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Effects of chain branching and chirality on liquid crystalline phases of bent-core molecules: blue phases, de Vries transitions and switching of diastereomeric states[†]

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Bent-core molecules based on a resorcinol bisbenzoate core with a series of distinct substituents in different positions at the central resorcinol core have been synthesized and characterized. The focus is on the effect of branched terminal groups in the racemic and chiral forms on the mesomorphic properties. These were investigated by differential scanning calorimetry, optical polarizing microscopy, X-ray diffraction, electro-optic and dielectric methods. Only bent-core mesogens derived from 4cyanoresorcinol exhibit liquid crystalline phases and the mesophases of these compounds are strongly influenced by the branching and enantiomeric composition of the terminal chains. Depending on the structure of the rod-like wings and the enantiomeric composition, cybotactic nematic phases (N_{cybC}), BPIII-like isotropic mesophases (BPIII_{cvbC}*) and various polar and apolar smectic phases (SmA, SmC, SmC^* , SmC_sP_A , $SmC_sP_A^*$) are formed. For one compound, a de Vries type smectic phase is observed and it appears that with decreasing temperature, order develops in two steps. First, at the SmA to SmC transition, the tilt direction becomes long range ordered and in a second step a long range ordering in bend direction takes place. Hence, for the optically active compound a transition from chirality induced polar switching to bend induced (shape induced) antiferroelectricity takes place. In this SmCsPA* phase a homogeneous layer chirality is induced under an applied electric field which interacts with the fixed molecular chirality leading to the energetically favoured diastereomeric state and giving rise to a field direction dependent uniform tilt director orientation. Field reversal induces a flipping of the layer chirality, which first leads to the less favorable diastereomeric state, and then this slowly relaxes to the more stable one by a spontaneous reversal of the tilt direction.

1. Introduction

Liquid crystal research on bent-core compounds has been given much attention over the past decade due to the discovery of outstanding properties of the new mesophases which differ significantly from mesophases of calamitic and disc-like compounds.^{1,2} The remarkable behaviour of liquid crystalline (LC) materials possessing a bent molecular shape is the spontaneous formation of polar order even without molecular chirality. This leads to antiferroelectric and ferroelectric switching smectic and columnar phases, and to spontaneous achiral symmetry breaking on a mesoscopic scale in tilted polar smectic phases.³ Chirality in LC phases of achiral bent-core molecules also arises due to frustration phenomena as for example reported for the so-called dark conglomerate phases.⁴ Moreover, helical conformers of bent-core mesogens⁵ seem to give rise to amplification of chirality and this could be of importance for chirality-related phenomena observed in some of their smectic and nematic phases.^{6,7} Recently, the focus in this field has shifted to nematic phases. Nematic phases of bentcore compounds are quite distinct from those formed by rod-like or disc-like mesogens. This is due to a special cluster structure of these nematic phases⁸⁻¹⁰ and the distinct shape of the molecules enabling restricted rotation and polar packing, which makes them candidates for biaxial¹¹ and ferroelectric nematic phases.¹²

Bent-core mesogens usually require at least five aromatic rings in order to show the specific properties described above.¹³ There are several studies on five-ring bent-core mesogens in which the central phenyl ring was substituted at different positions by polar groups.¹⁴ Especially substituents in the 4-position of the bent unit play an important role. It is known that five-ring bent-core mesogens with

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4-cyanoresorcinol as the central core and ester connecting groups between the aromatic rings are able to form polar and apolar smectic phases as well as nematic phases depending on the structure of the rod-like wing groups.^{8,15} As shown recently, the effect of a cyano substituent on the mesomorphic behaviour also depends on the length and type of the terminal groups; for example, alkyl substituted 4-cyanoresorcinol bisbenzoates show broader nematic phase ranges than related alkoxy substituted analogues.⁸

Chirality is well known to have a major influence on the selfassembly and properties of liquid crystals,¹⁶⁻¹⁸ thus chiral liquid crystals are widely studied. In particular, liquid crystals (LCs) of chiral molecules self-assemble into macroscopic chiral (in most cases helical) superstructures, as found in chiral nematic phases (N*), blue phases (BPs),¹⁹ ferroelectric switching chiral smectic C phases (SmC*), twist grain boundary phases (TGB) and other chirality induced 3D phases and isotropic phases.²⁰

As mentioned above, bent-core molecules can show spontaneous achiral symmetry breaking which is of general interest for the development of chirality in self-assembled systems.²¹ One open question concerns the interaction of molecular configurational and conformational chirality with chirality provided by the superstructures.²² Hence, it is of interest to introduce molecular chirality into bent-core molecules.²²⁻²⁴ This can be achieved by asymmetric centres in the tails^{22,24,25} or within the bent-core structure itself, either as linking group²⁶ or as a cholesteryl core unit in bent dimesogens.23a,27 Chirality was also induced by mixing achiral bent-core mesogens with chiral rodlike molecules.²⁸ Bent-core molecules with chiral tails can exhibit ordinary chiral smectic phases (SmC*) and polar banana phases such as SmCPA*,9,24-26 but also blue phases (BPs)28 and chiral nematic (N*) phases have been reported.9,23 Special attention is presently paid to blue phases, because of their application potential in new generations of fast switching displays.²⁹

Herein, the synthesis and characterization of new resorcinol based bent-core molecules with polar substituents in different positions at the central core and having branched terminal groups are reported (see Fig. 1). Many of the compounds show only crystalline phases, but the 4-cyanoresorcinol core turned out to be especially successful, as LC phases are obtained even for strongly branched molecules. Therefore, the focus of this contribution is on the effects of branched terminal groups in the

racemic and chiral form on the LC properties of bent-core compounds derived from 4-cyanoresorcinol. For this purpose, bent-core mesogens derived from 4-cyanoresorcinol with an (S)-2-methylbutoxy or (S)-3,7-dimethyloctyloxy group as a terminal substituent and their racemic mixtures were studied and the influence of molecular chirality on the mesophases was investigated.³⁰ As major results, it was shown that nematic phases are replaced by optically isotropic mesophases related to BPIII phases and a temperature dependent transition between chirality induced polar response and molecular-shape induced antiferroelectricity was observed in the smectic phases. For one compound, a de Vries type smectic phase is observed and it appears that with decreasing temperature, order develops in two steps. First, the tilt direction becomes long range ordered (SmA^(*) to SmC^(*) transition), and in a second step a long range ordering in bend direction takes place, leading to a SmC_sP_A^(*) phase. Moreover, a unique switching and reorientation process based on superstructural diastereomerism is observed in the SmC_sP_A* phase of the chiral compound.

2. Results and discussion

2.1 Synthesis

The synthesis of the bent-core compounds derived from 4-cyanoresorcinol, 3, 4 and 5 is shown in Scheme 1 and the different combinations of core and tails produced are summarized in Table 2. As reported previously,^{15b,31} 2,4-dihydroxybenzonitrile was prepared from commercially available 2,4-dihydroxybenzaldehyde by the formation of the oxime, followed by dehydration. Other starting materials for the synthesis of the 4substituted 4-benzoyloxybenzoic acids rac-1a, (S)-1a, rac-1b and (S)-1b and the 4-substituted biphenylcarboxylic acids rac-2b and (S)-2b were racemic 2-methylbutyl-1-tosylate, (S)-2-methylbutyl-1-tosylate, racemic 3,7-dimethyloctyl-1-bromide and (S)-3,7dimethyloctyl-1-bromide. The tosylates were prepared from the corresponding alcohols.³² Racemic and (S)-3,7-dimethyloctyl-1-bromide were prepared from racemic and (S)-3,7-dimethylpreviously.33 1-octanol, respectively, as described (S)-3,7-Dimethyl-1-octanol was obtained from (S)-(-)- β -citronellol by catalytic hydrogenation (H₂, Pd/C in MeOH).



Fig. 1 Structures of the bent-core compounds under investigation.



Scheme 1 Structures of the bent-core compounds 3–5 and their synthesis. *Reagents*: (i) (1) $NH_2OH \cdot HCl$, (2) Ac_2O , (3) KOH; (ii) DCC, DMAP, CH_2Cl_2 , r.t.

Specific optical rotations of the alcohols were measured using a Perkin-Elmer polarimeter in order to confirm enantiomeric purity or the absence of optical activity in the case of racemic chiral alcohols (see the ESI[†]). As the stereogenic centres of the chiral alcohols were not touched throughout the synthesis it can be assumed that the final products have approximately equal optical purity as the starting materials.

4-(4-Alkyloxybenzoyloxy)benzoic acids were synthesized according to the procedures described in the literature.^{34,35} In a first step ethyl 4-hydroxybenzoate was alkylated with the appropriate alkyl bromides or tosylates, followed by hydrolysis of the ester group. Esterification of the obtained 4-alkyloxybenzoic acids with 4-hydroxybenzaldehyde, followed by oxidation using sodium chlorite as oxidizing agent leads to the benzoyloxybenzoic acids rac-1a,³⁶ (S)-1a,³⁷ (S)-1b³⁸ and the new compound rac-1b. The synthesis of the 4'-alkyloxy-4-biphenylcarboxylic acids rac-2b and (S)-2b was carried out by using known procedures.³⁹ The experimental details and spectroscopic data (1H-, 13C-NMR and MS) of the substituted benzoic acids 1 and 2 are given in the ESI[†] and their phase transitions are shown in Table 1. For compound (S)-1b no phase transitions were provided in the previous report.³⁸ For this compound a SmC*-N* dimorphism was recorded in our investigations and the biphenyl based carboxylic acids rac-2b and (S)-2b, which represent new compounds, show a $SmI^{(*)}$ phase (see Fig. S5 and S6[†]) below a very small nematic or cholesteric phase region, respectively.

As shown in Scheme 1, the esterification of the appropriate 4-(4-alkyloxybenzoyloxy)benzoic acids or 4'-alkyloxy-4-biphenylcarboxylic acids with 4-cyanoresorcinol was performed by means of dicyclohexylcarbodiimide (DCC) in dichloromethane using 4-dimethylaminopyridine (DMAP) as catalyst.⁴⁰ The other bent-core compounds (6–15) derived from other differently substituted resorcinols (see Fig. 1) were prepared in a similar way from commercially available resorcinol, 4-chlororesorcinol, 4,6dichlororesorcinol, 4-bromoresorcinol, 2-methylresorcinol, 2-nitroresorcinol and 3,5-dihydroxybenzonitrile, respectively. All bent-core compounds were characterized by the common spectroscopic methods (¹H-, ¹³C-NMR and MS). The spectroscopic data of the materials are consistent with the proposed structures (see the ESI†).

2.2. Liquid crystalline properties—general trends

The mesomorphic properties of the obtained resorcinol based bent-core compounds **3–15** (see Tables 2 and 4) were investigated by polarised light optical microscopy (PM), differential

Table 1 Mesophases and phase transition temperatures of the benzoic acids 1 and $\mathbf{2}^a$

	RO	x{=			
a : $R = 1$, $R = 1$					
Compound	Х	R	<i>T</i> /°C		
rac-1a	COO	а	Cr 168 N 183 Iso		
(S)-1a	COO	а	Cr 168 N* 184 Iso		
rac-1b	COO	b	Cr 99 SmC 169 N 197 Iso		
(S)-1b	COO	b	Cr 98 SmC* 167 N* 194 Iso		
rac-2b	_	b	Cr 163 SmI 223 N 225 Iso		
(S)- 2b			Cr 163 SmI* 224 N* 226 Iso		

^{*a*} Abbreviations: Cr = crystalline solid; SmC = tilted smectic phase, SmC^{*} = tilted chiral smectic phase with helical superstructure, N = nematic phase; N^{*} = chiral nematic phase; SmI = SmI-type hexatic phase; SmI^{*} = chiral SmI phase; Iso = isotropic liquid phase. scanning calorimetry (DSC), some of them by X-ray diffraction, electro-optic measurement and dielectric studies. The bent-core compounds 6-15 with two branched terminal chains are nonmesomorphic if the resorcinol core is non-substituted (X=H) or the substituent is halogen, NO_2 or CH_3 (see Table 2). This indicates a relatively strong mesophase destabilizing effect of chain branching, as the related non-branched compounds 16-19 are known to form a variety of different mesophases (see Table 3).9a,b,14,15,41 Also CN substitution in 5-position14,42 leads to nonmesomorphic material (compound rac-15), whereas compounds 3 and 4 possessing cyano substitution at the 4-position of the central phenyl ring exhibit LC behaviour. Therefore, further attention was focussed on investigation of the racemic and chiral forms of the 4-cyanoresorcinol based mesogens 3, 4 (Table 2) and 5 (Table 4). Depending on the nature of branched terminal groups, bent-core compounds with phenylbenzoate rod-like wings (3, 4) show nematic and optically isotropic mesophases whereas bent-core compounds 5 with biphenyl based wings exhibit various smectic phases.

2.3 4-Cyanoresorcinols with 2-methylbutoxy substituted phenylbenzoate based rod-like wings (compounds 3)

The homogeneously chiral compound (S)-3 with (S)-configuration of the stereogenic centres in both 2-methylbutoxy chains as well as the racemic mixture of diastereomers assigned as *rac*-3 shows monotropic LC phases, as indicated by small exotherms in the DSC cooling curves at 63 and 55 °C, respectively. The transition enthalpies are relatively small and have comparable values for the racemic and enantiomerically pure compound around 0.42-0.43 kJ mol⁻¹ (see Fig. 2d). On cooling the racemic compound *rac-3* from the isotropic liquid Schlieren textures and marbled textures were observed under the polarizing microscope, as typical for nematic phases (Fig. 2a).

The homogeneously chiral compound (S)-3 behaves differently. With decreasing temperature, at 63 °C, a diffuse bluish colour starts appearing, which becomes brighter as the temperature is reduced further (Fig. 2b). The optical appearance of this mesophase is very similar to that of BPIII phases (blue fog phases) of calamitic compounds that represent a special type of double twisted nematic phase without long-range periodicity of the lattice of defects.^{16,28,43} However, this bluish appearance seems to occur only in relatively thick cells, whereas thin layers appear nearly isotropic in most cases. On further cooling, another monotropic mesophase M with unknown structure appears at 45 °C (Fig. 2c). A comparison of the mesomorphic properties of the enantiopure compound (S)-3 with the optically inactive mixture rac-3 shows that the nematic phase of the racemate is replaced by a kind of BPIII phase in (S)-3. In addition, the mesophase stability of the LC phase is about 8 K higher than that of the nematic phase of rac-3. Moreover, an additional mesophase occurs in the phase sequence of (S)-3 at 45 °C that is not observed for rac-3. However, as the mesophases of compounds rac-3 and (S)-3 are only monotropic and rapidly crystallize, more detailed investigation of these LC phases by XRD was not possible.

Table 2 Phase transitions of the resorcinol derivatives 3–15^a



Compound	Х	R	$T/^{\circ}$ C [$\Delta H/k$ J mol ⁻¹]
rac-3	4-CN	я	Cr 84 [21 6] (N _{mbc} 55 [0 3]) Iso
(S)-3	4-CN	a	Cr 87 [25.0] (M 45 [0.5]) BPUL _{wh} c^* 63 [0.3]) Iso
(S)-6	Н	a	Cr 145 [30.6] Iso
(S)-7	4-C1	a	Cr 120 [33 7] Iso
(S)- 8	4-Br	a	Cr 109 [32.5] Iso
rac-4	4-CN	b	Cr 84 [42, 2] (N_{evbC} 60 [0, 4]) Iso
(S)-4	4-CN	b	Cr_1 54 [13,4] Cr_2 80 [5,8] (M ₁ 42 [2,4] BPIII ₂₂₄ * 58 [0,3]) Iso
rac-9	Н	b	Cr 100 [38.6] Iso
rac-10	4-C1	b	Cr 70 [29.8] Iso
rac-11	4.6-Cl	b	Cr 106 [42.9] Iso
rac-12	4-Br	b	Cr 65 [14 6] Iso
rac-13	2-CH ₂	b	Cr 103 [31 0] Iso
rac-14	$2 - NO_2$	b	Cr 107 [14 3] Iso
rac-15	5-CN	b	Cr 71 [<i>13.9</i>] Iso

^{*a*} Enthalpy values in italics in brackets, obtained from first DSC heating scans (10 K min⁻¹, peak temperatures); abbreviations: N_{cybC} = nematic phase composed of cybotactic groups of the SmC type; M, M_1 = mesophases with unknown structures (M_1 phase of *rac*-4 can only be detected in the cooling scans, see Fig. 4d, due to crystallization); BPIII_{cybC}* = blue phase III-like phase composed of SmC*-type cybotactic clusters; for the other abbreviations, see Table 1; monotropic transitions are in parentheses.

Table 3 Phase transition temperatures of representative bent core mesogens with linear *n*-octyloxy chains (compounds 16–19), related to compounds (4, *rac*-9, *rac*-10 and *rac*-12) with branched terminal chains and the same number of C-atoms^{*a*}



^{*a*} Abbreviations: B₁ and Col represent modulated smectic phases (ribbon phases), for other abbreviations, see Tables 1 and 2.

2.4 4-Cyanoresorcinols with 3,7-dimethyloctyloxy substituted phenylbenzoate type rod-like wings (compounds 4)

Compounds (S)-4 and rac-4 with longer and more branched terminal chains behave similar to (S)-3 and rac-3. The racemic compound rac-4 forms a nematic phase and for the chiral compound (S)-4 a phase very similar to the BPIII-like phase of (S)-3 is observed (see Fig. 3). It initially appears optically isotropic but develops a bluish color upon shearing the sample. In addition, in the case of the chiral compound (S)-4 the transition from the isotropic liquid to the LC phase is broadened. Broad peaks were previously observed for other chirality induced isotropic mesophases, such as BPIII phases and chirality induced disordered smectic phases.⁴⁴⁻⁴⁶

Though the mesophases of *rac*-4 and (S)-4 are also monotropic, they can be supercooled more easily, and hence, investigation by XRD was possible in these cases. The 2D X-ray diffraction pattern of a magnetically aligned sample (B = 1 T) of *rac*-4 in the nematic phase range is shown in Fig. 4a and b. The



Fig. 2 Textures (between crossed polarizers) as seen for: (a) the N_{cybC} phase of *rac*-**3** at T = 53 °C; (b) the amorphous blue phase BPIII_{cybC}* of (*S*)-**3** at T = 61 °C and (c) the low temperature mesophase (M) at T = 42 °C; (d) DSC cooling traces (10 K min⁻¹).

scattering pattern is characterized by two diffuse scattering regimes. The diffuse scattering in the wide angle range at d = 0.47 nm is centred on the equator, confirming the liquid crystalline state and indicating an alignment of the molecules with their average long axes parallel to the magnetic field direction. The diffuse scattering in the small angle region forms four maxima at d = 3.8-3.9 nm between equator and meridian, indicating a nematic phase composed of SmC type cybotactic clusters and an average tilt of about 28° . The correlation lengths in parallel and longitudinal direction were estimated according to





^{*a*} Values were determined from the first heating and cooling DSC traces (10 K min⁻¹, peak temperatures); for abbreviations, see Table 2; additional abbreviations: SmA/SmA^{*} = de Vries type smectic phase; SmC_sP_A = synclinic tilted antiferroelectric switching smectic phase; $M_2 M_2'$ = mesophases with unknown structures (it appears that on cooling the racemic compound the transition to M_2 takes place in two steps *via* M_2' (see Fig. 6), but on heating only the direct M_2 -SmC_sP_A transition is observed); SmC_sP_A^{*} = antiferroelectric switching synclinic tilted chiral smectic phase. ^{*b*} Transitions were observed by polarizing microscopy and electro-optical experiments; detailed XRD data of *rac*-5 and (*S*)-5 are shown in the ESI (Fig. S3 and S4[†]).



Fig. 3 Textures as seen in transmission between crossed polarizers for: (a) the N_{cybC} phase of *rac*-4 at T = 53 °C; (b and c) the BPIII_{cybC}* phase of (S)-4 at T = 45 °C after shearing; (d) DSC cooling traces (10 K min⁻¹).



Fig. 4 2D-XRD patterns of magnetically aligned samples (B = 1 T, field direction is indicated by an arrow) of compound *rac*-4 (a and b) and (*S*)-4 (c and d); left complete diffraction patterns, right small angle regions at T = 50 °C.

 $\xi_{\parallel\perp} = 2/\Delta q$ from the full width at half maximum (FWHM, Δq) of the fitted curves.⁴⁷ The dimensions of the cybotactic clusters in longitudinal (L_{\parallel}) and transversal (L_{\perp}) direction can be approximated to three times the correlation lengths ξ_{\parallel} and ξ_{\perp} respectively.⁴⁸ The obtained values of $L_{\parallel} = 14$ nm and $L_{\perp} = 4$ nm at T = 50 °C indicate clusters incorporating on average 8 molecules organized side-by-side, assuming an average lateral molecular distance of approximately 0.47 nm (= maximum of the diffuse wide angle scattering).

The XRD pattern of the chiral compound (*S*)-4 at the same temperature is characterized by diffuse scattering maxima in the

same two regimes (d = 0.47 and 3.8 nm, respectively), but in contrast to the nematic phase of rac-4 no alignment was possible under the magnetic field (same strength as above) as indicated by the perfectly circular diffuse rings (Fig. 4c and d). This is in line with the proposed phase structure where the cybotactic clusters of the N_{CvbC} phase adopt a chirality induced disordered BPIIIlike organization. The average cluster size, estimated as described above from the FWHM of the diffuse small angle scattering, is L = 12 nm.⁴⁹ This is in the same range as for *rac*-4 and indicates that the cybotactic clusters have approximately the same size as in the N_{cvbC} phase of the racemic mixture. Due to the cybotactic cluster structure of the nematic phases of bent-core mesogens the formation of double twist cylinders seems to be distorted and a regular 3D lattice, similar to that of the type I and II blue phases (BPI, BPII), may not be possible.28 Instead, a disordered BPIII-like defect structure is formed, assigned here as BPIII_{cybC}*. The proposed phase structure is the same as reported previously for blue phases obtained by adding a chiral dopant to a nematic bent-core liquid crystal.²⁸

In the contact region between the nematic phase of the racemic compound rac-4 and its enantiomer (S)-4 the induction of a cholesteric phase is indicated by the typical oily streaks texture and the appearance of selective reflection (Fig. 5). With increasing concentration of (S)-4 the colour of the reflected light changes from red via yellow, green and blue to violet, indicating a decrease of the helical pitch with increasing concentration of (S)-4. The induced cholesteric phase appears optically isotropic in regions with highest (S)-4 concentration, as the pitch is in the range of the wavelength of UV-light. This observation is in line with the proposed phase structure (see above). There seems to be a strong helical twisting power of (S)-4 which leads to double twist for the pure enantiomer. By reducing the enantiomeric purity the twisting power is reduced and helix formation occurs in only one direction, leading to a cholesteric phase. As in the N_{cvbC} phase of the racemic mixture the cholesteric phase should be composed of N_{cybC} clusters and therefore it is assigned as N_{cvbC}*. The pitch length of the induced cholesteric phase increases with further decreasing (S)-4 concentration. As is often



Fig. 5 Induced cholesteric phase (N_{cybC}^*) as seen between crossed polarizers in the contact region between the achiral N_{cybC} phase of *rac*-4 (bottom right) and the BPIII_{cybC}* phase of (*S*)-4 (top left) (a) at $T = 54 \,^{\circ}$ C and (b) at $T = 45 \,^{\circ}$ C (same region as indicated in (a) by the dotted rectangle).

the case in chiral nematic the pitch increases with decreasing temperature as seen by the rainbow coloured band being shifted towards higher (S)-4 concentration (Fig. 5b).

2.5 4-Cyanoresorcinols with biphenyl wings (compounds 5)

Exchange of the phenylbenzoate units of compounds 4 by biphenyls leads to compounds 5. This structural variation causes a change of the LC phase type from nematic to smectic and the clearing as well as the melting point are raised by some 40 K. Both effects are reasonable considering that the biphenyl moieties in compounds 5 render the core stiffer (albeit somewhat shorter) than that of compounds 4, in which all phenyl rings are linked by semiflexible COO groups. The enantiopure compound (*S*)-5 as well as the mixture *rac*-5 form enantiotropic LC phases.

2.5.1 Racemic mixture *rac*-5—transition from nonpolar SmA/ SmC phases to a polar SmC_sP_A phase. Compound *rac*-5 exhibits three smectic phases and an additional low temperature phase M with unknown structure (see Table 4). On cooling from the isotropic liquid, the high temperature smectic phase develops a focal conic texture in planar alignment or an optically isotropic



Fig. 6 DSC cooling traces (10 K min⁻¹) of compounds (S)-5 and rac-5.

appearance in homeotropic alignment (layers parallel to the substrate surfaces), as typical for SmA phases. On further cooling, at T = 74 °C, a phase transition takes place at which a schlieren texture appears in the homeotropically aligned regions (see Fig. 7a and b), indicating a transition to an optically birefringent LC phase. However, this phase transition is not associated with a peak in the DSC traces, indicating a second order phase transition (Fig. 6).

As the temperature is lowered further, at T = 50 °C additional textural changes take place (compare textures in Fig. 7b and c), but again no transition enthalpy could be detected for this transition (Fig. 6). Upon further cooling, at T = 38 °C another textural transformation is observed, indicated by a slight change of the birefringent color (Fig. 7d), which is associated with a small enthalpy change ($\Delta H = 0.5$ kJ mol⁻¹), before crystallization occurs at T = 35 °C.

XRD investigations were carried out with surface aligned samples in the temperature range between 95 and 60 °C; below 60 °C crystallization sets in. In the whole investigated temperature range the XRD patterns (Fig. 8a-d) are characterized by two diffuse scattering maxima located on the equator (d = 0.47 nm)and two sharp layer reflections (together with a weak second order reflection) on the meridian, a pattern that at first sight might suggest that the smectic structure is orthogonal at all temperatures. However, another possibility is that the molecules are in fact tilted already in the SmA phase but in random directions, and the transition to SmC is characterized by the development of longrange order of the tilt directions. This type of 'de Vries' transition⁵⁰ from SmA to SmC would have no impact on the XRD pattern (even in the SmC phase we will have domains with different tilt directions within the beam, hence the experiment still averages over all tilt directions) and is thus essentially compatible with the data in Fig. 8. Below we will provide further evidence from the chiral compound that this phenomenon in fact takes place in racand (S)-5. It is however not the only process taking place at the phase transition: a slight broadening of the WAXS maxima in the low-temperature phase suggests that some additional molecule tilt does occur in the SmC phase.

On cooling, in the high-temperature SmA phase the *d*-value of the layer reflection (see Fig. 8e) at first slightly increases from d =3.82 nm at T = 95 °C to d = 3.84 nm at T = 80 °C and then decreases to d = 3.75 nm in the SmC phase at T = 60 °C. The first increase of the layer thickness could be explained by the increasing degree of orientational order on cooling from the isotropic phase, possibly also with a contribution from an improved packing of the aromatic cores which reduces chain folding. The decrease below 80 °C reflects the small additional tilt of the molecules that must also be the origin of the broadening of the wide-angle maxima. The additional tilt can be calculated through the layer shrinkage as $\theta_{add} = \arccos(3.75/3.82) \approx 11$ degrees. The optical tilt was estimated, as described below, to be about 20 degrees, substantially more than the additional molecule tilt detected by X-ray investigations. The transition thus indeed seems to be in part of 'de Vries' type, partly connected to regular increased molecule tilt.

Optical investigations of planar aligned samples (Fig. 7e–m) indicate the onset of an optic axis tilt of about 20° at T = 74 °C. As shown in Fig. 7e, above 74 °C the extinction is parallel to the polarizer, whereas below 74 °C it is generally impossible to get



Fig. 7 Textures as observed on cooling between crossed polarizer and analyzer (vertical and horizontal) for the mesophases of compound *rac*-5: (a–d) homeotropic alignment; (e–h) planar alignment, rubbing direction vertical; (i–m) planar alignment, rubbing direction 20° inclined anticlockwise to the direction of the polarizer; (a, e and i) SmA phase at 80 °C; (b, f and k) SmC phase at 62 °C; (c, g and l) SmC_sP_A phase at 45 °C; (d, h and m) M₂ phase at 35 °C.

extinction, indicating a twist of the optic axis from substrate to substrate. In a few regions the twist seems to be negligible, however, such that extinction is possible here and it is then found upon rotating the sample by 20° (Fig. 7f and k). This indicates a transition from a SmA high temperature phase to a slightly tilted SmC phase with synclinic tilt. The optical tilt is retained through both low temperature phases (see Fig. 7g–m).

Electro-optic investigations were carried out in 6 µm polyimide coated-ITO cells. No switching current response could be observed down to $T = 50 \,^{\circ}\text{C}$ (voltage up to 300 V_{pp}), indicating the absence of polar order in the two high temperature smectic phases (SmA, SmC). Only upon further cooling, at the transition to the low temperature phase at $T = 50 \,^{\circ}$ C two polarization current peaks per half cycle of the applied voltage waveform appeared (see Fig. 9a). This twin peak response clearly evidences antiferroelectric switching and quantitative analysis reveals a very large polarization value of 700–800 nC cm⁻². Hence, this mesophase is assigned as SmC_sP_A (synclinic tilt is confirmed by optical investigation described above, see Fig. 7g and l). By optical investigation of the switching process no difference between the texture of the two switched states could be seen (Fig. 9b-d). This observation, together with the confirmed synclinic tilt, indicates antiferroelectric switching by a collective rotation of the molecules around their long axis.

The non-polar nature of the SmA and SmC phases was verified also by dielectric spectroscopy, cf. Fig. 10. Below 50 °C the sample crystallized, hence the SmC_sP_A phase could not be investigated in this experiment. No collective polar mode was seen at any temperature, only a non-collective mode following an Arrhenius dependence on temperature. This is what one generally expects to see in a non-polar smectic phase, although the mode is unusually strong considering that the sample is essentially planar aligned. The strength of the mode within the SmA phase shows that the molecules are substantially tilted within the layers even in this phase, in line with the view of a de Vries type material. In the temperature range of the SmC phase we can understand the presence of the mode as a result of the twisted director geometry, leading to true planar alignment only at the two sample boundaries. In the sample bulk the molecules tilt out of the sample plane due to the twist and thereby they contribute to the mode.

2.5.2 The enantiomer (S)-5—transition from chirality induced polar switching on a cone to bent-shape induced antiferroelectric switching around the long axis. The unichiral compound (S)-5 exhibits a series of smectic phases with the same transition temperatures as observed for the racemic mixture (see Table 4). Also for (S)-5 the phase transitions at 74 and 50 °C are not



Fig. 8 X-Ray diffraction data from a surface aligned sample of compound *rac*-5: (a and c) original patterns; (b and d) patterns after subtraction of the diffraction pattern of the isotropic liquid at T = 105 °C; (a and b) SmA phase at T = 90 °C, and (c and d) SmC phase at T = 70 °C; (e) d = f(T) plot; for χ -scan over the small angle and wide angle scattering at different temperatures, see Fig. S3g⁺.

associated with any enthalpy change (Fig. 6). On cooling from the isotropic liquid, the SmA phase first occurs with a fan texture in planar alignment (Fig. 11a-c) and homeotropically aligned regions appearing completely dark, *i.e.* optically isotropic. In contrast to the achiral sample, the homeotropic sample remains dark also below the transition to the SmC phase at T = 74 °C. A birefringent schlieren texture can however be induced in the homeotropically aligned regions upon shearing the sample (see Fig. 12a) and in the planar-aligned sample a stripe pattern can be detected in some regions (Fig. 11d). The shear-induced birefringence of the homeotropic sample disappears soon after the shear force is released (Fig. 12b). These observations can be explained through the formation of a helical superstructure in the chiral SmC phase (SmC*) with a pitch length somewhat longer than the wavelength of visible light. It is long enough for a modulation in planar sample to be visible and for the



Fig. 9 (a) Switching current response on applying a triangular wave field (49 °C, 280 V_{pp}, 9 Hz, 5 k Ω , 6 μ m polyimide coated ITO cells, planar alignment) in the SmC_sP_A phase of compound *rac*-**5** and textures observed at *T* = 49.0 °C: (b) +20 V, (c) 0 V, (d) -20 V, respectively.

homeotropic sample not to reflect light, but not so long that the homeotropic sample starts displaying birefringence and optical activity. The helix is obviously distorted under shear forces, resulting in the shear-induced visible birefringence in the homeotropic samples. The time required for the shear induced birefringence to disappear increases with decreasing temperature without a distinct jump at the SmC*-SmC_sP_A* transition temperature. This means that also in the SmC_sP_A* phase the helical superstructure is retained. Only after transition to the low temperature phase M₂ at T = 38 °C does birefringence occur spontaneously in homeotropic alignment (Fig. 12c).

The de Vries nature of (S)-5 leaves a very clear fingerprint on the planar textures, as shown in Fig. 11. First we note that the color within the SmA* phase changes upon cooling from yellowgreen to orange (Fig. 11b and c), reflecting an increase in birefringence and thus an increased degree of orientational order. This is what is expected upon approaching a de Vries transition to a tilted phase and it also fits well with the increasing smectic layer thickness upon cooling seen in X-ray scattering, as mentioned above. As the sample is cooled into the SmC* phase the color again changes, now suddenly, from orange to green (Fig. 11d). This reflects a decreased effective birefringence which is to be expected as we in this chiral sample have a helical modulation of the tilt direction. By applying an electric field we can unwind the helix and then the color changes drastically to pink (Fig. 11e and h), reflecting a birefringence that is not just higher than the one of the helical state but also higher than that of the SmA* phase prior to the transition (Fig. 11c). Again, this is exactly what is expected in the low temperature phase following a de Vries transition. The ease in distorting the helix, the slow reformation of the helix through relaxation, and the many disturbances in the striped pattern in Fig. 11d, g and j-l are also



Fig. 10 (a and c) Dielectric absorption spectra obtained on cooling showing the imaginary part of the dielectric permittivity ε'' as a function of temperature and frequency for the racemic and unichiral versions of 5. Color coding: green-Iso; magenta-SmA/A*; yellow-SmC/C*; cyan-SmC_sP_A/C_sP_A*/crystal. (b and d) The temperature dependence of the frequency *f* of the main absorption peak, as obtained by fitting a Cole–Cole equation to the absorption data. By plotting ln *f vs.* 1/*T* linear curves result, indicating an Arrhenius dependence on temperature with activation energies varying from phase to phase, as indicated in the figure.

all well known from de Vries materials,⁵¹ indicating unusually weak interlayer correlations in tilt direction. The XRD patterns of a surface aligned sample were recorded in the temperature range between 95 °C and 60 °C (onset of crystallization) and the results are close to identical with those recorded for the racemic mixture (see Fig. S4⁺).

Similar to the racemic mixture rac-5 no polarization current response could be detected for the enantiomer (S)-5 under an applied triangular-wave field in the temperature range of the SmA* phase and in the SmC* phase down to T = 50 °C. Below this temperature antiferroelectric switching sets in with polarization values in the same range (700-800 nC cm⁻²) as observed for the racemic compound (Fig. 13). The antiferroelectric switching in the SmC_sP_A* phase again takes place by rotation around the long axis as was observed for the racemic mixture (see Fig. 14a-c). The reduced birefringence at 0 V (Fig. 14b) should result from the antiferroelectric structure and a reduction of the order parameter after removal of the alignment field, which is usually observed for polar switching phases of bent-core mesogens. However, there is another interesting and completely unexpected observation. After reversal of the DC field a slow change of the texture is observed, as shown in Fig. 14c-f; within about one minute the bright birefringent texture turns dark (Fig. 14f). Rotation of the sample between crossed polarizers leads to birefringence and indicates that the extinction is due to

a change of the tilt director orientation which is parallel to one of the polarizers. After field reversal the dark texture is retained (Fig. 14h) but after a while turns into the initial birefringent bright texture (Fig. 14a and h–j).

This slow transformation is not observed for the racemic compound rac-5 and therefore should be chirality related. In order to explain this unusual observation it must be considered that during the switching process the antiferroelectric $SmC_sP_A^*$ ground state is changed to a field induced polar SmC_sP_F* state. The field induced SmC_sP_F* state is unichiral due to layer chirality (see Fig. 14k) as well as due to the fixed molecular chirality. Hence, there are two energetically different diastereomeric structures: (+)-SmC_sP_F-(S)-5 (blue models) and (-)-SmC_sP_F-(S)-5 (red models). One of them (let us assume (+)-SmC_sP_F-(S)-5) is favoured under a positive voltage and therefore a nearly uniform director orientation (tilt direction) is observed for the field aligned sample (Fig. 14a). Reversing the field direction switches the molecules around their long axis. This rotation does not change the director tilt direction (and hence not the optic axis) and therefore the new switched state (Fig. 14c) cannot be distinguished optically from the initial field induced state (Fig. 14a). However, rotating the molecules around the long axis, as in this switching process, reverses layer chirality. The resulting new diastereomeric structure (-)-SmC_s P_{F} -(S)-5 does not correspond to a global energy minimum under the applied electric field



Fig. 11 Textures of a planar-aligned 6 μ m sample with (*S*)-5 upon cooling through the SmA* phase ((a) and (b): $T = 96 \,^{\circ}$ C; (c): $T = 78 \,^{\circ}$ C) to SmC* ((d)–(l): $T = 70 \,^{\circ}$ C). The polarizers are crossed horizontal/vertical except in (j) and (l), where the analyzer has been turned 20° in each direction, and the rubbing direction is aligned along the polarizer in (a), (d), (e), (g), (h) and (j–l), while it is rotated +20° in (b) and +15° in (c). In (e) and (f) a +10 V voltage is applied and the sample is rotated +20° to the new extinction orientation in (f). The corresponding images for $-10 \,$ V are shown in (h) and (i) the latter with the sample rotated -20° . In (j)–(l) the defect-rich helical modulation slowly appearing after removing the electric field is shown, and the presence of a director twist between the substrates is demonstrated by decrossing the polarizers in (j) and (l), opposite decrossing directions shifting the color towards green and pink, respectively.



Fig. 13 (a) Switching current response on applying a triangular wave field (49 °C, 202 V_{pp} , 9 Hz, 5 k Ω , cell thickness: 6 μ m) in the SmC_sP_A* phase of compound (*S*)-5.

and it is thus metastable and slowly relaxes (in about one minute, see Fig. 14c-f) by direct tilt reversal back to the more stable diastereomer (+)-SmC_sP_F-(S)-5. Note that this is not regular director rotation around the SmC tilt cone, as such rotation would also reverse the direction of the spontaneous polarization. Through the tilt reversal the direction of the optic axis changes such that it now coincides with the direction of the polarizer, resulting in the texture now appearing dark (Fig. 14f). Removing the field relaxes the synpolar state via rotation around the long axis in every second layer to the antipolar (+/-)-SmC_sP_A-(S)-5 state, which is racemic regarding layer chirality. Because the director tilt is unaffected the texture remains dark. If we now apply a positive +100 V field the system readopts a synpolar state via molecular long axis rotation in the layers that did not switch upon field removal. The optic axis is not affected and the texture thus remains dark (Fig. 14f-h), but the layer chirality is again changed to (-)-SmC_sP_F-(S)-5. Being in the metastable diastereomeric state the system again slowly transforms to the original field induced birefringent (+)-SmC_s P_{F} -(S)-5 state by tilt flipping (Fig. 14a and h-i).

To the best of our knowledge this is the first example of a field induced chirality flipping between two diastereomeric configurations resulting from the coupling of molecular chirality and layer chirality. As the molecular chirality is fixed a relaxation of the energetically less favorable diastereomer to the more stable one requires a spontaneous reversal of the tilt direction.

The absence of measurable spontaneous polarization in the SmC^* phase of (S)-5 is truly bewildering. This absence is further



Fig. 12 Polarised light optical photomicrographs of the mesophases of (*S*)-**5** as observed on cooling in homeotropic alignment; (a and b) SmC* phase at T = 71 °C after shearing and then 2 seconds of relaxation (a), and after 20 seconds of relaxation (b); (c) spontaneously formed schlieren texture of the M₂ phase at T = 38 °C.



Fig. 14 (a–j) Textures as observed for the SmC_sP_A* phase of compound (*S*)-**5** under an applied DC field at $T = 43 \,^{\circ}$ C; (a) and (h–j) +100 V; (c-f) –100 V and (b) and (g) after switching off the applied field (6 µm polyimide coated ITO cell, planar alignment); (c) and (h) were taken immediately after field reversal, whereas (d–f), (i) and (j) were taken with a time difference of 20 s between each photo; (k) shows the origin of chirality in tilted polar smectic phases due to the configuration provided by the specific combination of tilt direction and polar direction with respect to the layer normal. The models show a projection of the molecules along the polar axis (\bullet means that the apex is pointing outwards and *x* means that the apex is pointing backwards), red color means (–) layer chirality, blue color (+)-layer chirality. The field induced SmC_sP_F structures are homogeneously chiral and have uniform chirality in all layers, whereas in the racemic SmC_sP_A structures at 0 V the layer chirality changes between each layer. In the phase assignment "s" means synclinic tilt correlation, "A" indicates an "antiferroelectric" (antipolar) structure with opposite polar direction in adjacent layers, "F" indicates a "ferroelectric" (synpolar) structure with uniform polar direction in adjacent layers. The orientations of the layers and of the molecules in the layers are indicated by the models overlaying the textures.

corroborated by the dielectric spectroscopy data (Fig. 10) which reveal only a non-collective mode, any mode being related to a spontaneous polarization being too weak to be detected. Nevertheless, the textural response upon switching (Fig. 11e–f and h-i) is clearly polar in nature, with the optic axis rotating in opposite sense for opposite signs of the applied voltage, as expected for a chiral SmC* phase. Obviously, there is a very small spontaneous polarization present that couples to the applied field, inducing a rotation of the director around the smectic C tilt cone until the polarization is aligned with the field. This type of switching of a SmC* phase with very small value of the spontaneous polarization was previously reported for an achiral phenylpyrimidine mixture doped with a small quantity of naproxen as a rather weak chiral dopant.⁵² In the present case the behaviour is however much more surprising because this is a unichiral sample, which at lower temperatures, in the SmC₈P_A* phase, demonstrates very large spontaneous polarization values. One reason could be that the molecular chirality is "weak" as there are three very similar alkyl groups at the stereogenic centers and that two CH₂ groups decouple the stereogenic centers from the core structure.⁵³ Though the weak molecular chirality cannot induce significant polarization in the SmC* phase it can efficiently couple with the layer chirality.

In order to explain the unexpected absence of measurable spontaneous polarization in the SmC* phase we tentatively propose that the de Vries nature of compounds 5 is in fact of a new type, where the transition from disorder to order occurs in two steps. First, at the SmA*-SmC* transition the tilt directions become long-range ordered, as in previously studied de Vries materials. But as the molecule in this question has a bent core, we also have a freedom regarding the bend direction. We believe that the long-range ordering in bend direction occurs only at yet lower temperatures, at the transition to the SmC_sP_A* phase. In the SmC* phase the packing density of the aromatic cores is increased compared to the SmA* phase. A change of the molecular configuration from more rod-like to more bent-corelike takes place by reduction of the temperature,^{15b} which is combined with a further increase of the packing density at reduced temperature. The combination of these two contributions leads to the restriction of the molecular rotation around the long axis and hence to the appearance of order of the bend direction at the SmC*-to-SmCsPA* transition. Because the molecular dipole in bent-core molecules such as 5 is essentially along the bend, a lack of long-range order in bend direction leads to a loss of any substantial spontaneous polarization in the SmC* phase, although the symmetry of the phase allows the appearance of spontaneous polarization. Electrooptic and dielectric measurements thus reveal no sign of spontaneous polarization although a tiny residual spontaneous polarization in fact exists which is sufficient to allow the polar switching revealed in the texture studies.

3. Summary and conclusions

Bent-core molecules based on resorcinol derivatives with branched terminal chains in the racemic and enantiomeric forms and substituents in different positions at the central aromatic core have been investigated. With exception of cyano substitution in the 4-position, all other substituents and substitution patterns give no liquid crystalline properties. This confirms the exceptional properties of these 4-cyanoresorcinol based bent-core mesogens.^{8,54}

The benzoyloxybenzoates **3** and **4** exhibit isotropic blue phases composed of tilted smectic clusters (BPIII_{cybC}*) over wide temperature ranges. To the best of our knowledge, these are the first bent-core compounds showing BPIII phases without an accompanying cholesteric phase (N*) or any other blue phase with cubic defect lattice. This indicates the strong helical twisting power of the bent-core mesogens and the strong distortion of a cubic lattice, probably due to the cybotactic cluster structure of the nematic phase which distorts formation of double twist cylinders.

The related bent-core compounds **5** with a biphenyl core form a series of smectic phases: $SmA^{(*)}-SmC^{(*)}-SmC_sP_A^{(*)}$. It appears that the uniaxial smectic phase ($SmA^{(*)}$) is of the de Vries type. This is likely to be the result of the strong segregation of the rather rigid and extended aromatic cores from the branched and flexible terminal chains. Hence, layer formation is mainly due to segregation. In the layers order develops in two separate steps with decreasing temperature. First, at the SmA to SmC transition, the tilt direction becomes long range ordered and in a second step a long range ordering in bend direction takes place. Hence, this can be regarded as a new type of de Vries material bridging the classical rod-like de Vries materials and the randomly tilted phases of bent-core molecules.⁵⁵

For the optically active compound (*S*)-**5** this leads to a unique transition from chirality induced polar switching to bent-core-type antiferroelectricity. A related transition between bent-core-like and rod-like behaviour was observed for a rod–rod-dimesogen,²⁷ between a chiral nematic and a polar columnar or smectic phase. Herein this transition was for the first time observed within a series of smectic phases.

Moreover, as the switching in the $\text{SmC}_{s}P_{A}^{*}$ phase takes place by collective rotation around the long axis application of an electric field leads to the chiral $\text{SmC}_{s}P_{F}^{*}$ structure, and hence, induces layer chirality. The emerging layer chirality couples with the molecular chirality and gives rise to the more stable diastereomeric configuration. This provides a uniform tilt director orientation in the whole sample with the tilt director depending on the direction of the applied field. Field reversal switches the layer chirality by fast rotation around the long axis. As the molecular chirality is fixed this process leads to the other, less stable diastereomeric configuration, which is only metastable and then slowly relaxes to the more stable one by spontaneous director reorientation. This unique switching and reorientation process based on superstructural diastereomerism is observed for (*S*)-5 for the first time.

Both observed phase types, polar smectic phases as well as blue phases are of significant interest for the development of fast switching display.²⁹ Especially the blue phases are of contemporary interest as new LC (with switching times $<10^{-3}$ s) for sequential color and 3D-displays. For these purposes bent-core based blue phases might become especially useful due to their high tendency for blue phase formation over broad temperature ranges, also in mixtures with rod-like molecules,²⁸ combined with the shape induced polarization which could allow fast switching under relatively weak electric fields.

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- 1 T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, J. Mater. Chem., 1996, 6, 1231.
- 2 R. Amaranatha Reddy and C. Tschierske, J. Mater. Chem., 2006, 16, 907; H. Takezoe and Y. Takanishi, Jpn. J. Appl. Phys., 2006, 45, 597; J. Etxebarria and M. Blanca, J. Mater. Chem., 2008, 18, 2919; G. Pelzl and W. Weissflog, in Thermotropic Liquid Crystals: Recent Advances, ed. A. Ramamoorthy, Springer, Berlin 2007, ch. 1, pp. 1–58.
- 3 D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Körblova and D. M. Walba, *Science*, 1997, **278**, 1924.
- 4 L. E. Hough, M. Spannuth, M. Nakata, D. A. Coleman, C. D. Jones, G. Dantlgraber, C. Tschierske, J. Watanabe, E. Körblova, D. M. Walba, J. E. Maclennan, M. A. Glaser and N. A. Clark, *Science*, 2009, **325**, 452–456.
- 5 D. J. Earl, M. A. Osipov, H. Takezoe, Y. Takanishi and M. R. Wilson, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **71**, 021706; H. S. Jeong, S. Tanaka, D. K. Yoon, S.-W. Choi, Y. H. Kim, S. Kawauchi, F. Araoka, H. Takezoe and H.-T. Jung, *J. Am. Chem. Soc.*, 2009, **131**, 15055–15060; S. Kawauchi, S.-W. Choi, K. Fukuda, K. Kishikawa, J. Watanabe and H. Takezoe, *Chem. Lett.*, 2007, **36**, 750; S.-W. Choi, S. Kang, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe, *Chirality*, 2007, **19**, 250–254.
- 6 (a) G. Pelzl, A. Eremin, S. Diele, H. Kresse and W. Weissflog, J. Mater. Chem., 2002, 12, 2591; (b) T. Niori, J. Yamamoto and H. Yokoyama, Mol. Cryst. Liq. Cryst., 2004, 409, 475; (c) V. Görtz and J. W. Goodby, Chem. Commun., 2005, 3262; (d) C. Praasang, A. C. Whitwood and D. W. Bruce, Chem. Commun., 2008, 2137; (e) P. S. Salter, P. W. Benzie, R. A. Reddy, C. Tschierske, S. J. Elston and E. P. Raynes, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2009, 80, 031701.
- 7 J. Thisayukta, H. Niwano, H. Takezoe and J. Watanabe, J. Am. Chem. Soc., 2002, 124, 3354; M. Nakata, Y. Takanishi, J. Watanabe and H. Takezoe, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2003, 68, 041710.
- 8 C. Keith, A. Lehmann, U. Baumeister, M. Prehm and C. Tschierske, Soft Matter, 2010, 6, 1704–1721.
- 9 (a) S. Stojadinovic, A. Adorjan, S. Sprunt, H. Sawade and A. Jakli, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2002, 66, 060701;
 (b) D. Wiant, S. Stojadinovic, K. Neupane, S. Sharma, K. Fodor-Csorba, A. Jakli, J. T. Gleeson and S. Sprunt, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2006, 73, 030703; (c) N. Vaupotic, J. Szydlowska, M. Salamonczyk, A. Kovarova, J. Svoboda, M. Osipov, D. Pociecha and E. Gorecka, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2009, 80, 030701(R).
- 10 O. Francescangeli, F. Vita, C. Ferrero, T. Dingemans and E. T. Samulski, *Soft Matter*, 2011, 7, 895–901; O. Francescangeli and E. T. Samulski, *Soft Matter*, 2010, 6, 2413–2420.
- 11 C. Tschierske and D. J. Photinos, J. Mater. Chem., 2010, 20, 4283.
- 12 O. Francescangeli, V. Stanic, S. I. Torgova, A. Strigazzi, N. Scaramuzza, C. Ferrero, I. P. Dolbnya, T. M. Weiss, R. Berardi, L. Muccioli, S. Orlandi and C. Zannoni, *Adv. Funct. Mater.*, 2009, 18, 2592.
- 13 Less rings could be sufficient if packing is reinforced by H-bonding: R. Deb, R. K. Nath, M. K. Paul, N. V. S. Rao, F. Tuluri, Y. Shen, R. Shao, D. Chen, C. Zhu, I. I. Smalyukh and N. A. Clark, J. Mater. Chem., 2010, 20, 7332–7336.
- 14 (a) G. Pelzl, S. Diele and W. Weissflog, Adv. Mater., 1999, 11, 707–724; (b) W. Weissflog, H. Nadasi, U. Dunemann, G. Pelzl, S. Diele, A. Eremin and H. Kresse, J. Mater. Chem., 2001, 11, 2748–2758; (c) W. Weissflog, H. N. Shreenivasa Murthy, S. Diele and G. Pelzl, Philos. Trans. R. Soc. London, Ser. A, 2006, 364, 2657.
- 15 (a) L. Kovalenko, M. W. Schröder, R. A. Reddy, S. Diele, G. Pelzl and W. Weissflog, *Liq. Cryst.*, 2005, **32**, 857; (b) I. Wirth, S. Diele, A. Eremin, G. Pelzl, S. Grande, L. Kovalenko, N. Pancenko and W. Weissflog, *J. Mater. Chem.*, 2001, **11**, 1642.
- 16 H.-S. Kitzerow and C. Bahr, *Chirality in Liquid Crystals*, Springer-Verlag, NewYork, 2001.
- 17 R. Lemineux, Chem. Soc. Rev., 2007, 36, 2033-2045.
- 18 C. Tschierske, in *Chirality at the Nano Scale*, ed. D. B. Amabiliino, Wiley-VCH, Weinheim, 2009, p. 271.
- 19 H. Kikuchi, Struct. Bonding, 2008, 128, 99-117.
- 20 I. Nishiyama, Chem. Rec., 2009, 9, 340–355; I. Nishiyama, J. Yamamoto and H. Yokoyama, Mol. Cryst. Liq. Cryst., 2009,

498, 19–28; I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, *Mol. Cryst. Liq. Cryst.*, 2005, **443**, 25–41.

- 21 D. B. Amabiliino, *Chirality at the Nano Scale*, Wiley-VCH, Weinheim, 2009.
- 22 M. Nakata, D. R. Link, F. Araoka, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe, *Liq. Cryst.*, 2001, 28, 1301–1308. It is reported that the layer chirality alternates from layer to layer despite being composed of chiral mesogens.
- 23 (a) C. V. Yelamaggad, I. S. Shashikala, G. Liao, D. S. Shankar Rao, S. K. Prasad, Q. Li and A. Jakli, *Chem. Mater.*, 2006, **18**, 6101; (b) G. Liao, I. Shashikala, C. V. Yelamaggad, D. S. Shankar Rao, S. Krishna Prasad and A. J. Jákli, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2006, **73**, 051701; (c) C. V. Yelamaggad, G. Shanker, U. S. Hiremath and S. K. Prasad, *J. Mater. Chem.*, 2008, **18**, 2941.
- 24 K. Kumazawa, M. Nakata, F. Araoka, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe, J. Mater. Chem., 2004, 14, 157.
- 25 C. K. Lee, S. S. Kwon, T. S. Kim, E. J. Choi, S. T. Shin, W. C. Zin, D. C. Kim, J. H. Kim and L. C. Chien, *Liq. Cryst.*, 2003, **30**, 1401; S. K. Lee, C. W. Park, J. G. Lee, K. T. Kang, K. Nishida, Y. Shimbo, Y. Takanishi and H. Takezoe, *Liq. Cryst.*, 2005, **32**, 1205.
- 26 R. A. Reddy, B. K. Sadashiva and U. Baumeister, J. Mater. Chem., 2005, 15, 3303.
- 27 J. P. F. Lagerwall, F. Giesselmann, M. D. Wand and D. M. Walba, *Chem. Mater.*, 2004, 16, 3606–3615.
- 28 S. Taushanoff, K. V. Le, J. Williams, R. J. Twieg, B. K. Sadashiva, H. Takezoe and A. Jakli, *J. Mater. Chem.*, 2010, **20**, 5893–5898; M. Lee, S.-T. Hur, H. Higuchi, K. Song, S.-W. Choi and H. Kikuchi, *J. Mater. Chem.*, 2010, **20**, 5813–5816; K. V. Le, S. Aya, Y. Sasaki, H. Choi, F. Araoka, K. Ema, J. Mieczkowski, A. Jakli, K. Ishikawa and H. Takezoe, *J. Mater. Chem.*, 2011, **21**, 2855–2857.
- 29 S. Siemianowski, *Liq. Cryst. Today*, 2009, **18**, 66–67; PhysOrg: http:// www.physorg.com/news129997960.html; Digital Trends: http://news. digitaltrends.com/news-article/16726/samsung-shows-240-hz-bluephase display; Gizmodo: http://gizmodo.com/390255/samsungdevelopsnew-blue-phase-lcd-panel-for-tvs.
- 30 A 3,7-dimethyloctyloxy substituted bent-core LC with a biphenyl based core and Schiff base type wings was reported previously, but only in the racemic form: S. Rauch, C. Selbmann, P. Bault, H. Sawade, G. Heppke, O. Morales-Saavedra, M. Y. M. Huang and A. Jákli, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, 69, 021707.
- 31 (a) E. Marcus, Ber. Dtsch. Chem. Ges., 1891, 24, 3650; (b)
 J. L. Serrano, T. Sierra, Y. Gonzalez, C. Bolm, K. Weickardt,
 A. Magnus and G. Moll, J. Am. Chem. Soc., 1995, 117, 8312.
- 32 B. Otterholm, M. Nilsson, S. T. Lagerwall and K. Skarp, *Liq. Cryst.*, 1987, 2, 757.
- 33 P. C. Jocelyn and N. Polgar, J. Chem. Soc., 1953, 132-137.
- 34 V. Kozmik, A. Kovarova, M. Kuchar, J. Svoboda, V. Novotna, M. Glogarova and J. Kroupa, *Liq. Cryst.*, 2006, 33, 41–56.
- 35 R. Achten, A. Koudijs, M. Giesbers, A. T. M. Marcelis and E. J. R. Sudhölter, *Liq. Cryst.*, 2005, 32, 277–285.
- 36 K. Luo, Y. Li and M. Xie, *Huaxue Yanjiu Yu Yingyong*, 2001, 13, 673–674, 640.
- 37 (a) M. Xie, J. Qin, Z. Hu and H. Zhao, Chin. Chem. Lett., 1992, 3, 775–778; (b) J. Qin, M. Xie, Z. Hu and H. Zhao, Synth. Commun., 1992, 22, 2253–2258.
- 38 J. Barbera, L. Puig, P. Romero, J. L. Serrano and T. Sierra, J. Am. Chem. Soc., 2006, 128, 4487–4492.
- 39 T. Ohtake, M. Ogasawara, K. Ito-Akita, N. Nishina, S. Ujiie, H. Ohno and T. Kato, *Chem. Mater.*, 2000, **12**, 782–789.
- 40 C. Tschierske and H. Zaschke, J. Prakt. Chem., 1989, 331, 365.
- 41 (a) G. Pelzl, S. Diele, S. Grande, A. Jakli, C. Lischka, H. Kresse, H. Schmalfuss, I. Wirth and W. Weissflog, *Liq. Cryst.*, 1999, 26, 401–413; (b) U. Dunemann, M. W. Schröder, R. Amaranatha Reddy, G. Pelzl, S. Diele and W. Weissflog, *J. Mater. Chem.*, 2005, 15, 4051–4061; (c) R. A. Reddy and B. K. Sadashiva, *Liq. Cryst.*, 2003, 30, 1031–1050; (d) W. Weissflog, S. Sokolowski, H. Dehne, B. Das, S. Grande, M. W. Schröder, A. Eremin, S. Diele, G. Pelzl and H. Kresse, *Liq. Cryst.*, 2004, 31, 923–933.
- 42 W. Weissflog, C. Lischka, L. Benne, T. Scharf, G. Pelzl, S. Diele and H. Kruth, *Proc. SPIE*, 1998, **3319**, 14–19; R. A. Reddy and B. K. Sadashiva, *Liq. Cryst.*, 2004, **31**, 1069–1081.

- H.-S. Kitzerow, *ChemPhysChem*, 2006, 7, 63–66; S. Hekimoglu and J. Conn, *Liquid Crystals Today*, 2003, 12, 1–2; D. C. Wright and N. D. Mermin, *Rev. Mod. Phys.*, 1989, 61, 385–432; E. Grelet, *Liquid Crystals Today*, 2003, 12, 1–5.
- 44 H.-S. Kitzerow, Ferroelectrics, 2010, 395, 66-85.
- 45 M.-H. Li, V. Laux, H.-T. Nguyen, G. Sigaud, P. Barois and N. Isaert, *Liq. Cryst.*, 1997, **23**, 389.
- 46 J. W. Goodby, D. A. Dunmur and P. J. Collings, *Liq. Cryst.*, 1995, 19, 703–709.
- 47 A. Guinier, X-Ray Diffraction, Freeman, San Francisco, 1963.
- 48 O. Francescangeli, M. Laus and G. Galli, *Phys. Rev. E: Stat.,* Nonlinear, Soft Matter Phys, 1997, 55, 481-487.
- 49 In this case maily L_{\parallel} contributes to L.
- 50 J. P. F. Lagerwall and F. Giesselmann, ChemPhysChem, 2006, 7(1), 20-45.
- 51 J. P. F. Lagerwall, F. Giesselmann and M. D. Radcliffe, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2002, 66, 031703.

- 52 J. P. F. Lagerwall, A. A. Kane, N. A. Clark and D. M. Walba, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, 70, 031703.
- 53 In fact the polarization values obtained for rod-like ferroelectric LCs with the (S)-3,7-dimethyloctyl-1-oxy unit are low, ranging between a few and 10 nC cm⁻², see: E. Chin, J. W. Goodby, J. S. Patel, J. M. Geary and T. M. Leslie, *Mol. Cryst. Liq. Cryst.*, 1987, 146, 325–339.
- 54 C. Keith, M. Prehm, Y. P. Panarin, J. K. Vij and C. Tschierske, *Chem. Commun.*, 2010, 46, 3702–3704.
- 55 (a) G. Dantlgraber, U. Baumeister, S. Diele, H. Kresse, B. Lühmann, H. Lang and C. Tschierske, J. Am. Chem. Soc., 2002, **124**, 14852; (b) Y. Shimbo, E. Gorecka, D. Pociecha, F. Araoka, M. Goto, Y. Takanishi, K. Ishikawa, J. Mieczkowski, K. Gomola and H. Takezoe, Phys. Rev. Lett., 2006, **97**, 113901; (c) R. A. Reddy, U. Baumeister and C. Tschierske, Chem. Commun., 2009, 4236– 4238; (d) R. A. Reddy, J.-L. Chao, H. Kresse and C. Tschierske, J. Mater. Chem., 2010, **6**, 3883–3897.