar–H, J = 8,8 Hz), 4.00 (t, 4H, OCH$_2$, J = 6.5 Hz), 1.81 (m, 4H, $\mathrm{OCH_2C\underline{H_2}}$), 1.28 (m, 36H, CH$_2$), 0.89 (m, 6H, CH$_3$).

The phase transition temperatures were determined by calorimetry (DSC7, Perkin-Elmer) and by polarizing microscopy (Leitz Orthoplan). The polarizing microscope was also used for analysis of the textures. Preliminary X-ray diffraction measurements were carried out using a Guinier goniometer (HUBER Diffraktionstechnik) and a Guinier film camera.

In order to obtain information about the structure of the B$_7$ phase X-ray diffraction measurements were performed. In the X-ray pattern of a non-oriented sample a diffuse scattering in the wide angle region (~10°) was observed indicating a liquid-like order within the smectic layers. In the small angle region six sharp reflections were detected; these have not yet been assigned because we were unable to obtain well oriented monodomains (figure 1). But this pattern excludes a simple layer structure.

The microscopic texture of the B$_7$ phase is extraordinary and not comparable with the textures of other B phases. If the isotropic liquid is cooled down very fast, the B$_7$ phase appears as a cluster of thin thread-like or straight lancet-like nuclei (figure 2†) which coalesce to an unspecific texture. On very slow cooling, variety of texture variants is obtained, but these mostly occur simultaneously within the same preparation. In very thin sandwich cells (2 μm), the B$_7$ phase appears in some parts of the cell as a weakly birefringent fan-shaped texture which reminds one of the corresponding

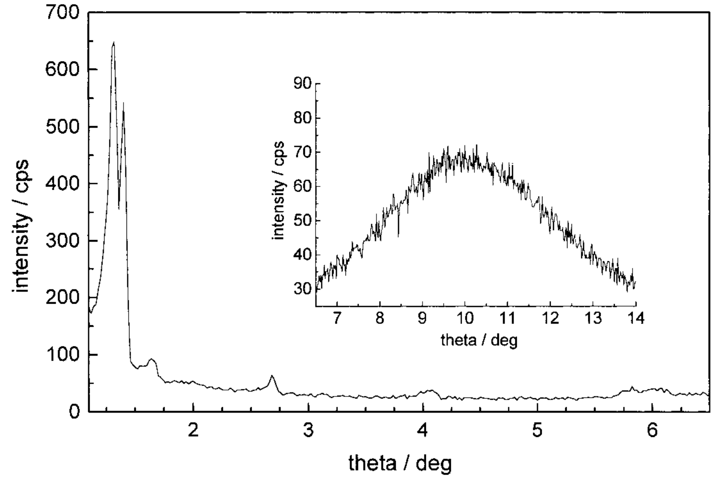


Figure 1. X-ray diffraction pattern of the B$_7$ phase of the octyloxy homologue (151°C).

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† All microphotographs relate to the octyloxy homologue.

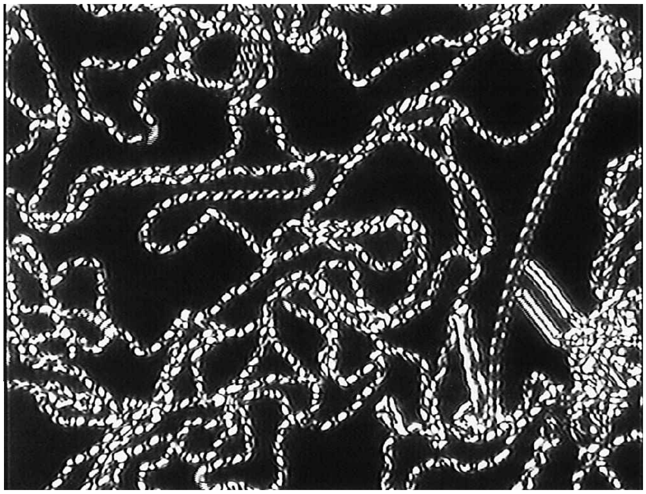

Figure 2. Growth of thread-like and spiral nuclei on cooling the isotropic liquid.

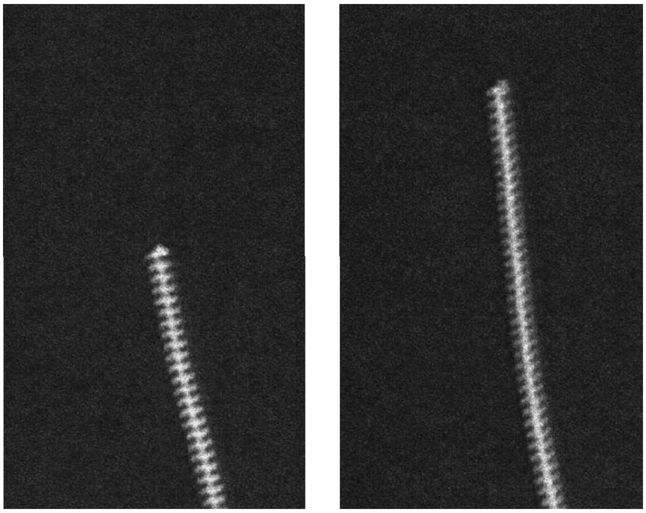

Figure 4. Growth of a spiral domain on cooling the isotropic liquid.

texture of a SmA phase (figure 3). Sometimes, but not always, within the fans equidistant black stripes are visible between crossed polarizers and do not disappear on rotating the sample. The period of the stripes is of the order 2 μm. Inserting a λ-plate between polarizer and analyser, it can be detected that the direction of the maximum refractive index for transmitted light is perpendicular to the black lines within the fans.

Also, on slow cooling of the isotropic liquid, the B_7 phase frequently forms elongated germs such as straight lancet-like or irregular thread-like germs. But frequently these germs have clearly a spiral or double-spiral character. Figure 4 shows the growth of a spiral germ. The handedness of the screw-like nuclei could be determined by adjusting the focus of the microscope. We found roughly an equal number of right-handed and left-handed helices within a given sandwich cell.

On the other hand, the B_7 phase frequently grows as oval or sometimes as circular domains. Such an oval domain shown in figure 5 exhibits equidistant stripes with a spacing of about 2 μm. Frequently texture variants are obtained which remind one of myelinic textures of lyotropic liquid crystals (figure 6). Figure 7 (*a*) shows a circular domain which grows like a spiral, in this case clockwise. This circular domain exhibits equidistant concentric rings which are also visible in natural light and which do not disappear on rotating the sample between crossed polarizers. The brushes of the extinction cross are parallel to the polarizer and analyser directions. It is seen from figure 7 (*b*) that, on cooling, the circular

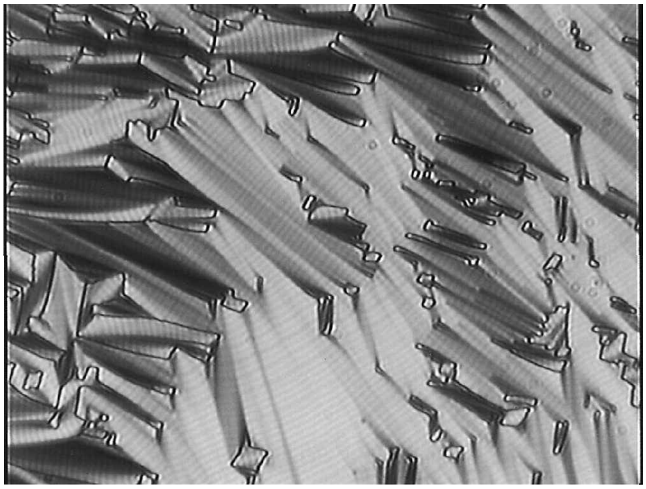

Figure 3. Fan-shaped texture of the B_7 phase (162°C, sample thickness 2 μm).

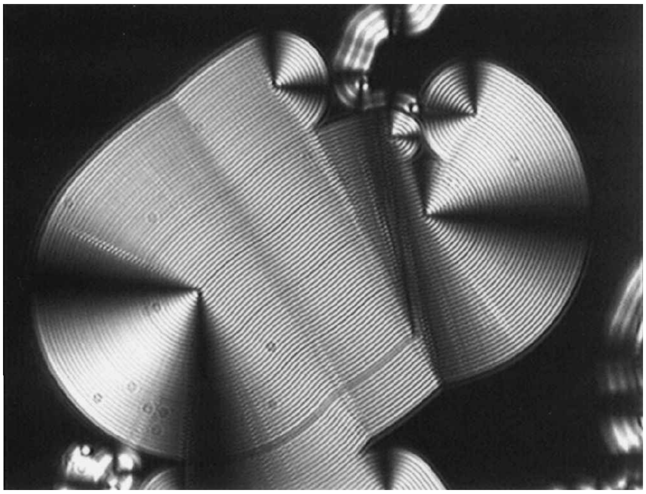

Figure 5. Oval domains with equistant stripes (175°C, sample thickness 2 μm).

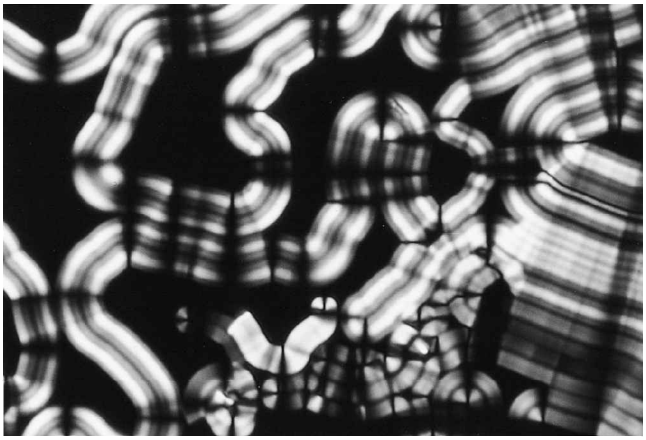

Figure 6. Myelinic texture of the B_7 phase (175°C).

domain is transformed into a rosette-shaped domain. Such behaviour is not restricted to circular domains. Generally, on cooling, one-dimensional periodic textures are transformed into a two-dimensional periodic pattern.

If all domains coalesce on cooling, very complicated and extraordinary textures are formed; some representative examples are shown in figures 8 (*a*, *b*, *c*). Often finely structured two dimensional mosaics can be observed where the optical axis alternates by about 90° from one mosaic element to the next, indicating a zig-zag alternation of the extinction direction.

The occurrence of spiral or double-spiral germs clearly points to a helical structure of the B_7 phase. But also, the equidistant stripes in the fan-shaped texture or the equidistant concentric circles are obviously the result of a helicoidal periodicity. This periodicity is probably due to a twisted distribution of the molecular tilt which corresponds to the pitch of the helical structure in chiral smectic phases. Similarly to the chiral SmC* phase, the equidistant circular lines can be explained by the presence of a screw line superimposed on the vertical focal conic line [9]. If successive smectic layers form semi-conical concentric ribbons, a spiral arrangement results where dark and bright bands are seen between crossed polarizers. When the preparation is rotated, the light bands become progressively dark and vice versa [9].

An attempt was made to obtain free-standing films of the B_7 phase. By continuous diminution of the film thickness, the film tears up into smaller pieces. In this way single thin threads with a diameter up to about 10 μm could be prepared. On shrinking, sometimes a screw-like thickening of these threads was observed.

The question is what is the origin of the helicoidal structure? It follows from the preliminary X-ray investigations that the molecules are tilted with respect to the layer normal. It can be assumed that similarly to the B_2 phase, a tilted arrangement of the bent molecules on the one hand and the polar ordering on the other hand cause a chirality of the smectic layers where the handedness is determined by the tilt direction [3]. Probably this chirality gives rise to the helicoidal superstructure, although the constituent molecules are achiral.

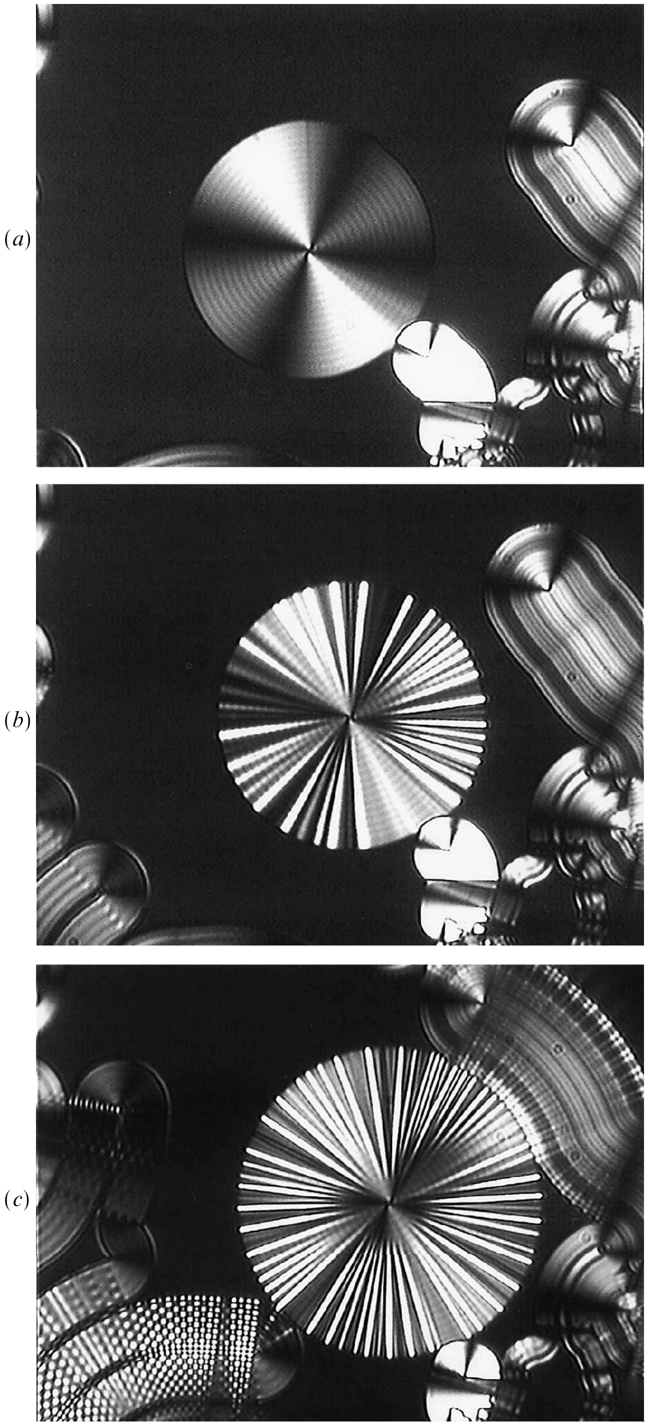

Figure 7. Growth of a circular domain on cooling the isotropic liquid (sample thickness 2 μm).

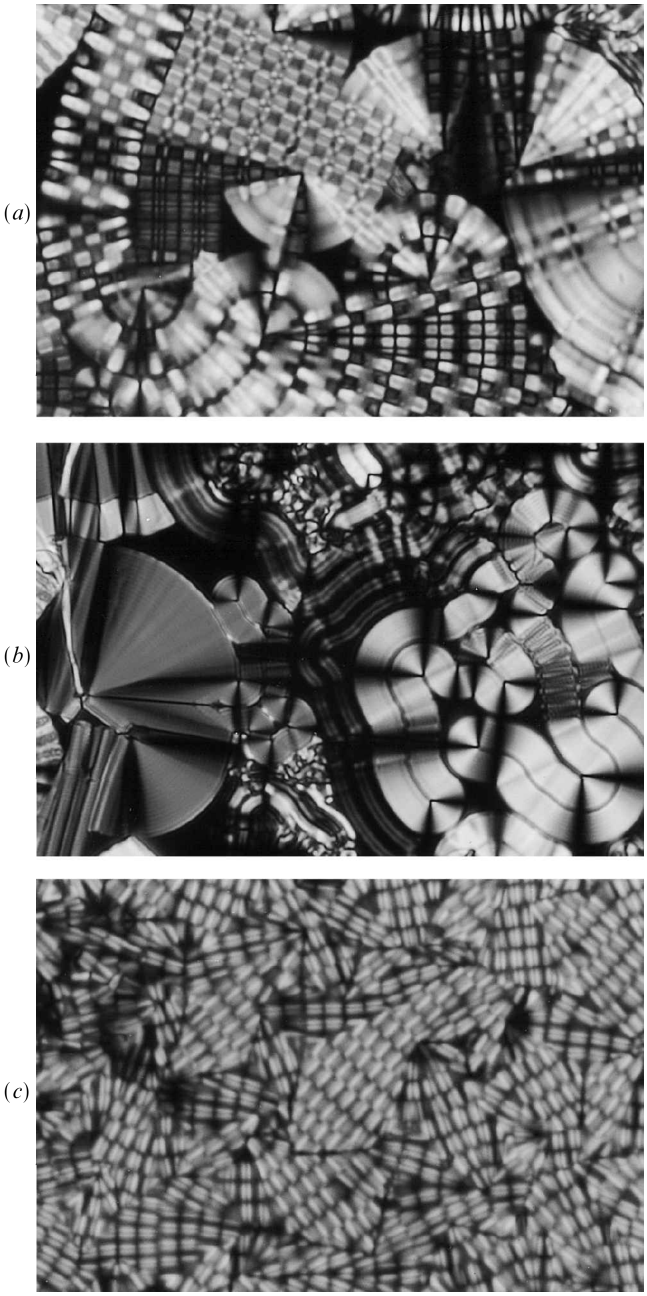

Figure 8. Texture variants of the B_7 phase.

It is striking that in the same sandwich cell there are analogous texture variants (fan-shaped texture, oval domains) which are weakly or more strongly birefringent. Furthermore, structureless elongated lancets occur simultaneously with spiral threads of different shape. This observation points to the coexistence of 'homochiral' and 'racemic' regions as discussed for the antiferroelectric B_2 phase [3]. As shown by [3], the 'racemic' ground state should possess a higher double refraction because of the uniform director tilt. On the other hand, it can be assumed that the racemic state cannot build up a helicoidal structure. Up to now the alignment of molecules in such a helical structure is an open equation. X-ray investigations on oriented samples and a careful analysis of the textures will be made to understand the properties of this peculiar mesophase in more detail.

References

[1] Collings, P., Heppke, G., Krüerke, D., Löhning, C., Rabe, J., and Stocker, W., 1997, in Abstracts of the Workshop on Banana-Shaped Liquid Crystals: Chirality of Achiral Molecules, December 1997, Berlin, p. 15.

[2] Heppke, G., and Moro, D., 1998, *Science*, **279**, 1872.

[3] Link, D. R., Natale, G., Shao, R., Maclennan, J. E., Clark, N. A., Körblova, E., and Walba, D. M., 1997, *Science*, **278**, 1924.

[4] Sekine, T., Niori, T., Watanabe, J., Fukukawa, T., Choi, S. W., and Takezoe, H., 1997, *J. mater. Chem.*, **7**, 1307.

[5] Weissflog, W., Lischka, Ch., Bennié, I., Scharf, T., Pelzl, G., Diele, S., and Kruth, H., 1997, *Proc. SPIE*, Liquid Crystals: Chemistry and Structure, **3319**, 14.

[6] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6**, 1231.

[7] Neises, B., and Steglich, W., 1978, *Angew. Chem.*, **90**, 556.

[8] Weissflog, W., Lischka, Ch., Diele, S., Pelzl, G., Wirth, I., Grande, H., Kresse, H., Schmalfuss, H., Hartung, H., and Stettler, A., *Mol. Cryst. liq. Cryst.* (submitted).

[9] Bourdon, L., Sommeria, I., and Kleman, M., 1982, *J. Phys. (Paris)*, **43**, 77.