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Kojic acid—a new fragment for the preparation of bent-core mesogens

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Kojic acid was used to synthesize bent-core mesogens. Antiferroelectric polar smectic mesophases, an oblique and a rectangular columnar mesophase were found. The mesophases were characterized by X-ray scattering, electro-optical measurements, polarizing microscopy and DSC. On the base of these measurements, models of the mesophases are proposed.

1. Introduction

Over the last decade the mesophases of bent-core compounds have attracted growing interest because of their unusual physical properties [1, 2]. Due to their bent molecular shape, the molecules favour a polar packing in layers, which gives rise to the existence of a spontaneous polarization of the layers and to ferro- and antiferro-electric properties. In tilted smectic phases the combination of polar order and director tilt leads to the formation of chiral structures [3], despite the arrangement involving exclusively achiral molecules. The most common switchable, polar chiral phase of bent-core mesogens is the SmCP phase. Predominately, this phase has an antiferroelectric ground state (SmCP$_A$ phase) which can be switched into ferroelectric states. Depending on the tilt directions (synclinic, anticlinic) these states can be racemic (this means that the handedness of the chiral alignment changes from layer to layer leading to a macroscopic achiral state), or homochiral (homogeneous handedness of the chiral alignment of successive layers in a domain).

The escape from a bulk spontaneous polarization cannot be achieved only by an antiferroelectric structure but also by a modulation of the layers leading to two-dimensional structures. Such columnar phases have been frequently observed among the phases of bent-core compounds. There are rectangular columnar phases (Col$_r$), formerly called 'B$_1$' phases; There are also several examples of the oblique columnar phase, being the high temperature phase above a SmCP phase. The columns are represented by layer fragments, whose polar axis is perpendicular to the lattice vectors.

Usually banana-shaped mesogens are built up from two mesogenic groups linked via a rigid group in such a way as not to be colinear. In most cases, such rigid central groups are aromatic one- or two-ring systems, e.g. 1,3-phenylene or 2,7-naphthylene units; but the insertion of other bent moieties has also been reported, for example Pelz *et al.* [4] started from 4-hydroxybenzyl alcohol as the central core. In the present paper kojic acid was used in the preparation of bent-core mesogens for the first time. It should be mentioned that liquid crystalline compounds derived from kojic acid have not been reported previously. Formally, the kojic acid unit introduces an additional dipole moment into the central part of the bent molecule. Furthermore, the aromatic character of the heterocyclic 4-pyrone is reduced in comparision with benzene. The insertion of heterocyclic rings in bent-core mesogens has been reported only relatively rarely [5–10].

2. Experimental

2.1. *Materials*

The compounds were synthesized by the esterification of one part kojic acid with two parts of the acyl chloride of the appropriate two-ring acid (see figure 1). The experimental procedure is given for compound **1a** together with analytical data. The compounds **1a**–**c** and **2a**–**c** are isomeric with each other and differ only in the direction of the carboxylic connecting group. The transition temperatures and enthalpies are given in table 1.

1a: *6-[4-(4-n-octyloxybenzoyloxy)benzoyloxymethyl]-4-oxo-4H-pyran-3-yl 4-(4-n-octyloxybenzoyloxy)benzoate.* To a slurry of 4-(4-*n*-octyloxybenzoyloxy)benzoic acid (0.93 g, 2.5 mmol) in dry dichloromethane, oxalyl chloride (1.27 g, 10 mmol) was added and the mixture

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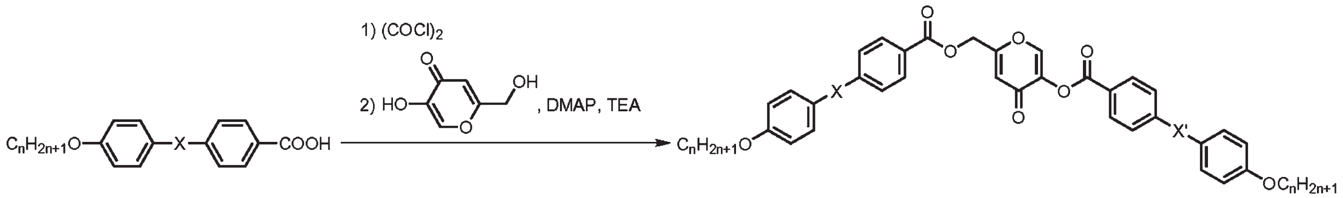


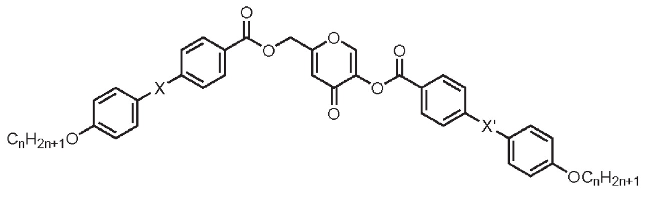
Figure 1. Synthesis of compound **1** (X=COO; X'=OOC) and compound **2** (X=OOC; X'=COO).

heated at reflux for 2 h. The solvent was evaporated under reduced pressure, dry toluene was added and the remaining oxalyl chloride removed under vacuum together with the solvent. The crude acid chloride was dissolved in dry toluene and kojic acid (0.14 g, 1 mmol) and a catalytic amount of DMAP added at 0°C, followed by triethylamine (0.25 g, 2.5 mmol) after 3 min. Stirring was continued for 10 min at room temperature and another 6 h at 65°C. After cooling, the reaction mixture was filtered and the solvent evaporated in vacuum. The crude compound was purified by column chromatography on silica gel 60 with $CHCl_3$/EtOAc (9/1) as eluant, and by recrystallization from DMF/EtOH; yield 0.80 g, 91%. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.83–0.92 (m, 6H, $2\times CH_3$), 1.22–1.52 (m, 20H, $2\times(CH_2)_5$), 1.77–1.86 (m, 4H, $2\times OCH_2\mathit{CH_2}$), 4.03 (t, ^3J=6.5 Hz, 4H, $2\times OCH_2$), 5.20 (s, 2H, CH_2OOC), 6.64 (s, 1H, 5-H of the γ-pyrone system), 6.96 (d, ^3J=8.9 Hz, 4H, Ar–H), 7.33 (d, ^3J=8.9 Hz, 2H, Ar–H), 7.34 (d, ^3J=8.9 Hz, 2H, Ar–H), 8.05 (s, 1H, 2-H of the γ-pyrone system), 8.08–8.17 (m, 6H, Ar–H), 8.23 (d, ^3J=8.9 Hz, 2H, Ar–H). ^{13}C NMR ($CDCl_3$, 100 MHz): 165.32, 164.18, 164.10, 163.79, 163.74, 163.47, 155.83, 155.20, 143.98, 141.84, 135.28, 134.04, 132.37, 132.33, 132.16, 131.32, 126.76, 125.68, 125.58, 125.36, 122.20, 122.00, 120.95, 120.88, 114.41, 114.38, 68.40, 64.89, 31.82, 29.34, 29.23, 29.12, 26.02, 22.68, 14.11.

2.2. *Methods*

The thermal behaviour of the compounds was studied using differential scanning calorimetry (DSC Pyris 1, Perkin Elmer). Phase assignments were made by the observation of textures under polarizing optical microscopy (POM) (Leitz Orthoplan) and from X-ray diffraction (XRD) patterns. XRD measurements on non-oriented samples were performed with a Guinier film camera (Huber Diffraktionstechnik GmbH). Oriented samples were obtained by annealing or very slow cooling of a drop of the isotropic liquid on a thin glas plate. The drop was irradiated parallel to the glass plate. The scattered radiation was detected by a two-dimensional detector (HI-Star, Siemens AG). The electro-optical measurements were carried out using commercial ITO cells with a gap of 6 µm (E. H. C. Co.). The switching polarization was measured using the triangular-wave method.

Table 1. Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) of compounds **1** and **2** taken from DSC measurements.



Compound	n	X	X'	Transition temperatures [enthalpies]
1a	8	COO	OOC	Cr 134 [35.5] Col$_r$ 146 [18.7] I
1b	12	COO	OOC	Cr 137 [29.8] SmCP$_A$ 140^a Col$_{ob}$ 142 [20.5] I
1c	16	COO	OOC	Cr 133 [32.6] SmCP$_A$ 147 [22.3] I
2a	8	OOC	COO	Cr 184 [60.5] Col 197 [21.1] I
2b	12	OOC	COO	Cr 172 [69.8] Col 196 [20.8] I
2c	16	OOC	COO	Cr 172 [73.4] Col 196 [22.7] I

[a]Taken from X-ray measurements.

3. Results

3.1. *Texture observations and electro-optical investigations*

On slowly cooling the isotropic liquid of compound **1a**, the mesophase appears as a mosaic texture growing dendritically from rhombohedric germs. This texture is characterized by large domains of almost uniform birefringence, see figure 2 (*a*). On faster cooling, some circular domains appear. This mesophase shows no electro-optical switching up to $E = 34\,\mathrm{V\,\mu m^{-1}}$.

The high temperature mesophase of compound **1b** appears clearly different from that of **1a**. The mosaic-like texture grows in spikes from circular germs. In comparision to compound **1a** the domains of compound **1b** are small and their birefringence less uniform, see figure 2 (*b*). Under POM there is no observable indication of the transition of the high temperature mesophase into the low temperature one, i.e. neither the birefingence nor the textures changes.

On fast cooling of the isotropic melt of compound **1b**, the formation of the high temperature phase is suppressed and the low temperature phase grows directly from the isotropic liquid. It appears as a non-birefringent texture. By turning one polarizer away from the crossed position by a few degrees in a clockwise direction, however, bright and dark domains are weakly visible. Turning in an anticlockwise direction, the brightness of these domains is exchanged. Such chiral domains have already been reported for other bent-core compounds [11–13]. This phenomenon can be explained by the existence of areas of opposite handedness. This mesophase is switchable by applying an electric field. The threshold voltage was found to be about $18\,\mathrm{V\,\mu m^{-1}}$. The current response curve shows two peaks per half-cycle of a triangular voltage, which

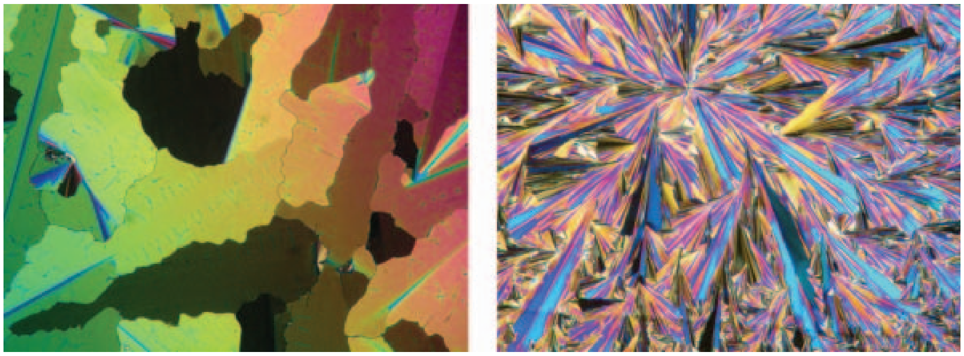

(*a*) (*b*)

Figure 2. Mosaic textures of the mesophases: (*a*) compound **1a**; (*b*) compound **1b**.

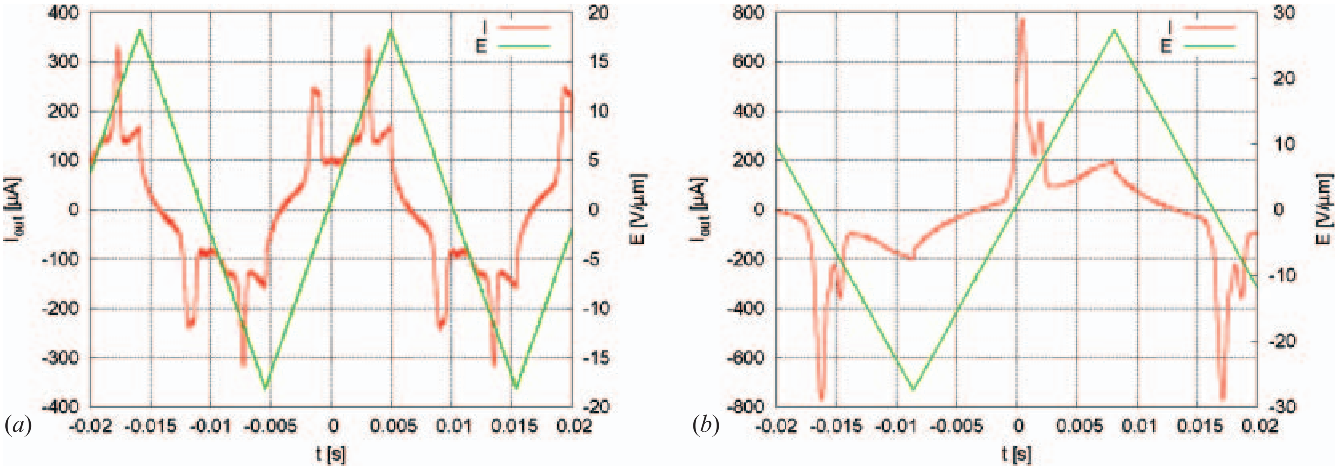


Figure 3. Current response curves to a triangular-wave field of the mesophases of **1b** and **1c**: (*a*) low temperature mesophase of compound **1b** ($E = \pm 18\,\mathrm{V\,\mu m^{-1}}$, $T = 120°\mathrm{C}$); (*b*) compound **1c** ($E = \pm 29\,\mathrm{V\,\mu m^{-1}}$, $T = 130°\mathrm{C}$).

indicates an antiferroelectric groundstate, see figure 3 (*a*).

The optical appearance of the mesophase of compound **1c** is very similar to that of the low temperature mesophase of compound **1b**. On cooling the isotropic liquid, it also occurs as a non-birefringent texture with homochiral domains, which are visible by decrossing one of the polarizers, although the contrast between domains of opposite handedness is very low. The mesophase of compound **1c** is switchable by applying an electric field. The switching process starts at a very high threshold voltage of about 28 V μm^{-1}. The fan-like textures of the switched states are independend of the polarity of the applied field and are of higher birefringence, see figure 4 (*b*). In the absence of the electric field it again appears as a weakly birefringent texture, figure 4 (*a*). The current response of compound **1c** shows two peaks per half-cycle of the triangular voltage, indicating an antiferroelectric groundstate, which is switched to the corresponding ferroelectric states, (see figure 3 (*b*)).

On cooling the isotropic liquids of the compounds **2a–c**, the mesophases appears as the texture shown in figure 5, growing from circular domains, which suggests columnar mesophases.

3.2. *X-ray diffraction measurements*

XRD measurements were performed for the compounds of series **1**. Bragg angles, layer spacings and cell parameters are summarized in table 2. In the case of the homologues **2a–c**, such investigations were not possible because of the high clearing points and a partial decomposition of the compounds.

Well oriented samples of the mesophases of compound **1a** show the scattering of a rectangular cell, i.e. of a Col_r phase, see figure 6 (*a*). The effect of special extinction rules is to be noted. The diffuse scattering is located orthogonal to the 0 *k* reflections, and therefore the mesogenic units are parallel to the *b*-axis of the cell.

An oriented sample of the high temperature mesophase of compound **1b** shows the scattering of an oblique cell, figure 6 (*b*). The *a**- and *b**-axes include an angle of about 85°. The direction of the outer diffuse scattering and the *a**-axis enclose an angle of about 25°. Thus, these data imply an oblique cell, the mesogenic units being inclined about 30° with respect to the *b*-axis.

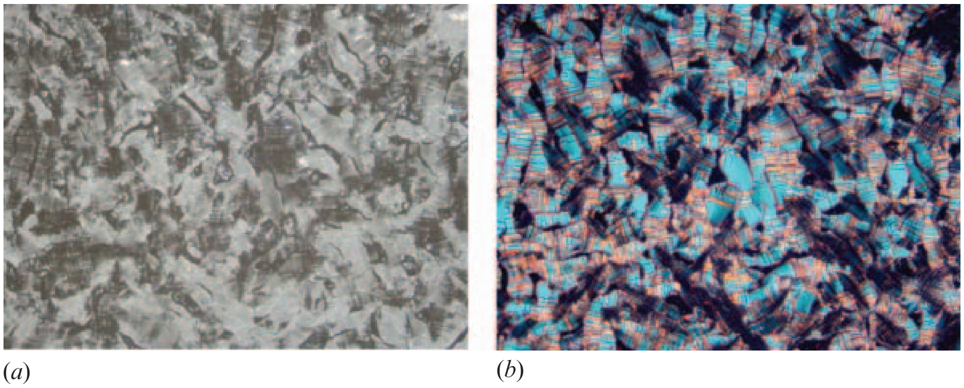

(*a*) (*b*)

Figure 4. Microscopic textures of the mesophase of compound **1c** at $T=130°C$: (*a*) $E=0\,V\,\mu m^{-1}$, (*b*) $E=\pm 29\,V\,\mu m^{-1}$.

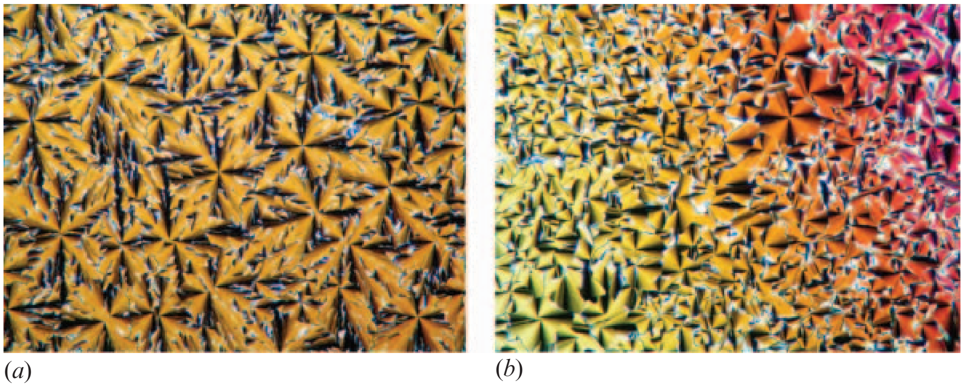

(*a*) (*b*)

Figure 5. Textures of the mesophases: (*a*) compound **2a** at 186°C; (*b*) compound **2b** at 180°C.

Table 2. Bragg angles, layer spacings and cell dimensions of compounds **1a**–**c** (only the Bragg angles used for the determination of the lattice parameters are given).

Compound	Phase	θ	Indices	Layer spacings resp. cell dimensions/Å
1a	Col_r	1.50	1 1	
		2.09	0 2	$a=40.7$, $b=42.3$
1b	Col_{ob}	1.05	2 0	
		1.94	0 2	
		1.15	1 1	$a=84.1$, $b=45.6$, $\gamma=95°$
1b	$SmCP_A$	1.15	0 1	$d=38.4$
1c	$SmCP_A$	1.01	0 1	$d=43.6$

During the transition of the high temperature mesophase to the low temperature mesophase of compound **1b**, the orientation of the sample is lost. Thus it was not possible to observe a tilt angle from the scattering diagram. The scattering pattern shows only the first order layer reflection. Assuming a very similar molecular structure of the mesogens in both phases, a tilt angle of about 40° can be estimated.

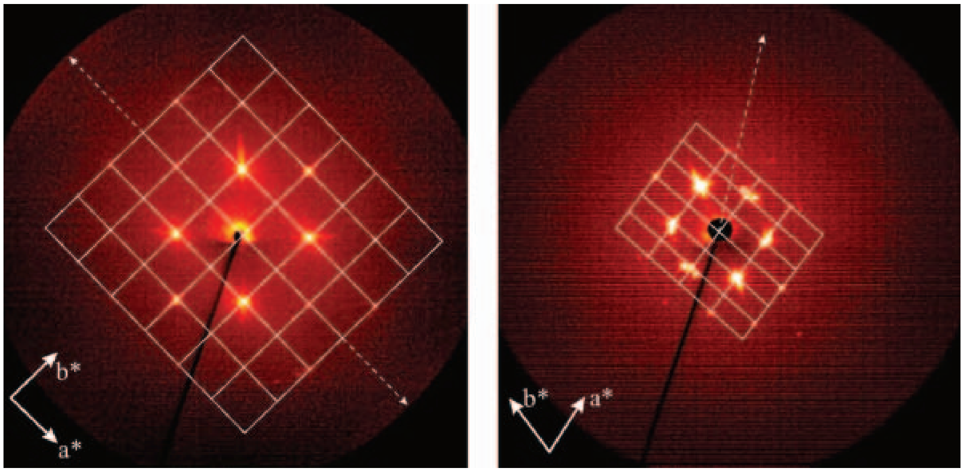
For the mesophase of compound **1c** it was impossible to obtain oriented or at least partially oriented samples. Therefore no tilt angle can be taken from the scattering pattern. As with the mesophase of compound **1b**, only the first order layer reflection occurs.

4. Discussion

This paper describes the use of kojic acid as a new synthon for bent-core mesogens. The liquid crystalline behaviour of compound **1a** seems to be quite similar to that of the corresponding 4-hydroxybenzylalcohol derivative [4]. Substituting the central 4-hydroxybenzyl alcohol fragment by kojic acid leads to slightly increased clearing temperatures.

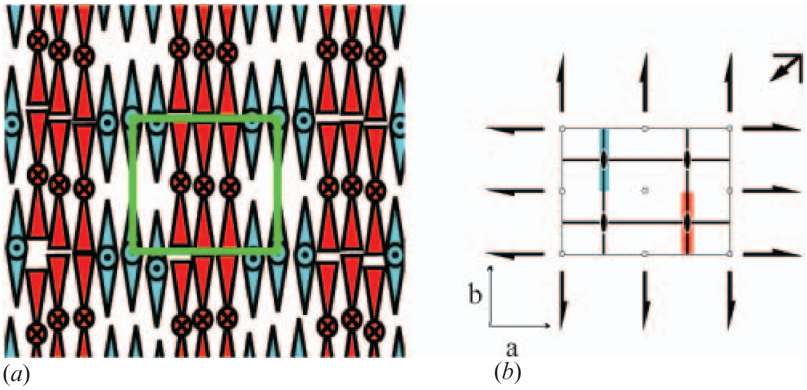
The XRD pattern of the mesophase of compound **1a** shows the typical scattering of a rectangular cell. The distinct extinction rules ($h0=2n$, $0k=2n$ and $h+k=2n$) imply a centred cell. Using plane group symmetry, only the group *c2mm* offers the necessary requirements to model such a phase. This purely two-dimensional approach however, does not take into account, that the columns (resp. layer fragments) have a certain polarization perpendicular to the *ab*-plane. From an antiferroelectric alignment of the columns and from the scattering patterns an arrangement using the symmetry of the layer group *pmmn* can be assumed [4] (figure 7). Thus this mesophase can be assigned as a columnar rectangular phase (Col_r) with an orthogonal arrangement of the mesogenic units in the rectangular cell ('B_1' phase). The molecular length obtained by semiempirical calculations (using MOPAC7, AM1 hamiltonian) is in good agreement with the findings of the X-raymeasurements ($L_{exp}=b=42.3$ Å; $L_{calc}=43.2$ Å, see figure 8).

In the case of compound **1b** a columnar oblique mesophase was found as the high temperature phase, followed by a SmCP phase. The high temperature phase shows the scattering of a two-dimensional oblique mesophase, whereas the low temperature phase exhibits only the scattering of a simple layer structure. If we consider the polar electro-optical response, this low temperature phase can be assigned as an antiferroelectric SmCP ($SmCP_A$) phase. The X-ray pattern of the columnar phase shows the scattering of an oblique cell, but with the appearance of special extinction rules. Together with the assumption of an antiferroelectric



(*a*) (*b*)

Figure 6. Small angle X-ray patterns of oriented samples of the columnar phases; lines represent the reciprocal lattice, dotted arrows illustrate the direction to the maxima of the diffuse scattering: (*a*) compound **1a** at 143°C; (*b*) compound **1b** at 140°C.



(*a*) (*b*)

Figure 7. Model of the columnar phase of compound **1a** and the symmetries of the appropriate layer group *pmmn*; the blue and red rectangles symbolize single mesogenic units of opposite bent direction; the symbols of the symmetry elements are according to there used in [14].

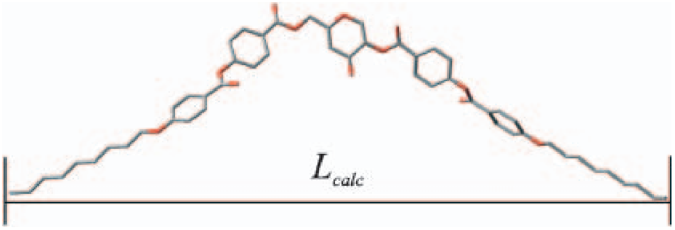
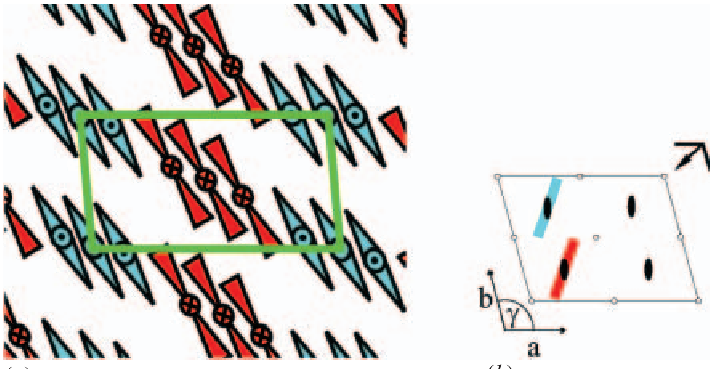


Figure 8. Conformation of a molecule of compound **1a**.

alignment of the columns, a model of this mesophase can be given according to the layer group *p*11*n* or *p*112/*n*. (see figure 9). The mesogenic units are inclined at about 30° with respect to the *b*-axis. The calculated length of the molecule is in good agreement with the findings of the X-ray measurements (L_{exp}=52.6 Å vs. L_{calc}=51.8 Å). Using this experimental length, a tilt angle of about 43° can be calculated for the SmCP phase of compound **1b**.

The XRD measurements on samples of compound **1c** point to a simple layer structure, which has an antiferroelectric order according to the electro-optical measurements. Thus, the phase can be assigned as a $\mathrm{SmCP_A}$ phase. Semiempirical calculations (MOPAC7, AM1 hamiltonian) give a molecular length of 60.5 Å. According to $\cos\theta = d/L$, a tilt angle of about 44° can be calculated. This tilt angle gives a good explanation of the weak birefringence of the groundstate of the



(*a*) (*b*)

Figure 9. Model of the columnar phase of compound **1b** and the symmetries of the appropriate layer group $p11\frac{2}{n}$.

switched texture: a tilt angle of 45° together with an anticlinic arrangement of successive layers leads to a so-called orthoconic structure, which is non-birefringent.

References

[1] T. Niori, J. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. *J. mater. Chem.*, **6**, 231 (1996).

[2] G. Pelzl, S. Diele, W. Weissflog. *Adv. Mater.*, **11**, 707 (1999).

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

[4] K. Pelz, S. Diele, U. Baumeister, W. Weissflog. *Liq. Cryst.*, **30**, 1151 (2003).

[5] D. Shen, S. Diele, G. Pelzl, I. Wirth, C. Tschierske. *J. mater. Chem.*, **9**, 661 (1999).

[6] T.J. Dingemans, E.T. Samulski. *Liq. Cryst.*, **27**, 131 (2000).

[7] J. Matraszek, J. Mieczkowski, J. Szydłowska, E. Gørecka. *Liq. Cryst.*, **27**, 429 (2000).

[8] H. Nozary, C. Piguet, J.-P. Rivera, P. Tissot, P.-Y. Morgantini, J. Weber, G. Bernardinelli, J.-C.G. Bünzli, R. Deschenaux, B. Donnio, D. Guillon. *Chem. Mater.*, **14**, 1075 (2002).

[9] M. Belloni, M. Manickam, J.A. Preece. *Ferroelectrics*, **276**, 103 (2002).

[10] J.A. Olivares, S. Stojadinovic, T. Dingemans, S. Sprunt, A. Jakli. *Phys. Rev. E*, **68**, 041704 (2003).

[11] G. Heppke, D.D. Parghi, H. Sawade. *Liq. Cryst.*, **27**, 313 (2000).

[12] G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl, C. Tschierske. *Angew. Chem.*, **114**, 2514 (2002).

[13] W. Weissflog, M.W. Schröder, S. Diele, G. Pelzl. *Adv. Mater.*, **15**, 630 (2003).

[14] V. Kopský, D.B. Litvin (Eds). *International Tables of Crystallography, Volume E, Subperiodic groups*, 1st Edn, Kluwer Academic Publishers, Dordrecht (2002).