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Spontaneous chiral ordering in the nematic phase of an achiral banana-shaped compound

G. Pelzl,* A Eremin, S. Diele, H. Kresse and W. Weissflog

Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, D-06108 Halle (Saale), Germany

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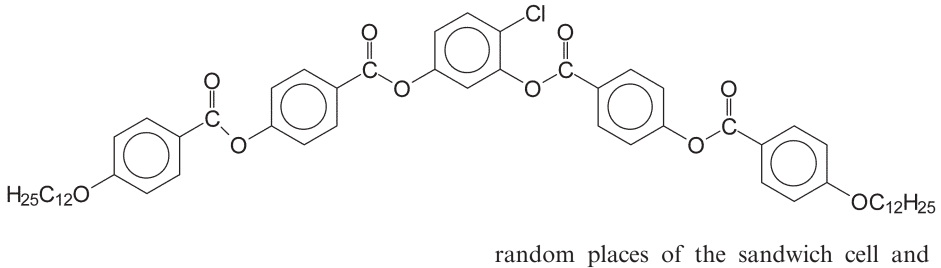
A new achiral banana-shaped mesogen is presented which exhibits a nematic phase and an isotropic mesomorphic phase with spontaneous chiral ordering.

Nematic phases are usually uniaxial. A non-polar biaxial nematic phase, theoretically predicted by Freiser[1] was experimentally discovered in lyotropic systems,[2] and later in liquid crystalline side-chain polymers.[3] As first discussed by Brand *et al.*[4] bent mesogens could be promising candidates for polar biaxial nematics. From the symmetry point of view, biaxial nematic phases with one, two, or three polar axes are, in principle, possible and would exhibit C_{2v}, C_{1h}, or C_1 symmetry, respectively. Similar to smectic phases of the same symmetry, polar biaxial nematics should possess ferro-, ferri-, or antiferroelectric properties.[5] Recently, a number of bent-core mesogens exhibiting the nematic phase have been reported in the literature. Some of these compounds form the nematic phase only.[6–8] Other compounds show the usual smectic and "banana phases" in addition to the nematic phase.[9–11] Until now, no noticeable anomalies were observed in these nematic phases, probably since in most cases the shape of the molecules can be regarded as approximately rod-like. Furthermore, computer simulations give evidence that bent molecules can form the nematic phase above a critical bending angle (which is the angle between the wings of the bent molecule).[12] It was shown by these simulations that the nematic phase can adopt a helical superstructure near to the transition into the polar smectic phase, which corresponds to a conical twist–bend deformation.

In this paper, we present a new achiral banana-shaped mesogen exhibiting a nematic phase with unusual optical and electro-optical properties. In addition, an unknown low temperature phase occurs, preliminarily designated as X. In the transition scheme, the numbers in square brackets under the transition temperatures are the transition enthalpies in kJ mol^{-1}. The parentheses indicate that the nematic and the X phases are monotropic.



$$\mathrm{Cr}\ \frac{98\ ^{\circ}\mathrm{C}}{[38.7]}\ (\mathrm{X}\ \frac{80\ ^{\circ}\mathrm{C}}{[9.1]}\ \mathrm{N}\ \frac{95\ ^{\circ}\mathrm{C}}{[0.65]})\ \mathrm{I}$$

The compound under study, 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate], was prepared by reaction of 4-chlororesorcinol with 4-(4-n-dodecyloxybenzoyloxy)benzoic acid in dichloromethane using 1,3-dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) as catalysts.

4-(4-n-Dodecyloxybenzoyloxy)benzoic acid (1.70 g, 0.004 mol) was added to a solution of 4-chlororesorcinol (280 mg, 0.002 mol), DCC (87 mg, 0.0042 mol), and DMAP (5 mg) in about 20 ml dry dichloromethane. The mixture was stirred for 24 h at room temperature. The solvent was evaporated and the solid was extracted with hot ethanol. The final product was recrystallized twice from a dimethylformamide–ethanol mixture. Yield: 770 mg (40.1%).

^{1}H NMR (200 MHz, $CDCl_3$) δ/ppm (J/Hz): 8.29 (d, J = 8.5, 2H, arom. H), 8.24 (d, J = 8.5, 2H, arom. H), 8.13 (d, J = 8.3, 4H, arom. H), 7.53 (d, J = 8.7, 1H, arom. H), 7.37 (d, J = 8.7, 2H, arom. H), 7.36 (d, J = 8.7, 2H, arom. H), 7.28 (d, J = 2.5, 1H, arom. H), 7.16 (dd, 1H, arom. H), 6.97 (d, J = 8.9, 4H, arom. H), 4.04 (t, J = 6.5, 4H, CH_2O), 1.81 (m, 4H, CH_2CH_2O), 1.26–1.52 (m, 36H, CH_2), 0.87 (t, J = 6.3, 6H, CH_3); IR ν(C=O)/cm^{-1}: (CCl_4) 1744.5; (Nujol) 1728.8, 1739.2, 1745.3; Elemental Analysis: calculated for $C_{58}H_{69}O_{10}Cl$, M_w 961.58, C 72.44, H 7.23, Cl 3.69; found C 72.40, H 7.11, Cl 4.05%

In the nematic phase, regions with different optical properties were observed by polarizing microscopy over the whole temperature range of the nematic phase. Starting from the crossed position of the polarizers and rotating one polarizer clockwise by a small angle (10–20°) dark and light domains become visible. Rotating the polarizer anticlockwise by the same angle causes the effect to be reversed, *i.e.* the previously dark domains now appear light and *vice versa* (see Fig. 1). In addition, these domains can also be distinguished by illuminating the cell with left or right circular polarized light in the reflection mode of the microscope. In the nematic phase, the formation of regions with opposite handedness is obviously the result of spontaneous macroscopic twist. We found that domains of opposite handedness are formed with equal probability. It should be noted that these domains occur in random places of the sandwich cell and can be altered by mechanical stress or by temperature change. The pitch of the twisted domains is clearly larger than the sample thickness, so that the texture corresponds to a nematic phase. The absence of a layer structure is indicated by X-ray investigations, but the existence of cybotactic smectic groups is clearly proven on the

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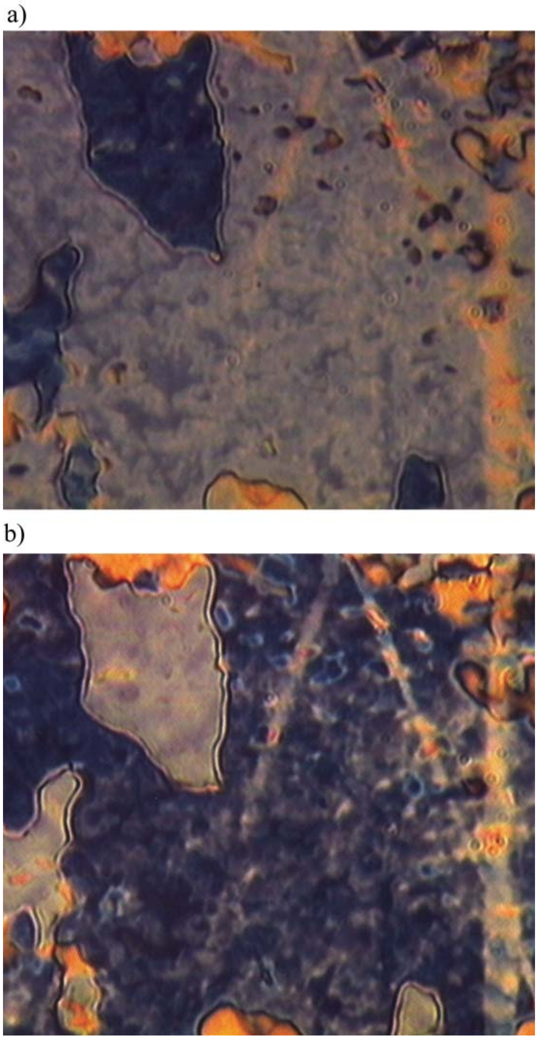

Fig. 1 Texture of the nematic phase observed by rotating one polarizer by 15° (a) clockwise and (b) anticlockwise from the crossed polarizer position, indicating domains of opposite handedness.

base of well-oriented samples. It should be noted that, recently, in the SmC phase of achiral bent mesogens containing a 1,5-disubstituted 2,3,4-trifluorophenyl unit, oppositely handed regions were also observed.[13]

Another interesting finding should be mentioned at this point. On applying a dc field to the planar oriented nematic phase, a domain pattern with equidistant stripes parallel to the original director orientation appears, but this pattern is disturbed by electrohydrodynamic processes as a consequence of the relatively high conductivity. With increasing voltage, the long wave nematic director fluctuations become weaker and a myeline texture with fine equidistant stripes arises, which is transformed into a fan-shaped texture with further increasing voltage (see Fig. 2 and 3). This field-induced fan-shaped texture, which is reminiscent of a smectic phase, is observed in the whole existence region of the nematic phase. If the electric field is removed, the texture of the planar oriented nematic phase reappears. Although the field-induced formation of a smectic phase cannot be excluded, it is more probable that the originally partially twisted sample is deformed by the electric field in such a way that a fan-shaped texture is built up which is also characteristic of a cholesteric phase, but we have no explanation for the mechanism by which such fan-shaped texture can be generated. We were not able to detect polar switching. Furthermore, dielectric measurements gave no evidence for a positive dipole correlation.

Spontaneous twisting is also manifested in the low temperature phase X. This phase is highly viscous and shows

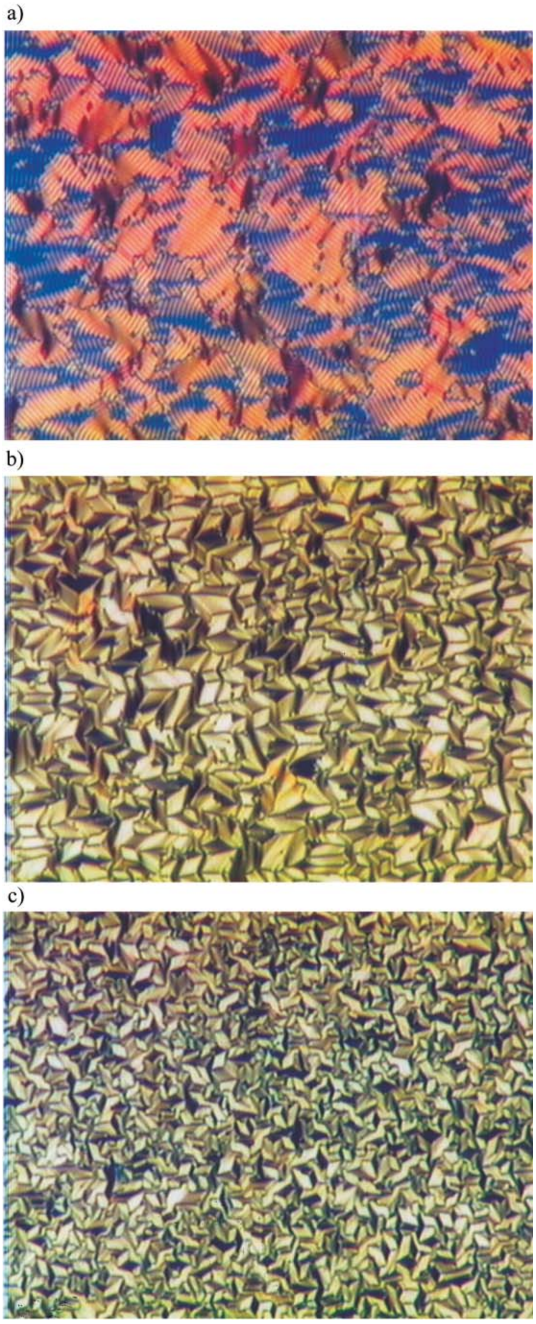

Fig. 2 Field-induced texture change of the nematic phase (90 °C, cell thickness 6 μm): (a) 17; (b) 25; (c) 50 V.

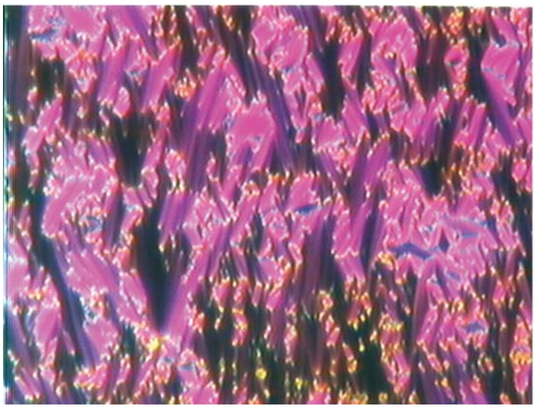

Fig. 3 Field-induced fan-shaped texture in the nematic phase (90 °C, cell thickness 10 μm, applied voltage 100 V).

complete extinction between crossed polarizers. Closer optical examinations gave evidence that this phase is isotropic. It spontaneously forms randomly distributed domains of opposite handedness, visible by rotating one polarizer from the crossed polarizer position. These domains are much more pronounced if this phase is formed in the presence of an electric field. In the X phase, the X-ray pattern displays a closed ring in the small angle region and diffuse scattering in the wide angle region. Although well-oriented samples have been obtained in the nematic phase, the alignment is completely lost in the X phase. The full width at half maximum of the inner ring is in between that of the nematic and usual smectic phases (about 4 times the instrumental resolution). This indicates that the structure of the X phase has no long range order. The formation of spontaneously twisted structures in nematic phases of banana-shaped compounds is obviously a result of the shape of the molecules. Such behaviour was predicted by computer simulations with banana-shaped molecules; according to the simulations, a temperature-driven transition from uniform nematic to a nematic phase with macroscopic twist can take place.[12] As recently shown by Dozov,[14] the bent shape of the molecules can induce a local bend of the director, giving rise either to a splay–bend deformation or a conical twist–bend helix. The latter should be two-fold degenerate, since the molecules are achiral. The highly viscous X phase possesses an isotropic structure and spontaneously forms chiral domains, which is reminiscent of a cholesteric blue phase. Further investigations are necessary (NMR, SHG study, dielectric measurements) to understand these experimental results in more detail.

Acknowledgements

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