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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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

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Online publication date: 01 November 2006

**To cite this Article** Pelzl, G. , Diele, S. , Jákl, A. , Weissflog, W. , Pelzl, G. , Diele, S. , Jákl, A. , Lischka, Ch. , Wirth, I. and Weissflog, W. (2006) 'Preliminary communication Helical superstructures in a novel smectic mesophase formed by achiral banana-shaped molecules', *Liquid Crystals*, 33: 11, 1513 – 1523

**To link to this Article:** DOI: 10.1080/02678290601140514

**URL:** <http://dx.doi.org/10.1080/02678290601140514>

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# The mysterious B<sub>7</sub> phase: from its discovery up to the present stage of research

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A Commentary on the paper “Helical superstructures in a novel smectic mesophase formed by achiral banana-shaped molecules”, by G. Pelzl, S. Diele, A. Jáklí, Ch. Lischka, I. Wirth, and W. Weissflog. First published in *Liquid Crystals*, **26**, 135–139 (1999).

Inspired by the lecture of Prof. H. Takezoe at the International Liquid Crystal Conference in Kent in 1996 and by the corresponding article in the *Journal Materials Chemistry* [1] the Halle group started research on bent-core mesogens at the beginning of 1997. In order to make the first step towards this new and fascinating field Weissflog and his coworkers synthesized a variety of new bent-core compounds by modifying the structure of the parent series [1] by lateral substituents at the central core and by the introduction of different linkage groups [2]. Among these first materials there was also a five-ring bent-core mesogen derived from 2-nitroresorcinol which forms an unknown mesophase preliminarily designated as M<sub>2</sub>. We found that on slowly cooling the isotropic liquid, spiral or double spiral nuclei arise which coalesce to a variety of optical textures such as striped focal conics, checkerboard textures, banana-leaf-like textures and circular domains (see figure 1). Although in Halle there is a very long tradition in the field of liquid crystals and in the analysis and classification of the optical textures, we had never seen such beautiful and exotic textures before and we were really enthusiastic.

The X-ray pattern of a non-oriented sample displayed, in addition to a diffuse wide-angle scattering, several small-angle reflections which could not be attributed to a simple layer structure. These findings clearly point to a new so-called banana phase. According to the recommendation made at the International Workshop on Banana-Shaped Liquid Crystals in Berlin in 1997 we designated this unusual phase (in the sequence of its discovery) as B<sub>7</sub> [3, 4].

Since we attempted for a long time to obtain well-oriented samples for X-ray diffraction measurements (unfortunately without success) we submitted our manuscript relatively late to *Liquid Crystals*, that is not before July 1998 [3]. Two years later Jakli *et al.* [5] showed that the spiral domains consist of smectic filaments forming single, double or triple coils. Yusuf *et al.* [6] studied the electric-field mediated growth of the habits of the B<sub>7</sub> phase in more detail. After 1999 further compounds exhibiting a B<sub>7</sub> phase were synthesized [7–20]. Starting from the original B<sub>7</sub> compound (formula I: Z=NO<sub>2</sub>; A=H, E=H [3]), the chemical structure can be varied in a limited way without the loss of this phase. The nitro group can be exchanged by a cyano group (Z=CN; A=H; E=H) [14], additionally halogen atoms can be attached in the neighbourhood of the terminal chains (A=F, Cl) [9]. It is also possible to vary the position and/or direction of the connecting groups between the aromatic rings of such 2-nitro and 2-cyano-substituted compounds [15, 19]. Furthermore, the number of aromatic rings can be increased to seven and fluorine atoms can be attached to different rings [12, 13].

But also compounds without a polar nitro- or cyano-group in the obtuse angle of the bent mesogens are able to form this B<sub>7</sub> phase. Shankar Rao *et al.* [10] reported a B<sub>7</sub> phase for compounds with inverse azomethine groups between the outer rings, the stability of which is increased by hydroxy groups in the ortho position. In compounds investigated by Bedel *et al.* [7, 11] the positions of the carboxylic and azomethine connecting groups are exchanged in comparison to formula I and additionally, the outer rings are substituted with fluorine atoms. But also seven ring compounds without any lateral substituents can exhibit a B<sub>7</sub> phase [8].

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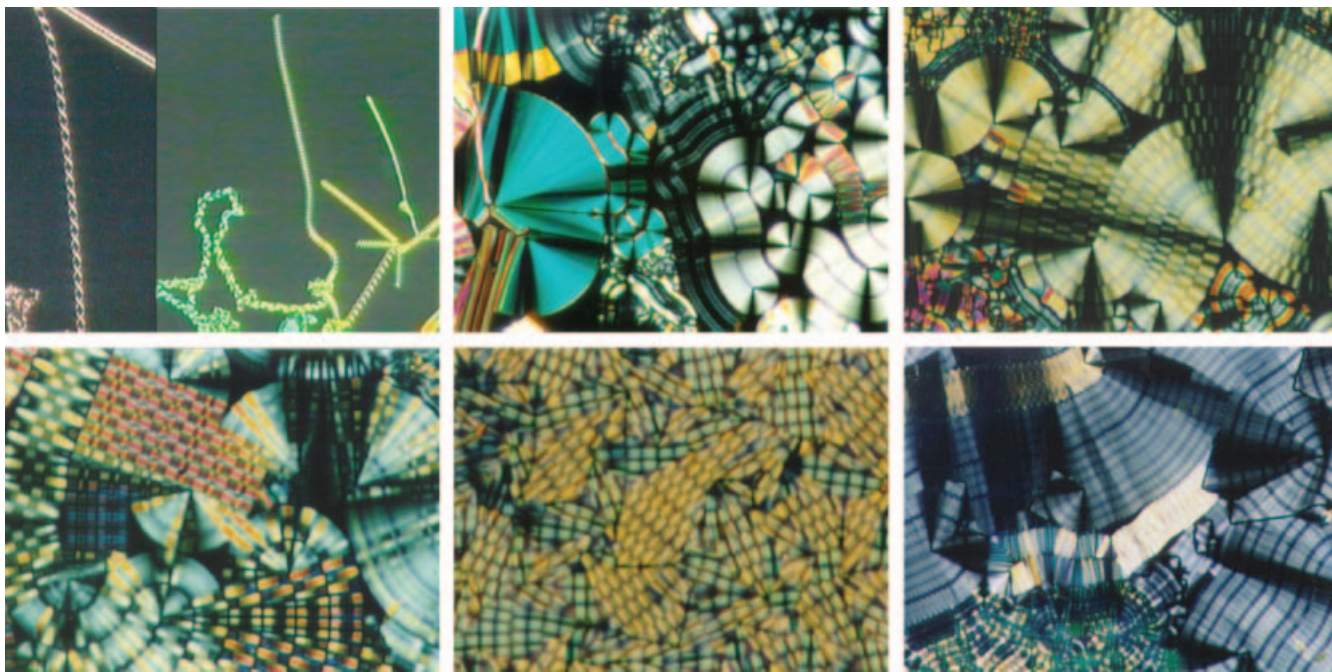


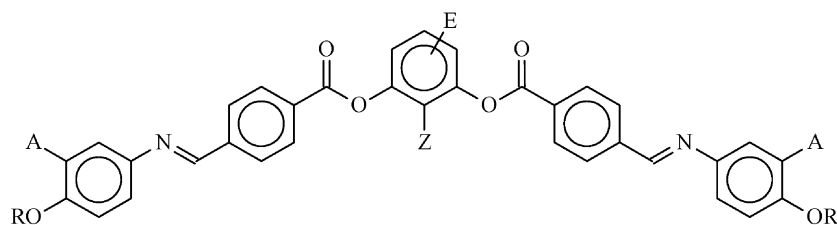
Figure 1. Unfortunately, in our paper from 1999 the textures of the  $B_7$  phase were shown in black and white. Now we present some of these microphotographs in the original coloured version in order to demonstrate the extraordinary beauty of these textures.

It is interesting that a bent compound consisting of two mesogenic units connected by an odd membered spacer also exhibits a  $B_7$  phase [20].

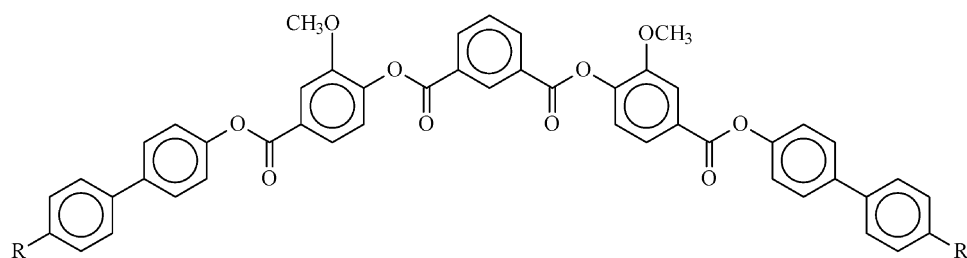
Recently, it has been found in two series that the  $B_7$  phase can also occur as a low temperature phase of the  $SmCP_A$  phase [16, 17, 18]. In this case the  $B_7$  phase does not form screw-like domains but paramorphotic textures of the  $SmCP_A$  phase. The compounds of the first series are related to formula I with  $Z=H$  and  $E=5-F$ .

Additionally, chlorine atoms are attached in both positions A [16]. The second series has a molecular design which is absolutely different (see formula II [17, 18]). In most cases  $B_7$  phases are non-switchable even at high electric fields. But there are also  $B_7$  phases with ferroelectric [7, 11, 16] or antiferroelectric switching [10, 15].

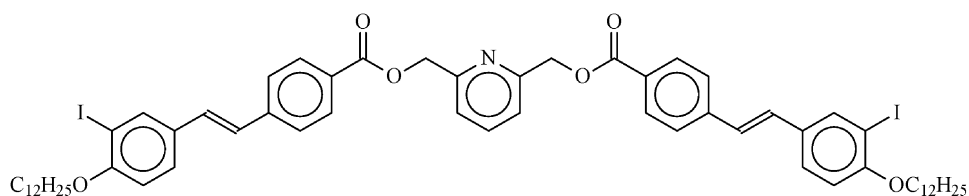
It is interesting that nearly simultaneously with the discovery of the  $B_7$  phase in 1999 another banana phase



**Formula I**



**Formula II**



Formula III

was reported [22] which was later designated with the code letter  $B_7'$  [21]. This phase also exhibits helical nuclei and a domain morphology quite similar to the original  $B_7$  phase [9, 22–40].

The  $B_7'$  phase has been reported for bent mesogens with quite different structures. In some cases the molecules forming a  $B_7'$  phase have a chemical structure similar to formula I. For example, the direct connection of the outer rings of the nitro compounds ( $Z=NO_2$ ) without linking group using biphenyl units [35] or the substitution of the central 2-nitro-1,3-phenylene moiety by a 1-nitro- and 1-cyano-2,7-naphthylene unit [33, 38] result in a  $B_7'$  phase. Furthermore, it is of interest that for seven-ring compounds the shift of the cyano group from the 2-position to the top of the bent molecule (position 5) changes the phase type from  $B_7$  to  $B_7'$  [36]. For compounds without a polar group at the central ring, a simple variation of the terminal groups, for example, the connection of the hydrocarbon chains to the outer rings by means of sulphur or a carboxylic group [25, 40] or the use of branched terminal chains, can result in materials having a  $B_7'$  phase [26, 30, 39]. For several compounds having fluorine, chlorine, bromine and iodine atoms, respectively, in both positions A,  $B_7'$  phases were also found [22–24, 27–29, 31, 32, 37].

The chemical structure of the derivative shown in formula III is remarkable. Here not only the central aromatic ring is a pyridine ring, but also both legs are linked with the central ring by three-membered connecting groups [34]. At the moment, it is not possible to find common structural features for all bent-core mesogens forming  $B_7'$  phases [55].

In most cases the  $B_7'$  phase shows an antiferroelectric or ferroelectric switching. But in contrast to the original  $B_7$  phase this phase possesses either a simple layer structure or an undulated layer structure. The undulation of the smectic layers was first detected by Coleman *et al.* [30]. Using a high resolution synchrotron X-ray diffraction with a micro-beam collimation, satellites of weak intensity behind the layer reflection were observed indicating the layer undulation of supramolecular length (15...70 nm). Since in most cases satellites behind the layer reflections cannot be detected by standard X-

ray techniques it could be that  $B_7'$ -like phases with a simple layer structure show also an undulation of the layers with a relatively large period ( $>100$ nm).

Coleman *et al.* [30] have not only carried out high-resolution synchrotron and microbeam X-ray experiments but also freeze-fracture electron microscopy and careful electro-optical investigations. On the basis of the experimental results a plausible structural model of the  $B_7'$  phase has been proposed which can be described by a synclitic ferroelectric  $SmCP$  structure ( $SmC_S P_F$ ). In order to avoid macroscopic polar order a splay of the polarization occurs giving rise to an undulation of the smectic layers and in this way to a lowering of the free energy. In the ferroelectric domain stripes with preferred polarization splay occur which are separated by defect walls. Two types of defect walls can be distinguished: those where the chirality and clinicity changes between neighbouring stripes and those where the clinicity changes and the chirality remains. According to ref. [30] the non-undulated  $SmC_S P_F$  structure is metastable and can appear by quenching from the isotropic liquid or can be induced by the application of an electric field larger than a threshold value. The metastable state thermally returns to the stable polarization-splay-modulated state on the removal of the field as experimentally proved by X-ray microbeam studies of Nakata *et al.* [39]. Recently Vaupotic and Copic [41] presented a theoretical model which describes the transition of the  $SmC_S P_F$  phase to the layer-undulated and polarization modulated  $B_7'$  phase. It is shown that this transition is driven by the coupling between the polarization splay and the tilt of the molecules. Since this coupling depends strongly on the specific structure of the constituent molecules it is plausible that minor structural changes can significantly influence the threshold required to suppress the undulated structure. The authors also give an estimation of the undulation period as well as of the width of the walls between two domains of opposite chirality.

It should be noted that a fractal dimensional analysis has been employed to characterize the ordering of the  $B_7'$  phase by its formation from the isotropic liquid [42]. Recently, AFM and scanning electron microscopy

investigations have been performed to study the growth of screw-like filaments in droplets and thin films confined by a substrate [43].

The  $B_7'$  phase can occur together with a  $SmCP_A$  phase but in this case it is the high-temperature phase with respect to the  $SmCP_A$  phase [28, 31, 32]. The initial assignment of this  $B_7'$  phase as a  $SmCG$  phase could not be confirmed by later investigations.

As shown by Coleman *et al.* [30] the splay modulation plays an important role for the stabilization of the helical filament structures. But it should be emphasized that the occurrence of helical filaments is not a sufficient criterion for the assignment of a  $B_7$  respectively  $B_7'$  phase. It is known from the literature that any layer instability can lead to the formation of helical filaments during the growing process, also in the absence of molecular chirality [44–47].

In contrast to the  $B_7'$  phase where the structure is well understood, a convincing and uniform structure model of the original  $B_7$  phase has not been established up to now. Due to the absence of well-developed monodomains all structural investigations were carried out on non-oriented samples. In this case the lattice and the symmetry of the structure have to be assumed in the process of the evaluation of the X-ray patterns and cannot be directly deduced from the patterns. This problem is compounded by the fact that the small-angle reflections of the pattern obtained from non-oriented samples with conventional techniques, are often not well resolved. Therefore the assumed lattice cannot be proved with certainty. In addition, the X-ray patterns of the  $B_7$  phase mostly display reflections in the middle range of the scattering angle ( $2\theta=12^\circ\dots14^\circ$ ) which have to fit the proposed model.

The first structural model of the  $B_7$  phase was presented by Brand *et al.* [48]. On the basis of theoretical (symmetry) considerations they assumed a polar columnar structure. Although the constituent molecules are achiral the proposed structure has no mirror plane and corresponds to a chiral phase divided into domains of opposite handedness. The absence of a mirror plane (i. e. a structure with  $C_1$  symmetry) is only possible when the polarization includes an angle different from  $0^\circ$  or  $90^\circ$  with the column axes.

The high-resolution X-ray studies by Coleman *et al.* [30] yielded an interdigitated two-dimensional oblique lattice for the original  $B_7$  phase. For two further bent-core mesogens exhibiting the dimorphism  $B_7$ – $SmCP_A$  also an oblique cell was proposed for the  $B_7$  phase [16, 17]. Folcia *et al.* [49] performed detailed X-ray investigations on the octyloxy homologue of the parent series derived from 2-nitroresorcinol [3]. They also described the structure of the  $B_7$  phase by an oblique

two-dimensional cell but in contradiction to ref. [30] they discarded a centro-symmetric structure and proposed a two-dimensional lattice with  $p121$  symmetry. Using additional information from SHG and considering space filling conditions, four possible structural models were presented where the building units are  $SmC_A P_A$  or  $SmC_A P_F$  fragments. It is interesting that according to Coleman *et al.* [30] the rectangular phase of a bent mesogenic twin [20] can also be regarded as a  $B_7$  phase. In this case no helical filaments are observed but splay stripe textures occur indicating a polarization modulated structure.

A detailed analysis of the optical textures of the  $B_7$  phase as well as the study of the growth features and annealing processes has been done by Nastishin *et al.* [50, 51]. The most striking textural feature – the helical ribbons – are described as a screw dislocation with a giant Burgers vector split into two helical disclination lines of strength  $\frac{1}{2}$  which bound the ribbons. The Burgers vector is equal to the pitch of the helices and the smectic layers adopt the shape of nested parallel helicoids.

Dielectric investigations on the  $B_7$  phase give controversial results which may be related to different substructures. In the octyloxy homologue of the parent series the  $B_7$  phase only shows the collective mode **A** which is difficult to separate from the conductivity [52]. The reorientation of the whole molecule about the long axis (mode **B**) could not be seen, probably due to a compensation of the perpendicular dipole components of the core. The introduction of a fluorine atom in each of the outer rings makes the situation clearer. In this case mode **A** with a static dielectric permittivity of 25 and a high frequency limit of 11 was observed [53]. Mode **B** appears at higher frequencies out of the measuring range ( $f>3\text{MHz}$ ). At the transition into a low temperature phase mode **B** was clearly detected. In a substance with the polymorphism  $SmCP_A$ – $B_7$  [16] mode **A** could be separated from the conductivity only in the  $SmCP_A$  phase whereas mode **B** was found in both mesophases [54]. In contradiction to the former experiments the intensity of mode **B** decreases within the  $B_7$  phase and reaches the intensity of zero at the phase transition temperature into an additional low temperature phase. The third and fast relaxation mode **C**, seen also in the  $B_7$  phase, is related to the dynamics of the terminal groups and reduces the dielectric permittivity to about 2.5 – the expected optical limit.

Although the  $B_7$  phase was discovered only seven years ago the little plantlet  $B_7$  has grown to a tree with many branches. Some unusual properties of single “branches” have been clarified, but on the other hand, many questions have not yet been answered and further

research should shed more light on this matter. We are sure that also in the next years the mesophases of the “B<sub>7</sub>-family” will give rise to many surprises. For the future we wish our fellow-researchers as much pleasure with this subject as we had.

## References

- [1] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. *J. Mater. Chem.*, **6**, 1231 (1996).
- [2] W. Weissflog, C. Lischka, I. Benné, T. Scharf, G. Pelzl, S. Diele, H. Kruth. *Proc. SPIE: Int. Soc. Opt. Eng.*, **3319**, 14 (1998).
- [3] G. Pelzl, S. Diele, A. Jakli, Ch. Lischka, I. Wirth, W. Weissflog. *Liq. Cryst.*, **26**, 135 (1999).
- [4] G. Pelzl, S. Diele, W. Weissflog. *Adv. Mater.*, **11**, 707 (1999).
- [5] A. Jakli, Ch. Lischka, W. Weissflog, G. Pelzl, A. Saupe. *Liq. Cryst.*, **27**, 1405 (2000).
- [6] Y. Yusuf, Y. Hidaka, S. Kai, H.R. Brand, P.E. Cladis, W. Weissflog, G. Pelzl. *Ferroelectrics*, **276**, 171 (2002).
- [7] J.P. Bedel, J.C. Rouillon, J.P. Marcerou, M. Laguerre, H.T. Nguyen, M.F. Achard. *Liq. Cryst.*, **27**, 1411 (2000).
- [8] V. Prasad. *Liq. Cryst.*, **28**, 1115 (2001).
- [9] W. Weissflog, H. Nadasi, U. Dunemann, G. Pelzl, S. Diele, A. Eremin, H. Kresse. *J. Mater. Chem.*, **11**, 2748 (2001).
- [10] D.S. Shankar Rao, Geetha G. Nair, S. Krishna Prasad, S. Anita Nagamani, C.V. Yelamaggad. *Liq. Cryst.*, **28**, 1239 (2001).
- [11] J.P. Bedel, J.C. Rouillon, J.P. Marcerou, M. Laguerre, H.T. Nguyen, M.F. Achard. *J. Mater. Chem.*, **12**, 2214 (2002).
- [12] R. Amaranatha Reddy, B.K. Sadashiva. *Liq. Cryst.*, **29**, 1365 (2002).
- [13] R. Amaranatha Reddy, B.K. Sadashiva. *Liq. Cryst.*, **30**, 273 (2003).
- [14] H.N. Shreenivasa Murthy, B.K. Sadashiva. *Liq. Cryst.*, **30**, 1051 (2003).
- [15] H.N. Shreenivasa Murthy, B.K. Sadashiva. *J. Mater. Chem.*, **13**, 2863 (2003).
- [16] G. Pelzl, M.W. Schröder, U. Dunemann, S. Diele, W. Weissflog, C. Jones, D. Coleman, N.A. Clark, R. Stannarius, J. Li, B. Das, S. Grande. *J. Mater. Chem.*, **14**, 2492 (2004).
- [17] V. Novotna, V. Hamplova, M. Kaspar, M. Glogorova, K. Knizek, S. Diele, G. Pelzl, C. Jones, D. Coleman, N.A. Clark. *Liq. Cryst.*, **32**, 967 (2005).
- [18] V. Novotna, V. Hamplova, M. Kaspar, M. Glogorova, D. Pociecha. *Liq. Cryst.*, **32**, 1115 (2005).
- [19] S. Umadevi, B.K. Sadashiva. *Liq. Cryst.*, **32**, 1233 (2005).
- [20] S.-W. Choi, M. Zennyoji, Y. Takanishi, H. Takezoe, T. Niori, J. Watanabe. *Mol. Cryst. Liq. Cryst.*, **328**, 185 (1999).
- [21] R. Amaranatha Reddy, C. Tschierske. *J. Mater. Chem.*, **16**, 907 (2006).
- [22] C.K. Lee, L.C. Chien. *Liq. Cryst.*, **26**, 609 (1999).
- [23] C.K. Lee, L.C. Chien. *Ferroelectrics*, **243**, 231 (2000).
- [24] G. Heppke, D.D. Parghi, H. Sawade. *Ferroelectrics*, **243**, 269 (2000).
- [25] G. Heppke, D.D. Parghi, H. Sawade. *Liq. Cryst.*, **27**, 313 (2000).
- [26] D.M. Walba, E. Körblova, R. Shao, J.E. MacLennan, D.R. Link, M.A. Glaser, N.A. Clark. *Science*, **288**, 2181 (2000).
- [27] C.-K. Lee, A. Primak, A. Jakli, E.-J. Choi, W.-C. Zin, L.-C. Chien. *Liq. Cryst.*, **28**, 1293 (2001).
- [28] A. Jakli, D. Krüerke, H. Sawade, G. Heppke. *Phys. Rev. Lett.*, **86**, 5715 (2001).
- [29] J. Mieczkowski, J. Szydłowska, J. Matraszek, D. Pociecha, E. Gorecka, B. Donnio, D. Guillon. *J. Mater. Chem.*, **12**, 3392 (2002).
- [30] D.A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Z. Takanishi, E. Körblova, D.R. Link, R.-F. Shao, W.G. Jang, J.E. MacLennan, O. Mondain-Monval, C. Boyer, W. Weissflog, G. Pelzl, L.-C. Chien, J. Zasadzinski, J. Watanabe, D.M. Walba, H. Takezoe, N.A. Clark. *Science*, **201**, 1204 (2003).
- [31] A. Jakli, G.G. Nair, H. Sawade, G. Heppke. *Liq. Cryst.*, **30**, 265 (2003).
- [32] A. Eremin, S. Diele, G. Pelzl, H. Nadasi, W. Weissflog. *Phys. Rev. E*, **67**, 021702 (2003).
- [33] J. Svoboda, V. Novotna, V. Kozmik, M. Glogorova, W. Weissflog, S. Diele, G. Pelzl. *J. Mater. Chem.*, **13**, 2104 (2003).
- [34] J. Mieczkowski, K. Gomola, J. Koseska, D. Pociecha, J. Szydłowska, E. Gorecka. *J. Mater. Chem.*, **13**, 2132 (2003).
- [35] K. Fodor-Csorba, A. Vajda, A. Jakli, C. Slugovec, G. Trimmel, D. Demus, E. Gacs-Baitz, S. Kolly, G. Galli. *J. Mater. Chem.*, **14**, 2499 (2004).
- [36] R. Amaranatha Reddy, B.K. Sadashiva. *Liq. Cryst.*, **31**, 1069 (2004).
- [37] P. Pyc, J. Mieczkowski, J. Pociecha, E. Gorecka, B. Donnio, D. Guillon. *J. Mater. Chem.*, **14**, 2374 (2004).
- [38] V. Kozmik, M. Kuchar, J. Svoboda, V. Novotna, M. Glogorova, U. Baumeister, S. Diele, G. Pelzl. *Liq. Cryst.*, **32**, 1151 (2005).
- [39] M. Nakata, D.R. Link, Y. Takanishi, Y. Takahashi, J. Thisayukta, H. Niwano, D.A. Coleman, J. Watanabe, A. Iida, N.A. Clark, H. Takezoe. *Phys. Rev. E*, **71**, 011705 (2005).
- [40] S. Umadevi, A. Jakli, B.K. Sadashiva. *Soft Matter*, **2**, 215 (2006).
- [41] N. Vaupotic, M. Copic. *Phys. Rev. E*, **72**, 031701 (2005).
- [42] I. Dierking, H. Sawade, G. Heppke. *Liq. Cryst.*, **28**, 1767 (2001).
- [43] A. Eremin, L. Naja, A. Nemes, R. Stannarius, M. Schulz, K. Fodor-Csorba. *Liq. Cryst.*, **33**, 789 (2006).
- [44] C.E. Williams. *Philos. Mag.*, **32**, 313 (1975).
- [45] M. Kleman, O.D. Lavrentovich. *Soft Matter Physics: An Introduction*. Springer, New York (2003).
- [46] J. Tsafirir, M.-A. Guedeau-Boudeville, D. Kandel, J. Stavans. *Phys. Rev. E*, **63**, 031603 (2001).
- [47] C.D. Santangelo, P. Pincus. *Phys. Rev. E*, **66**, 061501 (2002).
- [48] H.R. Brand, P.E. Cladis, H. Pleiner. *Europhys. Lett.*, **57**, 368 (2002).
- [49] C.L. Folcia, J. Etxebarria, J. Ortega, M.B. Ros. *Phys. Rev. E*, **72**, 041709 (2005).
- [50] Y.A. Nastishin, M.F. Achard, H.T. Nguyen, M. Kleman. *Eur. Phys. J. E*, **12**, 581 (2003).
- [51] M.F. Achard, M. Kleman, Y.A. Nastishin, H.T. Nguyen. *Eur. Phys. J. E*, **16**, 37 (2005).
- [52] H. Schmalfuss, A. Hauser, H. Kresse. *Mol. Cryst. Liq. Cryst.*, **351**, 221 (2000).

- [53] J. Salfetnikova, H. Nadasi, W. Weissflog, A. Hauser, H. Kresse. *Liq. Cryst.*, **29**, 115 (2002).
- [54] H. Kresse, Z. Vakhovskaya, U. Dunemann, W. Weissflog, A. Hauser. *Mol. Cryst. Liq. Cryst.*, **449**, 1 (2006).
- [55] A table of nearly all compounds exhibiting a  $B_7$  or  $B_7'$  phase is given in the ESI of the review article in ref. [21]. It should be mentioned that not in all cases is the phase classification in agreement with the literature.



## Preliminary communication

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

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(Received 27 July 1998; accepted 10 September 1998)

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<sub>4</sub> 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<sub>4</sub> phase. The chirality of smectic layers constituted by banana-shaped molecules was first detected by Link *et al.* [3] for the antiferroelectric B<sub>2</sub> 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<sub>7</sub>. 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<sub>7</sub> phase is not miscible with other B phases or with any known smectic phase of calamitic compounds.

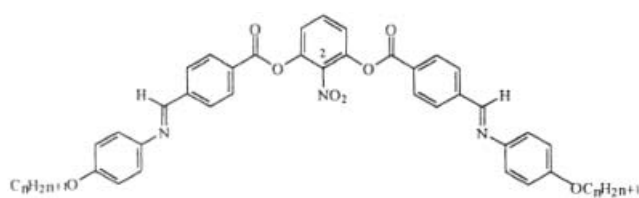
The synthesis of 2-nitro-1,3-phenylene bis[4-(4-*n*-alkyl-oxyphenyliminomethyl)benzoates] was achieved by esterification of 2-nitroresorcinol with 4-(4-*n*-alkyloxyphenyliminomethyl)benzoic acids using dicyclohexylcarbodiimide in the presence of dimethylaminopyridine in dichloromethane according to Steglich 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*-alkyloxy-anilines 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

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



<i>n</i>	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	• <sup>a</sup>	• 174 [30.20]	•
12	• 85 [13.92]	• 173 [28.41]	•

<sup>a</sup>The melting point could not be determined either by calorimetry or by polarizing microscopy.

mmol) 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:  $\text{C}_{58}\text{H}_{71}\text{N}_3\text{O}_8$  ( $M_m$ : 938.22), calc: C=74.25, H=7.63, N=4.48; found: C=74.22, H=7.45, N=4.46%.  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.59 (s, 2H,

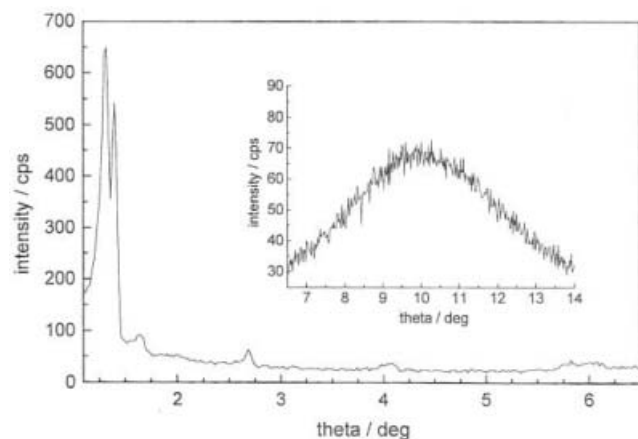


Figure 1. X-ray diffraction pattern of the  $B_7$  phase of the octyloxy homologue ( $151^{\circ}\text{C}$ ).

$\text{CH}=\text{N}$ ), 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,  $\text{OCH}_2$ ,  $J=6.5$  Hz), 1.81 (m, 4H,  $\text{OCH}_2\text{CH}_2$ ), 1.28 (m, 36H,  $\text{CH}_2$ ), 0.89 (m, 6H,  $\text{CH}_3$ ).

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 ( $\sim 10^{\circ}$ ) 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<sup>†</sup>) 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 ( $2\ \mu\text{m}$ ), the  $B_7$  phase appears in some parts of the cell as a weakly birefringent fan-shaped

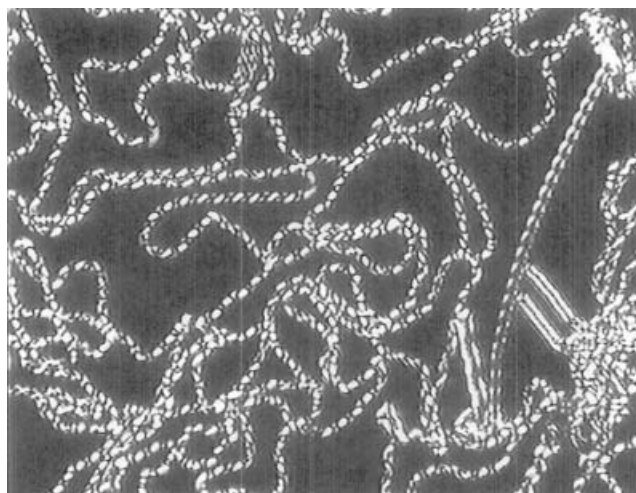


Figure 2. Growth of thread-like and spiral nuclei on cooling the isotropic liquid.

<sup>†</sup> All microphotographs relate to the octyloxy homologue.

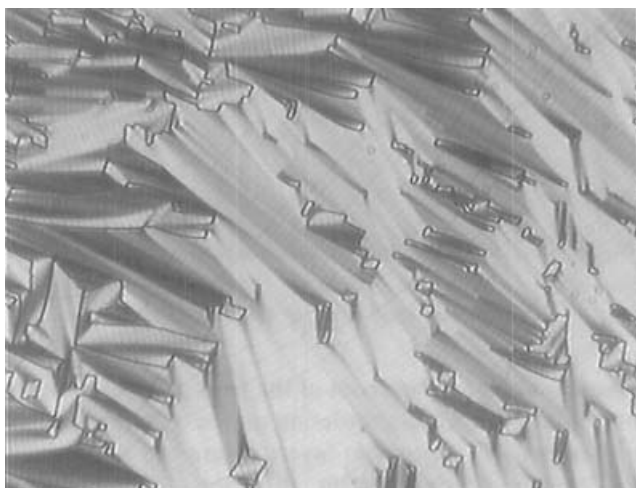


Figure 3. Fan-shaped texture of the  $B_7$  phase (162°C, sample thickness 2  $\mu\text{m}$ ).

texture which reminds one of the corresponding 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  $\mu\text{m}$ . Inserting a  $\lambda$ -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.

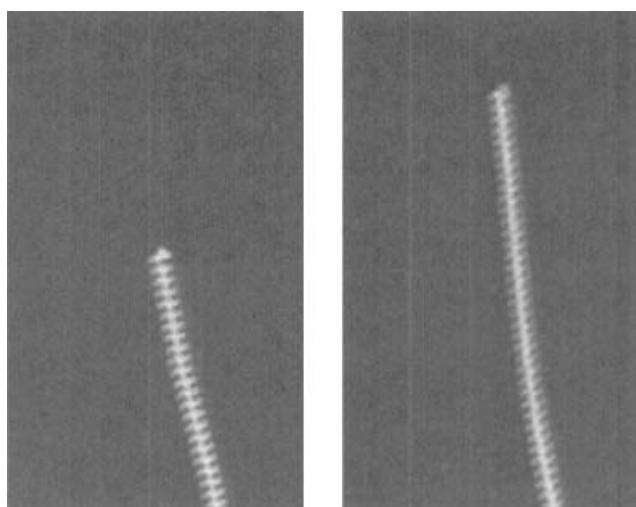


Figure 4. Growth of a spiral domain on cooling the isotropic liquid.

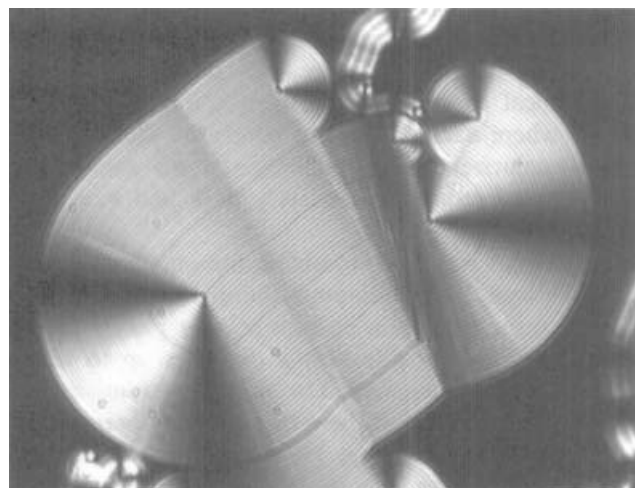


Figure 5. Oval domains with equidistant stripes (175°C, sample thickness 2  $\mu\text{m}$ ).

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  $\mu\text{m}$ . 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

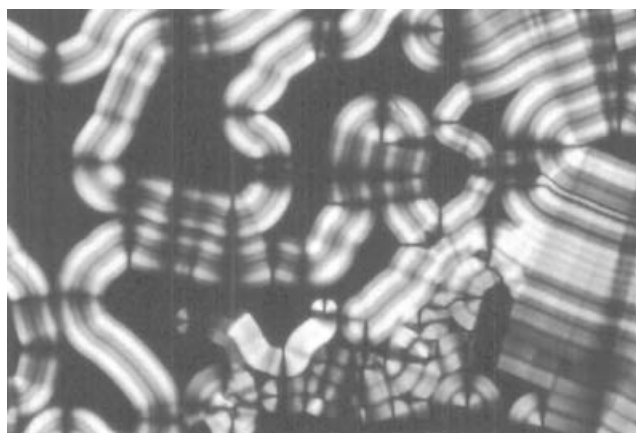


Figure 6. Myelinic texture of the  $B_7$  phase (175°C).

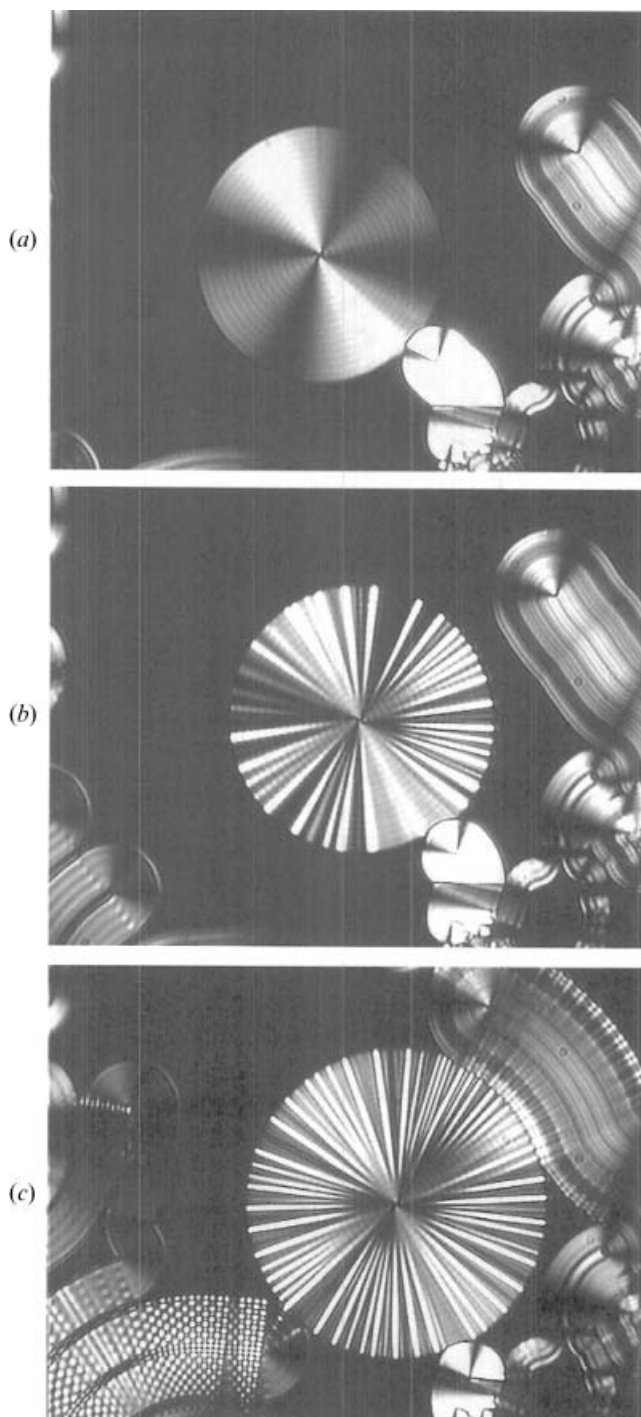


Figure 7. Growth of a circular domain on cooling the isotropic liquid (sample thickness  $2\ \mu\text{m}$ ).

figure 7(b) that, on cooling, the circular 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.

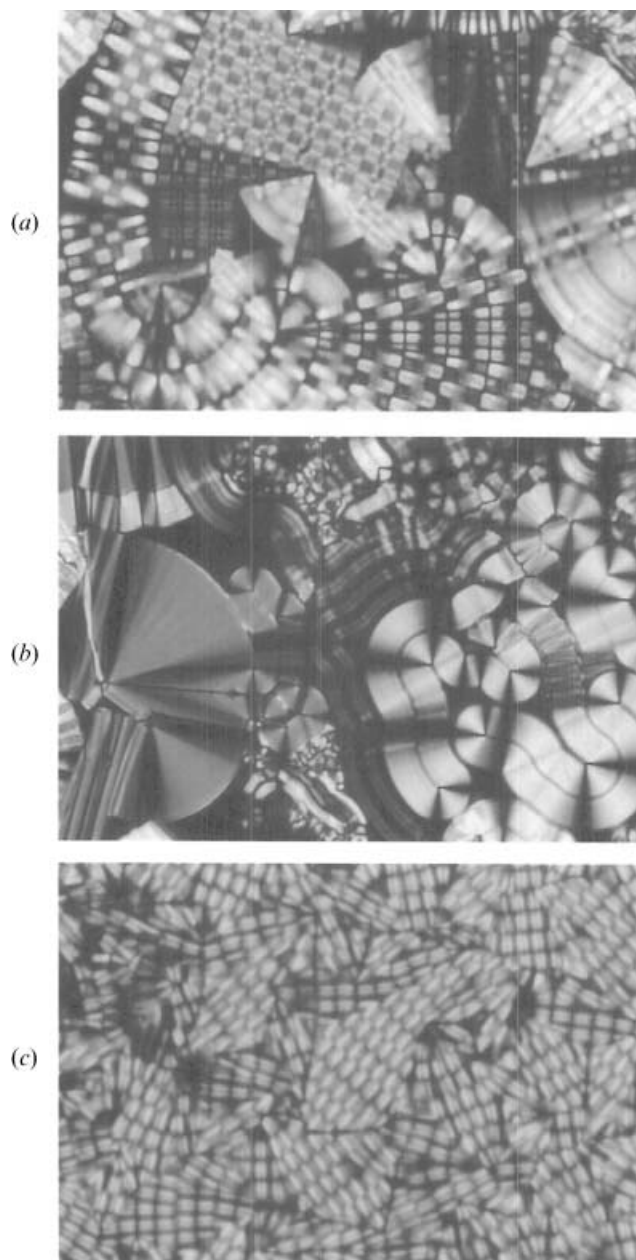


Figure 8. Texture variants of the  $B_7$  phase.

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  $90^\circ$  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  $\text{SmC}^*$  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  $\text{B}_7$  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  $10\ \mu\text{m}$  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  $\text{B}_2$  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.

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  $\text{B}_2$  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] P. Collings, G. Heppke, D. Krüerke, C. Löhning, J. Rabe, W. Stocker. in Abstracts of the Workshop on Banana-Shaped Liquid Crystals: Chirality of Achiral Molecules, December 1997, Berlin, p. 15 (1997).
- [2] G. Heppke, D. Moro. *Science*, **279**, 1872 (1998).
- [3] D.R. Link, G. Natale, R. Shao, J.E. MacLennan, N.A. Clark, E. Körblova, D.M. Walba. *Science*, **278**, 1924 (1997).
- [4] T. Sekine, T. Niori, J. Watanabe, T. Fukukawa, S.W. Choi, H. Takezoe. *J. mater. Chem.*, **7**, 1307 (1997).
- [5] W. Weissflog, Ch. Lischka, I. Bennié, T. Scharf, G. Pelzl, S. Diele, H. Kruth. *Proc. SPIE Liquid Crystals: Chemistry and Structure*, **3319**, 14 (1997).
- [6] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. *J. mater. Chem.*, **6**, 1231 (1996).
- [7] B. Neises, W. Steglich. *Angew. Chem.*, **90**, 556 (1978).
- [8] W. Weissflog, Ch. Lischka, S. Diele, G. Pelzl, I. Wirth, H. Grande, H. Kresse, H. Schmalfuss, H. Hartung, A. Stettler, *Mol. Cryst. liq. Cryst.* (submitted).
- [9] L. Bourdon, I. Sommeria, M. Kleman. *J. Phys. (Paris)*, **43**, 77 (1982).