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Liquid Crystals

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Chiral domains of the SmCP$_A$ phase formed by cooling the isotropic liquid or by field-induced nucleation above the clearing temperature

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Chiral domains of the SmCP$_A$ phase formed by cooling the isotropic liquid or by field-induced nucleation above the clearing temperature

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Three homologues belonging to a new class of achiral and asymmetric bent-core mesogens have been synthesized. The mesophase behaviour was investigated using polarizing optical microscopy, and by X-ray and electro-optical measurements. On cooling the isotropic liquid, the SmCP$_A$ phase of the dodecyloxy homologue forms a non-birefringent texture which exhibits randomly distributed domains of opposite handedness. Surprisingly, such chiral domains could also be induced above the clearing temperature using a sufficiently high electric field.

1. Introduction

The discovery of polar switching in the smectic phase of achiral bent-core mesogens opened a new area in the study of polar order and chiral structures in liquid crystals [1]. The long-range polar order in such compounds gives rise to new mesophases with ferroelectric or antiferroelectric properties [2]. Furthermore, the combination of polar order and director tilt, characteristic of the SmCP phase, can lead to the chirality of smectic layers although the molecules are achiral [3, 4]. All layers of a macroscopic domain can have layer chirality of the same sign (homochiral state) or the chirality can alternate from layer to layer (racemic state) [3].

The chirality of smectic layers is obviously the reason for the occurence of helical superstructures which have been observed for several 'banana' phases. For example, helical superstructures are indicated by the growth of screw-like or telephone wire-like nuclei on slow cooling of the isotropic liquid. Such nucleation was observed in B$_7$ phases [5–9] as well as in undulated SmCP phases [10–13]. Since the molecules are achiral, right-handed and left-handed helices occur with equal probability. On the other hand, some bent-core mesogens are able to form weakly birefringent textures of the SmCP phase which contain domains of opposite handedness. Such domains can arise spontaneously on cooling the isotropic liquid [14–19] or by relaxation of the switched ferroelectric state [20–24]. In this case, also domains of opposite chirality are formed with equal probability.

The mesophase behaviour of three new homologous asymmetric bent-core compounds has been studied by polarizing optical microscopy, calorimetry, X-ray diffraction and electro-optically. The hexyloxy homologue displays a dimorphism SmA–N, characteristic for a calamitic compound. The octyloxy and dodecyloxy homologues show a SmCP$_A$ phase typical for a bent compound. It was found that the SmCP$_A$ phase of the dodecyloxy homologue can form chiral domains of opposite handedness, not only on cooling the isotropic liquid, but also by application of a sufficiently high electric field at temperatures above the clearing temperature.

2. Materials

The compounds under investigation belong to a new class of bent-core mesogens in which the central fragment consists of a benzoyl derivative of a secondary cyclic amine. In these compounds the bending of the molecules is not achieved by 1,3-substitution of a central aromatic ring, but by a carbonyl group which links the phenyl ring of one leg to the nitrogen of a piperazine ring which is part of the second leg of the bent-core mesogens (see figure 1). The phase behaviour and transition enthalpies of the investigated compounds are summarized in table 1.

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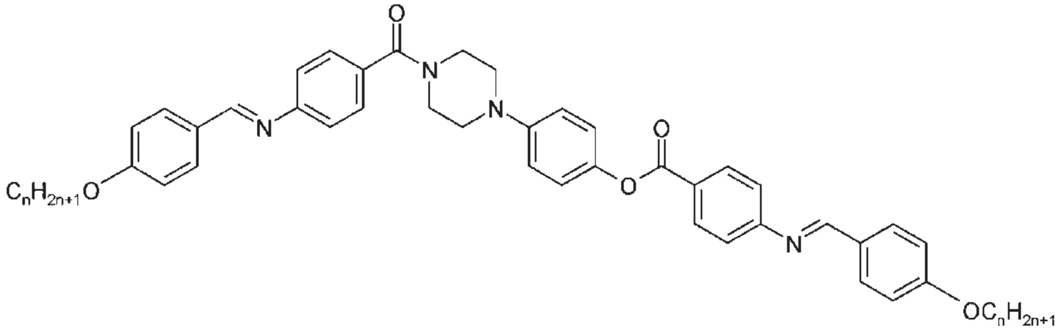


Figure 1. Chemical structure of the investigated compounds ($n=6$, 8, 12).

Table 1. Phase behaviour of the investigated compounds. Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) in square brackets. The temperature in parentheses indicates a monotropic transition.

Compound	n	Cr		SmA		SmCP$_A$		N		I
1	6	•	187 [28.3]	(•	178) [0.2]	—		•	201 [0.2]	•
2	8	•	177 [30.6.]	—		•	198 [8.7]	•	201 [0.6]	•
3	12	•	164 [47.4]	—		•	215 [13.8]	—		•

2.1. *Synthesis*

A mixture of 4-(1-piperazino)phenol (0.36 g, 2 mmol), the corresponding 4-[4-*n*-alkyloxybenzylideneamino]-benzoic acid (4 mmol) [25], DCC (1 g, 4.8 mmol) and DMAP as catalyst in 120 ml dichloromethane was stirred for 24 h at room temperature. The precipitate was filtered off and the solvent evaporated. The products were recrystallized several times from a DMF/ethanol mixture. Yields: 13–28%.

Analytical data are given for compound **3**. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 0.86 (t, $^3J=6.8$ Hz, 6H, $2\times CH_3$), 1.25–1.46 (m, 36H, $2\times$ $(CH_2)_9$), 1.79 (m, 4H, $2\times OCH_2C\underline{H_2}$), 3.19 (broad, 4H, piperazine), 3.83 (broad, 4H, piperazine), 4.02 (t, $^3J=6.4$ Hz, 4H, $2\times OCH_2$), 6.66 (dd, $^3J=8.7$ Hz, $^4J=2.3$ Hz, 2H, Ar–H), 6.97 (d, $^3J=8.7$ Hz, 4H, Ar–H), 7.12 (d, $^3J=8.5$ Hz, 2H, Ar–H), 7.29 (d, $^3J=8.7$ Hz, 2H, Ar–H), 7.48 (d, $^3J=8.3$ Hz, 2H, Ar–H), 7.80 (dd, $^3J=8.9$ Hz, $^4J=2.1$ Hz, 4H, Ar–H), 7.97 (d, $^3J=8.7$ Hz, 2H, Ar–H), 8.19 (d, $^3J=8.7$ Hz, 2H, Ar–H), 8.38 (s, 2H, CH=N). Elemental analysis: $C_{62}H_{80}O_5N_4$, $M_m=961.3$ g mol^{-1}, calcd, C 77.5, H 8.33, N, 5.83; found, C 77.7, H 8.23, N 5.91%.

2.2. *Characterization*

The phase transition temperatures were determined by calorimetry (DSC Pyris 1, Perkin-Elmer) and by polarizing microscopy (Leitz Orthoplan). The polarizing microscope was also used for examination of the optical textures.

X-ray diffraction measurements on powder-like samples were carried out using a Guinier goniometer (Huber Diffraktionstechnik) and a Guinier film camera. Electro-optical investigations were performed using a conventional experimental set-up. The switching polarization was measured by the triangular wave voltage method.

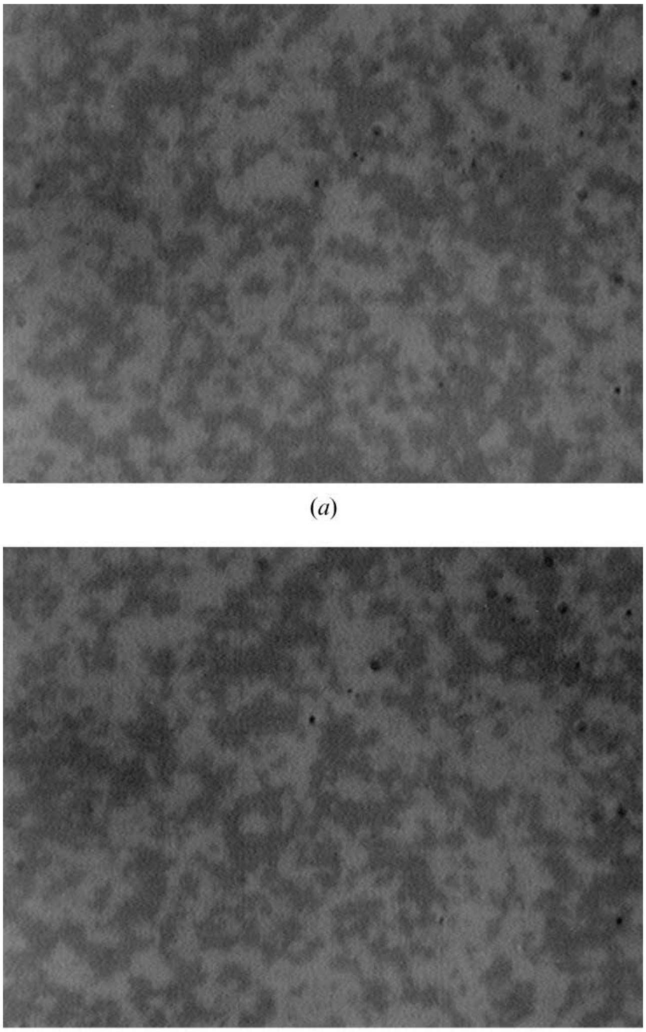
3. Results

3.1 *Texture observations*

As seen from table 1, compounds **1** and **2** form a nematic phase. If a marbled or planar nematic texture of compound **1** is cooled, the low temperature phase adopts a fan-like texture. If the low temperature phase of compound **1** is formed on cooling from a homeotropically oriented nematic phase, the low temperature phase also exhibits a homeotropic texture. This finding suggests a smectic A phase, but we cannot exclude that the low temperature phase is a N_X phase—a new kind of nematic phase—which has been observed for the short chain members of structurally quite similar compounds [25]. This phase exhibits the textural features of a smectic phase, but by X-ray investigations the absence of in-plane order could be shown clearly. Unfortunately, we are unable to distinguish between these possibilities, since this phase is monotropic and crystallizes immediately after its formation.

In contrast to compound **1**, the low temperature phase of compound **2** exhibits a non-specific grainy texture on cooling the nematic phase.

The dodecyloxy homologue **3** does not exhibit a nematic phase, so that the smectic phase is formed directly on cooling the isotropic liquid. In this case the texture shows complete extinction between crossed polarizers. If one polarizer is rotated clockwise by a small angle (5°–10°) with respect to the crossed position, however, bright and dark domains can be distinguished. Rotating the polarizer anticlockwise by



(*a*)

(*b*)

Figure 2. Optical texture with domains of opposite handedness obtained on cooling the isotropic liquid. One polarizer is rotated (*a*) clockwise and (*b*) anticlockwise by 10° from the crossed position (compound **3**, 170°C).

the same angle, we observed exactly the reverse effect: the dark domains become bright and *vice versa* (see figure 2). This finding points to a spontaneous formation of domains of opposite handedness. It should be noted that this texture does not change when the sample is rotated on the heating stage of the microscope. The domains can be destroyed by a strong mechanical stress but the texture remains dark between crossed polarizers. If the mesophase arises on melting the crystalline state a birefringent non-specific texture is obtained.

3.2 *X-ray investigations*

Table 2. Layer spacing d, molecular length L and tilt angle ϑ of the SmCP phase of compounds **2** and **3**.

Compound	d/Å	L/Å	ϑ/°
2	38	51	42
3	42	55	40

The X-ray patterns of the non-oriented smectic phase of compounds **2** and **3** were found to be quite similar, consisting of strong commensurable Bragg reflections in the small angle region and a diffuse scattering maximum in the wide angle region, which indicates a smectic layer structure without in-plane order. From the small angle Bragg reflections the layer spacing d could be calculated (see table 2). For comparison, the molecular lengths L are listed in table 2 which were determined from CPK-models assuming a bending angle (angle between the wings of the bent molecule) of 120°. It is seen that the layer spacing is clearly smaller than the molecular length which indicates a tilted arrangement of the molecules within the smectic layers. From the ratio d/L, a tilt angle ϑ of about 40° could be estimated using via $\cos\vartheta = d/L$.

3.3 *Electro-optical investigations*

If an electric field is applied to the grainy texture of the SmCP phase a reorientation into a stronger birefringent fan-like texture is observed above a threshold field (2–4 V μm^{-1}). This fan-like texture remains after removing the field (figure 3). In some regions the texture of the switched state clearly depends on the polarity of the field, which is indicative of homochiral domains. In the case of the dark texture of compound **3** obtained on cooling the isotropic liquid, the application of the field leads to a disappearance of the chiral domains, and after removing the field the original dark texture does not reappear. The current response to a triangular voltage shows two peaks per half period, indicating an antiferroelectric ground state of the SmCP phase (figure 4). The switching polarization obtained by integrating the area under the current peaks was found to be 480 and 670 nC cm^{-2} for compounds **2** and **3**, respectively.

An interesting electro-optical effect was observed in the isotropic state above the clearing temperature of compound **3**. Above a sufficiently high electric field, a birefringent texture of the SmCP phase grows within the isotropic liquid, and if the field is high enough the mesophase covers the whole viewing field of the microscope. This effect is accompanied by strong electrohydrodynamic motions. In contrast to the non-birefringent texture obtained on cooling the isotropic liquid, the field-induced texture is weakly birefringent. If the field is switched off, the mesophase immediately reappears. No such enhancement of the clearing

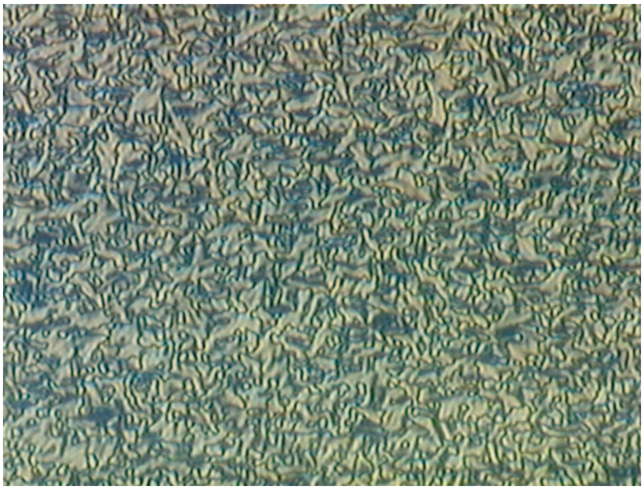


Figure 3. Fan-like texture obtained after removing the applied electric field (compound **3**, 180°C).

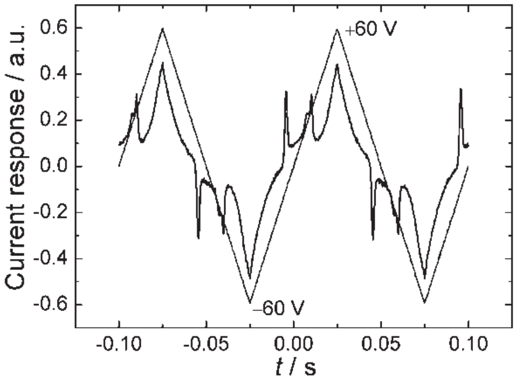


Figure 4. Current response to a triangular voltage (compound **3**, sample thickness 10 μm; applied voltage 120 V_{PP}; frequency 10 Hz; temperature 170°C).

temperature was observed for compounds **1** and **2** where the nematic phase is the high temperature phase. We found that the threshold field above which the smectic nuclei are generated, increases with increasing T–T_{cl}, where T_{cl} is the clearing temperature and T the actual temperature. For example, at 2 K above the clearing temperature the nucleation starts at 15 V μm^{-1}, whereas at 5 K above the clearing temperature a field of 40 V μm^{-1} is necessary. The field-induced nucleation of a 'banana' phase clearly above the clearing temperature was first described in [24, 26]. This effect is obviously due to the field-induced reorientation of ferroelectric clusters which already exist in the isotropic liquid [24]. But in the case of compound **3**, domains of opposite handedness can be clearly distinguished in the field-induced texture by a slight decrossing of the polarizers (figure 5). The occurrence of chiral domains in the field-induced $SmCP_A$ phase was observed for the first time.

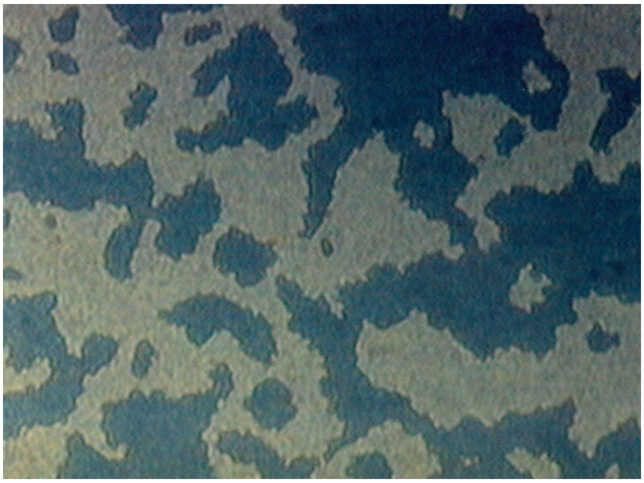


Figure 5. Optical texture of compound **3** obtained 2 K above the clearing temperature by application of an electric field of 25 V μm^{-1}. One polarizer is rotated by +5° from the crossed position.

4. Discussion

To date the structure of the chiral domains has yet to be established. As mentioned already, the texture with chiral domains does not change when the sample is rotated between crossed polarizers. This finding indicates a symmetry axis perpendicular to the substrates, and this symmetry axis can be a helix axis. Recently the texture with chiral domains has been explained by the existence of small domains with a helicoidal arrangement of the bent-core molecules in the homochiral antiferroelectric configuration, whereby the pitch is clearly smaller than the optical wavelength [27].

Another interesting point is the formation of the $SmCP_A$ phase up to 5 K above the clearing temperature under electric field application. Such behaviour has already been described for other bent-core compounds [24, 26], but in the case of compound **3** the field-induced $SmCP_A$ phase shows, in addition, chiral domains of opposite handedness. The origin of this unusual observation is not yet known. Possibly the asymmetric molecular shape of compound **3** is responsible for the preferred formation of a helical superstructure also in the field-induced state.

References

[1] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6,** 213.
[2] Pelzl, G., Diele, S., and Weissflog, W., 1999, *Adv. Mater.*, **11,** 707.
[3] Link, D. A., Natale, G., Shao, R., Maclennan, J. E., Clark, N. A., Körblova, E., and Walba, D. M., 1997, *Science*, **278,** 1924.
[4] Brand, H. R., Cladis, P. E., and Pleiner, H., 1998, *Eur. Phys. J. B*, **6,** 347.

[5] Pelzl, G., Diele, S., Jakli, A., Lischka, C., Wirth, I., and Weissflog, W., 1999, *Liq. Cryst.*, **26,** 135.

[6] Jakli, A., Lischka, C., Weissflog, W., Pelzl, G., and Saupe, A., 2000, *Liq. Cryst.*, **27,** 1405.

[7] Bedel, J. P., Rouillon, J. C., Marcerou, J. P., Laguerre, M., Nguyen, H. T., and Achard, M. F., 2000, *Liq. Cryst.*, **27,** 1411.

[8] Rao, D. S. S., Nair, G. G., Prasad, S. K., Nagamani, S. A., and Yelamaggad, C. V., 2001, *Liq. Cryst.*, **28,** 1239.

[9] Reddy, R. A., and Sadashiva, B. K., 2002, *Liq. Cryst.*, **29,** 1365.

[10] Walba, D. M., Körblova, E., Shao, R., Maclennan, J. E., Link, D. R., Glaser, M. A., and Clark, N. A., 2000, *Science*, **288,** 2181.

[11] Lee, C. K., and Chien, L.-C., 1999, *Liq. Cryst.*, **26,** 609.

[12] Heppke, G., Parghi, D. D., and Sawade, H., 2000, *Ferroelectrics*, **243,** 269.

[13] Coleman, D. A., Fernsler, J., Chattham, N., Nakata, M., Takanishi, Y., Körblova, E., Link, D. R., Shao, R. F., Jang, W. G., Maclennan, J. E., Mondainn-Monval, O., Boyer, C., Weissflog, W., Pelzl, G., Chien, L. C., Zasadzinski, J., Watanabe, J., Walba, D. M., Takezoe, H., and Clark, N. A., 2003, *Science*, **301,** 1204.

[14] Thisayukta, J., Nakayma, Y., and Watanabe, J., 2000, *Liq. Cryst.*, **27,** 1121.

[15] Thisayukta, J., Nakayma, Y., Kawauchi, S., Takezoe, H., and Watanabe, J., 2000, *J. Am. chem. Soc.*, **122,** 7441.

[16] Murthy, H. N. S., and Sadashiva, B. K., 2002, *Liq. Cryst.*, **29,** 1223.

[17] Eremin, A., Diele, S., Pelzl, G., Nadasi, H., and Weissflog, W., 2003, *Phys. Rev. E*, **67,** 21702.

[18] Dantlgraber, G., Eremin, A., Diele, S., Hauser, A., Kresse, H., Pelzl, G., and Tschierske, C., 2002, *Angew. Chem.*, **41,** 2408.

[19] Pelzl, G., Eremin, A., Diele, S., Kresse, H., and Weissflog, 2002, *Liq. Cryst.*, **12,** 2591.

[20] Heppke, G., Parghi, D. D., and Sawade, H., 2000, *Liq. Cryst.*, **27,** 313.

[21] Bedel, J. P., Rouillon, J. P., Marcerou, J. P., Laguerre, M., Achard, M. F., and Nguyen, H. T., 2000, *Liq. Cryst.*, **27,** 103.

[22] Fodor-Csorba, K., Vajda, A., Galli, G., Jakli, A., Demus, D., Holly, S., and Gacs-Baitz, E., 2002, *Macromol. Chem. Phys.*, **203,** 1556.

[23] Etxebarria, J., Folcia, C. L., Ortega, J., and Ros, M. B., 2003, *Phys. Rev. E*, **67,** 042702.

[24] Weissflog, W., Schröder, M. W., Diele, S., and Pelzl, G., 2003, *Adv. Mater.*, **15,** 630.

[25] Schröder, M. W., Diele, S., Pelzl, G., Dunemann, U., Kresse, H., and Weissflog, W., 2003, *J. mater. Chem.*, **13,** 1877.

[26] Bourny, V., Lorman, V., Pavel, J., Mettout, B., and Nguyen, H. T., 2003, *Ferroelectrics*, **276,** 127.

[27] Ortega, J., Folcia, C. L., Etxebarria, J., Gimeno, N., and Ros, M. B., 2003, *Phys. Rev. E*, **68,** 011707.