

Liquid-Crystalline Dimers Composed of Bent-Core Mesogenic Units

B. Kosata,[†] G.-M. Tamba,[†] U. Baumeister,[†] K. Pelz,[†] S. Diele,[†] G. Pelzl,[†] G. Galli,[‡]
S. Samaritani,[‡] E. V. Agina,[§] N. I. Boiko,[§] V. P. Shibaev,[§] and W. Weissflog^{*,†}

*Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Muehlpforte 1,
D-06108 Germany, Dipartimento di Chimica e Chimica Industriale, Università de Pisa, via Risorgimento
35, 56126 Pisa, Italy, and Chemistry Department, Moscow State University, Lenin Hills,
119992 Moscow, Russia*

Received August 25, 2005. Revised Manuscript Received November 23, 2005

Systematic studies on symmetric twin molecules composed of two bent-core mesogenic units are reported for the first time. It is shown that the formation of mesophases mainly depends on the chemical structure of the spacer. A sufficiently flexible spacer containing dimethylsiloxane units allows a decoupling of the mesogenic moieties; the related compounds exhibit a ferroelectric SmCP phase proved by electro-optical measurements. On the basis of X-ray data, a plausible structure model is presented. The connection of two bent-core mesogenic units by means of a tetraethylene glycol spacer results in dimers, which are able to form columnar phases. For twins containing a simple hydrocarbon chain as spacer, in most cases liquid-crystalline behavior could not be detected. These general tendencies remain valid if the bent-core unit is changed, e.g., by increasing the number of aromatic rings, by lateral substitution, and by inversion of the direction of one of the connecting groups between the aromatic rings, respectively. The mesophase behavior of the new dimers is compared with that of the corresponding single-unit compounds as well as a related dendrimer and a polymer. It is of interest that the antiferroelectric switching behavior found for the nonchiral “monomeric” compounds is changed to a ferroelectric behavior for the dimeric compounds.

1. Introduction

Mesogenic dimers contain two mesogenic units linked via a flexible spacer. Such compounds have attracted growing attention because their mesophase behavior can be clearly different from that of the corresponding monomers and they can be regarded as model compounds for main-chain liquid-crystal polymers.^{1–4} In general, the mesophase behavior of mesogenic dimers depends on several factors: especially on the structure and size of the mesogenic units and on the structure and parity of the spacer.^{5–8} The transition temperature and the phase behavior are often affected by the parity of the spacer.^{5,6,9} Also, the ratio between the length of the spacer and the length of the terminal chains can strongly influence the structure of the mesophases.^{9–12}

The aim of the paper was to synthesize mesogenic dimers which are built up by bent-core mesogenic units. Bent-core mesogens have attracted considerable interest in recent years because they are able to form new smectic mesophases with a polar structure.^{13–15} The polar structure is provided by a dense packing of the bent molecules, giving rise to a restricted rotation around the molecular long axis and therefore to a macroscopic polarization in the smectic layers which can be reversed by the application of an external electric field. In the ferroelectric phases the polarization is uniform in adjacent layers whereas in antiferroelectric phases the polarization alternates from layer to layer. Furthermore, in tilted smectic phases formed by bent-core molecules the combination of polar order and director tilt leads to a chiral structure of the layers without any molecular chirality.¹⁵ To avoid bulk polarization, an antiferroelectric ground state occurs in most cases.¹⁴ Another way to escape from bulk polarization is achieved by the break of the layers into two-dimensional modulated structures^{15–20} or by a splay of the polarization within the smectic layers.²¹ Note that bent-core

* Corresponding author. E-mail: wolfgang.weissflog@chemie.uni-halle.de.

[†] Martin-Luther-Universität Halle-Wittenberg.

[‡] Università de Pisa.

[§] Moscow State University.

- (1) Imrie, C. T.; Henderson, P. A. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 298.
- (2) Watanabe, J.; Hayashi, M. *Macromolecules* **1989**, *22*, 4083.
- (3) Watanabe, J.; Hayashi, M.; Morita, A.; Niori, T. *Mol. Cryst. Liq. Cryst.* **1992**, *254*, 221.
- (4) Watanabe, J.; Nakata, Y.; Simizu, K. *J. Phys. II France* **1994**, *4*, 581.
- (5) Niori, T.; Adachi, S.; Watanabe, J. *Liq. Cryst.* **1995**, *19*, 139.
- (6) Date, R. W.; Imrie, C. T.; Luckhurst, G. R.; Seddon, J. M. *Liq. Cryst.* **1992**, *12*, 203.
- (7) Date, R. W.; Luckhurst, G. R.; Shuman, M.; Seddon, J. M. *J. Phys. II France* **1995**, *5*, 587.
- (8) Weissflog, W.; Lischka, C.; Diele, S.; Wirth, I.; Pelzl, G. *Liq. Cryst.* **2000**, *27*, 43.
- (9) Watanabe, J.; Komura, H.; Niori, T. *Liq. Cryst.* **1993**, *3*, 455.
- (10) Watanabe, J.; Niori, T.; Choi, S.-W.; Takahashi, Y.; Takezoe, H. *Jpn. J. Appl. Phys.* **1988**, *37*, L401.

- (11) Choi, S.-W.; Zennoji, M.; Takahashi, Y.; Takezoe, H.; Niori, T.; Watanabe, J. *Mol. Cryst. Liq. Cryst.* **1999**, *328*, 185.
- (12) Attard, G. S.; Date, R. W.; Imrie, C. T.; Luckhurst, G. R.; Roskilly, S. J.; Seddon, J. M.; Taylor, L. *Liq. Cryst.* **1994**, *16*, 529.
- (13) Niori, T.; Sekine, T.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231.
- (14) Link, D. R.; Natale, G.; Shao, R.; MacLennan, J. E.; Clark, N. A.; Körblova, E.; Walba, D. M. *Science* **1997**, *278*, 1924.
- (15) Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707.
- (16) Watanabe, J.; Niori, T.; Sekine, T.; Takezoe, H. *Jpn. J. Appl. Phys.* **1998**, *37*, L139.
- (17) Pelz, K.; Diele, S.; Baumeister, U.; Weissflog, W. *Liq. Cryst.* **2003**, *30*, 1151.

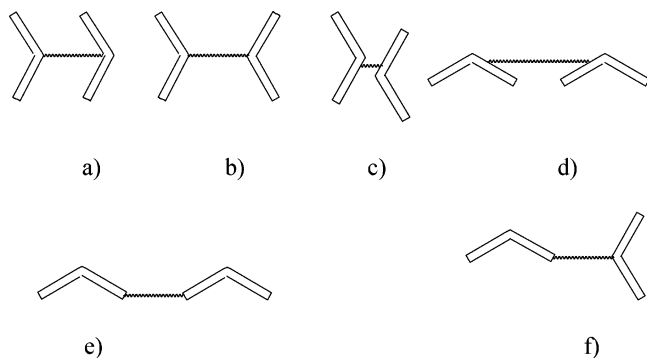


Figure 1. Several topological possibilities to connect two bent-core mesogens.

mesogens are not only interesting from the scientific point of view but they also have a potential for practical application, e.g., for materials with large second-order NLO effects.^{22,23} There are different possibilities for linking the mesogenic units as schematically sketched in Figure 1. Until now dimers of type c have been reported,²⁴ where the bent-core units are laterally linked by a relatively short and rigid spacer (sulfonyl or sulfide). These dimers form nematic, SmA, or SmC phases. This finding is not surprising since the mesogenic units within the twin molecule possess opposite bent directions. The first mesogenic dimers composed of terminally linked bent monomers (type e) were reported by Dantlgraber et al.²⁵ Depending on the number of dimethylsiloxane units in the spacer, either a ferroelectric or an antiferroelectric SmCP phase has been obtained.

In this paper we present symmetric dimeric liquid crystals where several bent-core mesogenic units are terminally linked with different flexible spacers. In addition, a bent-core mesogenic monomer is used to prepare a side-chain polymer as well as a dendrimer composed of eight monomers which allow comparison of the liquid crystalline behavior with the corresponding twin molecule.

The mesophase behavior of the synthesized compounds has been investigated by polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction, and electro-optical measurements. Structure–property relationships will be discussed on the basis of the experimental results.

2. Experimental Section

The thermal behavior was investigated using a Perkin-Elmer DSC Pyris 1. The optical textures and the field-induced changes of the

textures were examined using a polarizing microscope (Leitz Orthoplan) equipped with a Linkam THM 600/S hot stage. X-ray diffraction measurements on nonoriented samples were carried out using a Guinier film camera and a Guinier goniometer. X-ray investigations on oriented samples were done using a 2D detector (HI-Star, Siemens AG). The electro-optical properties were studied using commercial cells (E. H. C. Corp., Japan) with rubbed polyimide layers. The triangular wave method²⁶ was used to study the switching current response.

3. Results and Discussion

Synthesis. To prepare symmetric twin molecules, a convergent reaction path is advantageous. Therefore, compounds **1–3** have been synthesized as sketched in Scheme 1. The substituted phenol **1a** was reported.^{27,28} Compounds **1b** and **1c** were prepared analogously to compound **1d**, which was recently published by us.²⁹ Esterification of the phenols **1a–d** with 4-benzyloxybenzoic acid and then deprotection using ammonium formate and palladium on carbon as a catalyst results in compounds **1a–d**.

The alkylene-spacered bisbenzoic acid **III-1**³⁰ and the bisbenzoic acid **III-2** containing a tetraethylene glycol spacer³¹ are described. The bisbenzoic acid **III-3** with a spacer containing siloxane units was prepared analogously to that reported by Guillon et al.³² for shorter chain homologues.

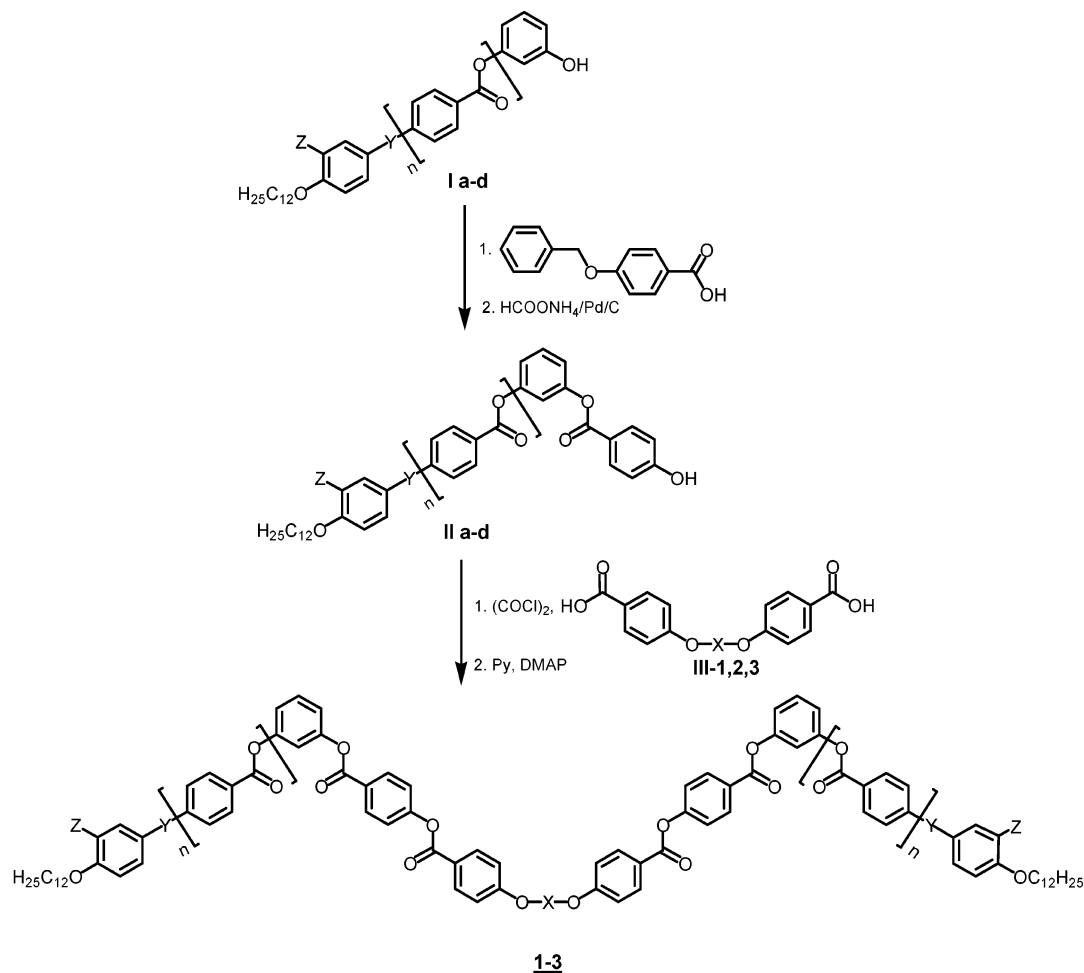
Reaction with oxalyl chloride results in the corresponding acid chlorides, which were esterified with the phenols **1a–d** to give the final compounds **1a–d**, **2a–d**, and **3a–d**.

In compound **1e** the carboxylic connecting groups between the “inner” phenyl rings are arranged in an inverse direction in comparison to the isomer **1a**. Therefore, the bent four-ring intermediate **IV** contains the carboxylic group, whereas the compound **V** containing the alkylene spacer represents a bisphenol. Final reaction between the intermediates **IV** and **V** yielded compound **1e**, as shown in Scheme 2.

To prepare the cyano-substituted compound **5a**, mono-protected 4-cyanoresorcinol **VI** was synthesized using the steps sketched in Scheme 3. Esterification of **VI** with 4-(4-*n*-octyloxybenzoyloxy)benzoic acid and following deprotection results in compounds **VII** and **VIII**. Reaction with 4-benzyloxybenzoic acid and hydrogenolysis yielded the cyano-substituted four-ring compound **IX**. Acylation of the phenol **IX** with the bis-benzoic acid **III-2** results in the twin molecule **5**.

- (18) (a) Szydłowska, J.; Mieczkowski, J.; Matraszek, J.; Bruce, D. W.; Gorecka, E.; Pocięcha, D.; Guillon, D. *Phys. Rev. E* **2003**, *67*, 031702. (b) Gorecka, E.; Pocięcha, D.; Cepic, M.; Mieczkowski, J. *Chem-PhysChem* **2005**, *6*, 1087.
- (19) Amaranatha Reddy, R.; Sadashiva, B. K. *J. Mater. Chem.* **2002**, *12*, 2214.
- (20) Amaranatha Reddy, R.; Sadashiva, B. K.; Raghunathan, V. A. *Chem. Mater.* **2005**, *17*, 274.
- (21) Coleman, D. A.; Fernsler, J.; Chattham, N.; Nakata, M.; Takanishi, Y.; Körblová, E.; Link, D. R.; Shao, R.-F.; Jang, W. G.; MacLennan, J. E.; Mondainn-Monval, O.; Boyer, C.; Weissflog, W.; Pelzl, G.; Chien, L.-C.; Zasadzinski, J.; Watanabe, J.; Walba, D. M.; Takezoe, H.; Clark, N. A. *Science* **2003**, *301*, 1204.
- (22) Kentischer, F.; Macdonald, R.; Warnick, P.; Heppke, G. *Liq. Cryst.* **1998**, *25*, 341.
- (23) Choi, S.-W.; Kinoshita, Y.; Park, B.; Takezoe, H.; Niori, T.; Watanabe, J. *Jpn. J. Appl. Phys.* **1998**, *37*, 3408.

- (24) Dehne, H.; Pötter, M.; Sokolowski, S.; Holzlehner, U.; Reinke, H.; Weissflog, W.; Diele, S.; Pelzl, G.; Wirth, I.; Kresse, H.; Schmalfluss, H.; Grande, S. *Proceedings of the Freiburger Arbeitstagung Flüssigkristalle*, Freiburg, March 2000, poster.
- (25) Dantlgraber, G.; Diele, S.; Tschierske, C. *Chem. Commun.* **2002**, 2768.
- (26) Miyasato, K.; Abe, S.; Takezoe, H.; Fukuda, A.; Kuze, E. *Jpn. J. Appl. Phys.* **1983**, *22*, L661.
- (27) Shreenivasa Murthy, H. N.; Sadashiva, B. K. *Liq. Cryst.* **2004**, *31*, 1347.
- (28) Achten, R.; Cuypers, R.; Giesbers, M.; Koudijs, A.; Marcelis, A. T. M.; Sudhölter, E. J. R. *Liq. Cryst.* **2004**, *31*, 1167.
- (29) Weissflog, W.; Naumann, G.; Kosata, B.; Schröder, M. W.; Eremin, A.; Diele, S.; Kresse, H.; Friedemann, R.; Rama Krishnan, A. *J. Mater. Chem.* **2005**, *15*, 4328.
- (30) Donahoe, H. B.; Benjamin, C. E.; Fennoy, L. V.; Greiff, D. *J. Org. Chem.* **1961**, *26*, 474.
- (31) Lu, X.-H.; He, C.-B.; Griffin, A. C. *Macromolecules* **2003**, *36*, 5195.
- (32) Guillon, D.; Osipov, M. A.; Mery, S.; Siffert, M.; Nicoud, J.-F.; Bourgojne, C.; Sebastiao, P. *J. Mater. Chem.* **2001**, *11*, 2700.

Scheme 1. Convergent Synthesis of the Dimers 1–3 Consisting of Two Bent-Core Moieties^a

Comp	-O-X-O-	No.	n	Y	Z
1; III-1	-O-(CH ₂) ₁₀ -O-	a	1	COO	H
2; III-2	-O-(CH ₂ CH ₂ O) ₄ -	b	1	COO	Cl
3; III-3	-OC ₁₁ H ₂₂ -Si(CH ₃) ₂ [OSi(CH ₃) ₂] ₂ -C ₁₁ H ₂₂ O-	c	2	COO	H
		d	1	OOC	H

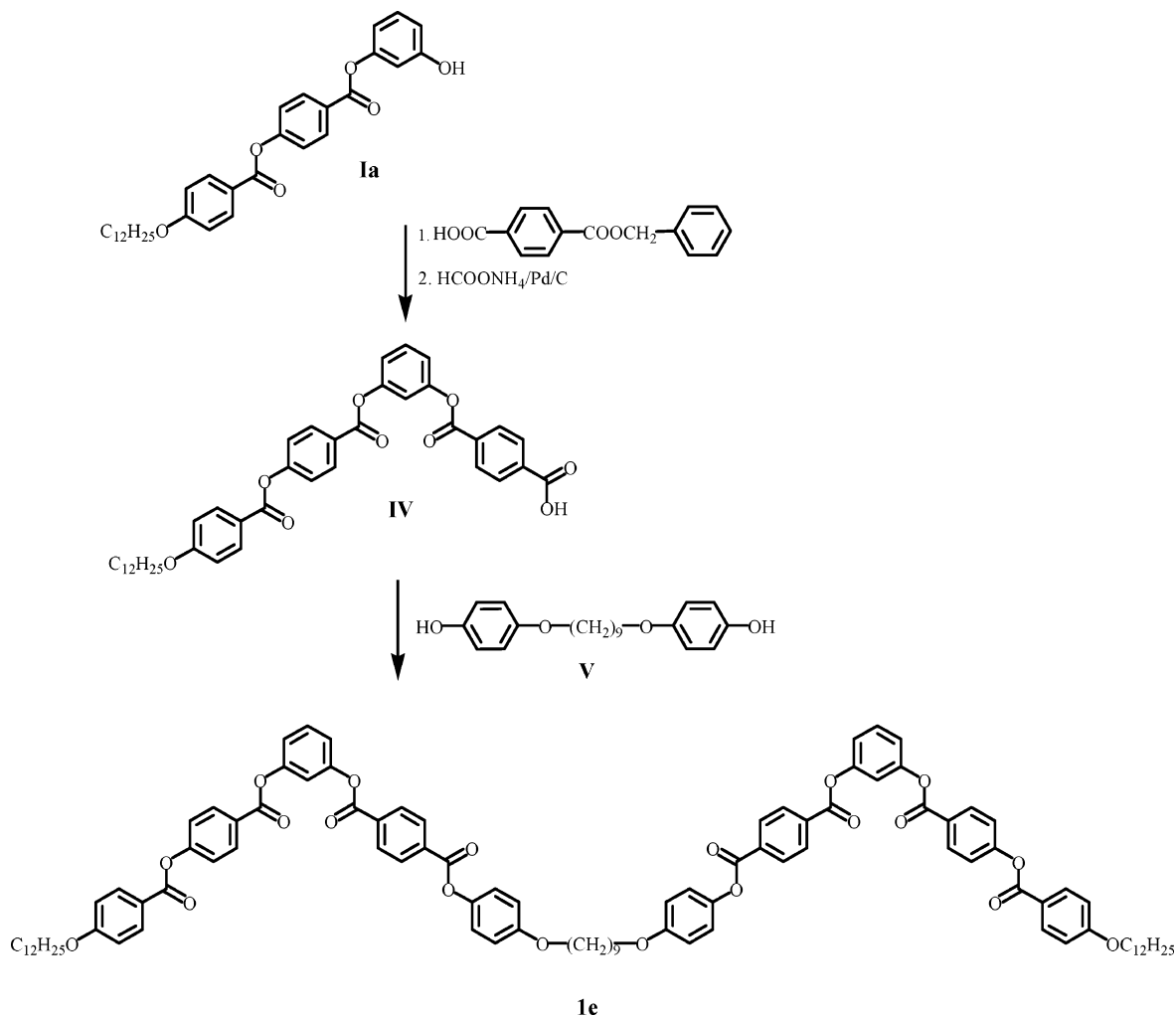
^a The indication **a-d** is valid for the compounds **Ia-d**, **IIa-d**, **1a-d**, **2a-d**, and **3a-d**.

The ω -unsaturated five-ring compound **6**, necessary for the synthesis of the polymer **7** and the dendrimer **8**, was prepared by reaction of the four-ring compound **IIa** with 4-*n*-undecenyloxybenzoic acid. Hydrosilylation of compound **6** with poly(H-siloxane) (35 Si-H-units) yielded the side-chain polymer **7**.

The dendrimer **8** was synthesized according to Scheme 4. A general approach to dendrimers of such structure was elaborated by Shibaev and co-workers.³³ It consists of a modification of the mesogen in such a way that it has a spacer

with an active terminal Si-H group capable of reaction with the terminal allyl groups of a carbosilane dendritic matrix. To realize this method, compound **6** underwent a hydrosilylation reaction with a 3-fold excess of dimethylchlorosilane. The completion of the reaction was checked by the disappearance of the NMR resonance assigned to the protons of a terminal carbon-carbon double bond. The product was not isolated because of the high hygroscopicity of chlorosilane derivatives. By the cohydrolysis of the obtained silane chloride in 40-fold excess of dimethylchlorosilane and in the presence of equal quantities of pyridine and water, the target silane compound **X** was obtained, which was purified by column chromatography on silica gel.

(33) Ponomarenko, S. A.; Rebrov, E. A.; Boiko, N. I.; Muzafarov, A. M.; Shibaev, V. P. *Vysokomol. Soedin. Ser. A* **1998**, *40*, 1253; *Polym. Sci. Ser. A* **1998**, *40*, 763.

Scheme 2. Synthesis of the Dimer **1e**, Having an Inverse Carboxylic Connecting Group between the “Inner” Phenyl Rings

Coupling of the silane **X** to the dendritic matrix of first generation having 8 terminal allyl groups was carried out using hydrosilylation reaction in the presence of platinum catalyst. A 1.5-fold excess of the silane **X** was used to ensure the complete addition, which was checked by NMR again. When the reaction was finished, the excess of the silane **X** was removed by column chromatography on silica gel. The final purification of the dendrimer **8** was performed by preparative GPC. The individuality and purity of the synthesized dendrimer **8** was proved by GPC. The GPC curve of compound **8** has a symmetric peak; the molecular-mass distribution (M_w/M_n) was 1.02, confirming the monodispersity of the product.

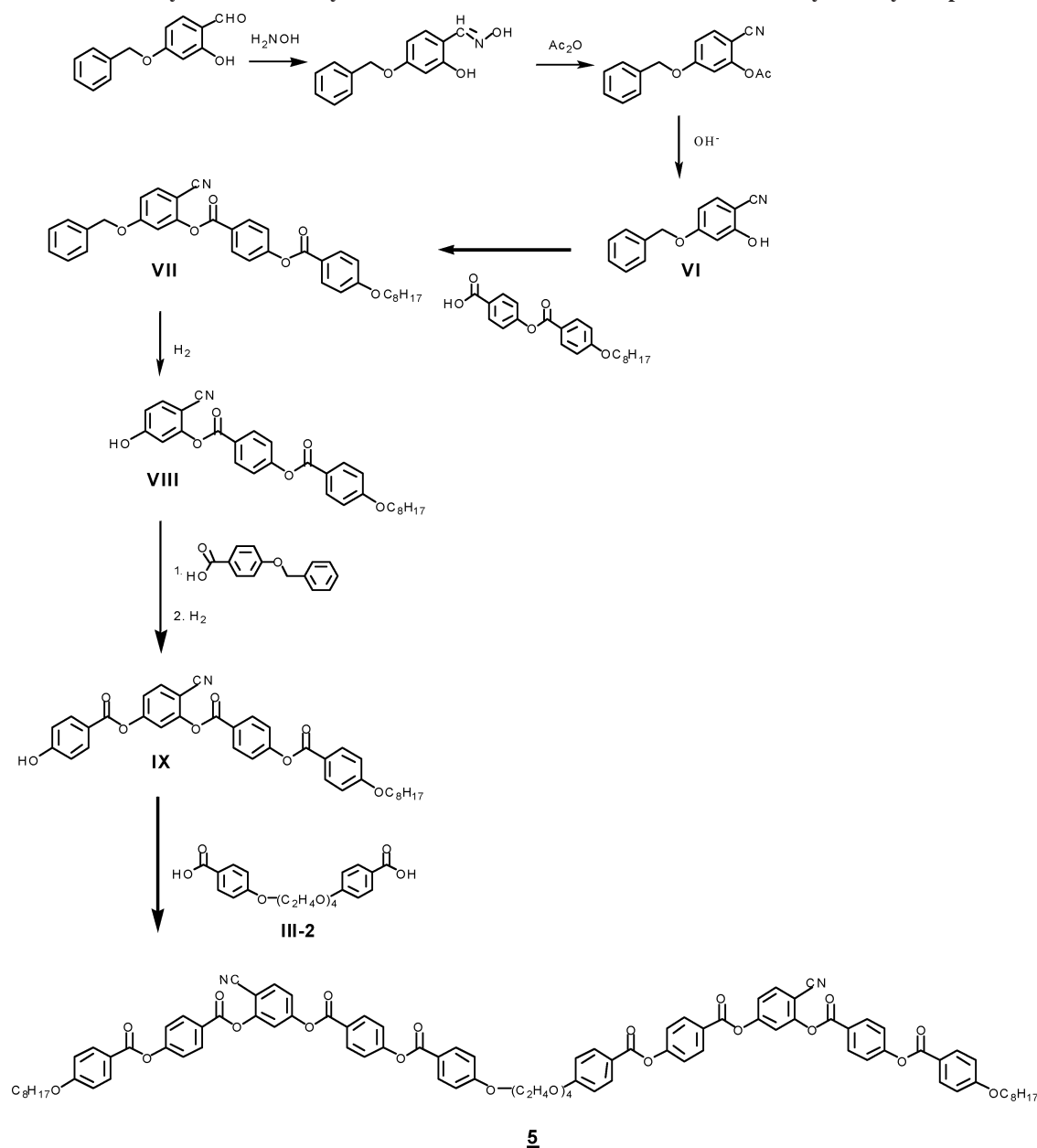
Experimental details concerning the synthesis of the materials are given in the Supporting Information.

Mesophase Behavior of the Materials. In Table 1 the transition temperatures and the phase behavior of 12 symmetric dimers are presented where 4 different mesogenic units were linked with 3 different connecting groups. It is seen from Table 1 that the mesophase behavior of the dimers is strongly different and depends on the chemical structure of the mesogenic units as well as on the type of the spacer. We have prepared additionally the single-unit bent-core mesogens to discuss these two effects separately. In Table 2 the transition temperatures of the corresponding single bent-core mesogens **4a–d** are listed. All of the compounds **4**

exhibit $SmCP_A$ phases, which are proved by X-ray and electro-optical measurements.

When one looks at the mesophase stability, one can see the influence of different molecular fragments is comparable for the “monomeric” (**4a–d**) and dimeric molecules (**2a–d**, **3a–d**). A lateral chlorine atom at the outer rings does not influence significantly the clearing temperatures (compare **2a–b**; **3a–b**; **4a–b**). An enlargement of the mesogenic unit from a five-ring to a six-ring core leads to a clear enhancement of the clearing temperatures (dimer **2a** to **2c** by 47 K; dimer **3a** to **3c** by 39 K; monomer **4a** to **4c** by 35 K). The inversion of one of the outer carboxylic groups increases the mesophase stability in all cases; compare the isomeric compounds: **2a** and **2d** by 15 K; **3a** and **3d** by 15 K; **4a** and **4d** by 14 K.

In principle, it is known that the connection of two mesogenic units to form a twin molecule is associated with an increase of the mesophase stability. This relationship is also true for bent-core mesogens. The scale of the effect depends on the length and type of the aliphatic spacer. For the dimers **2a–d** containing the tetraethylene glycol spacer, the increase of the clearing temperatures amounts to 28–42 K in comparison to the single compounds **4a–d**. For the siloxane-containing dimers **3a–d**, the stabilization effect caused by the dimerization is a little lower and amounts to 20–24 K.

Scheme 3. Synthesis of the Cyano-Substituted Twin Molecule **5** with a Tetraethylene Glycol Spacer

It is seen from Table 1 that the dimers linked by a hydrocarbon spacer (compounds **1a–d**) do not show any mesophase. It should be noted, however, that the melting points are relatively high and supercooling the isotropic melts is possible only for a few degrees. In contrast, analogous dimers linked by a tetraethylene glycol spacer form a columnar phase (compounds **2a–d**). The insertion of siloxane units into the spacer results in polar smectic phases (compounds **3a–d**).

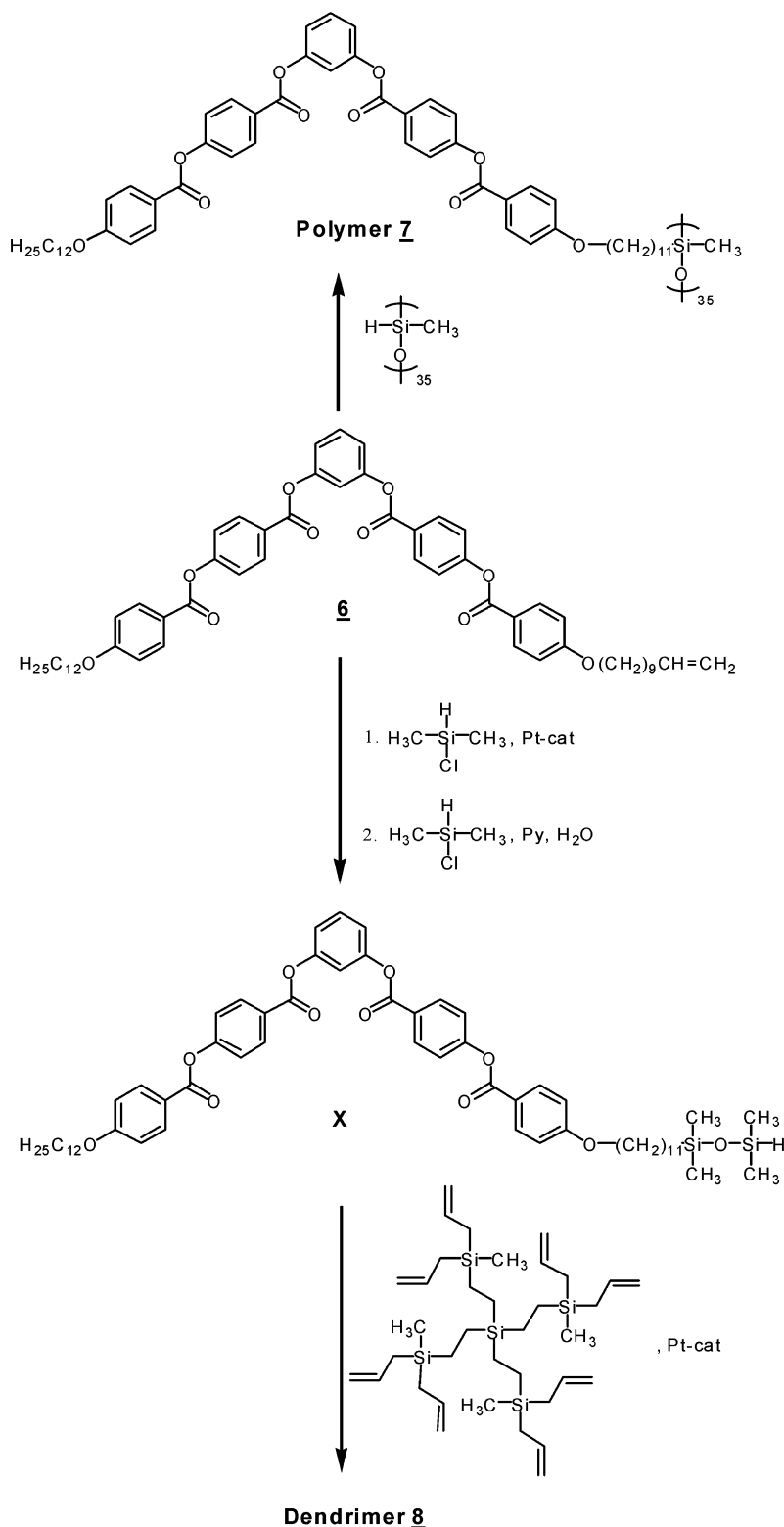
Let us start with the investigation of the tetraethylene glycol spacers compounds **2a–d**. The textures of the mesophases remind one of crystalline-like phases and contain oval, circular, and mosaic-like domains (Figure 2). No electro-optical response could be found up to 35 V/ μm .

The X-ray diffraction measurements of compounds **2a–d** suffer from the complexity of the diagrams. The patterns of nonoriented samples show several reflections in the small-angle range besides the outer diffuse scattering. These

patterns rule out a simple layer structure and suggest a columnar structure. In this way the patterns of compound **2b** have been evaluated based on a rectangular or on an oblique lattice (Figure 3a). But a careful reinvestigation displayed very weak additional reflections which do not fit the two-dimensional lattice (Figure 3b). Therefore, a three-dimensional structure cannot be ruled out with certainty.

Dimers with a spacer containing dimethyl siloxane units are listed in the third column of Table 1 (compounds **3a–d**). As shown by the X-ray investigations, these compounds form a tilted smectic phase. Compound **3c** has the highest clearing temperature. The X-ray patterns of the mesophases show a diffuse scattering maximum in the wide-angle region and strong layer reflections up to the third order in the small-angle region. This indicates a well-defined layer structure with liquidlike order within the layers. The layer spacing d (43–47 Å) was found to be clearly smaller than the half molecular length $L/2$ (~60 Å). With use of these data, a tilt

Scheme 4. Reaction Path To Prepare a Side Chain Polymer 7 and the Dendrimer 8 Containing Bent-Core Mesogenic Units



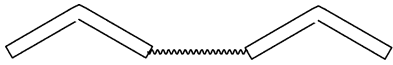
angle of about 45° can be estimated. Based on the X-ray data, a structure model was proposed as shown in Figure 4.

It is assumed that the monomeric units of the dimers intercalate into the neighboring layer and are inclined by an angle of about 45° with respect to the drawing plane. That means that the thickness of the smectic layer is determined by the length of one monomeric unit (including the chain and the spacer) and the smectic layers are separated by the

siloxane sublayers. The model with the orthoconic alignment of the molecules in the layer (tilt angle about 45°) could explain the nearly optically isotropic texture observed.

We found that this smectic phase shows unusual optical textures. On cooling the isotropic liquid into the smectic phase, the texture remains optically isotropic; that means, there is complete extinction between crossed polarizers. If one polarizer is rotated by a small angle ($\sim 5\text{--}10^\circ$), dark

Table 1. Transition Temperatures (°C) and Enthalpies (J/g) of the Compounds 1a–d, 2a–d, and 3a–d



mesogenic unit — spacer — mesogenic unit

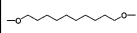
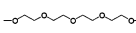
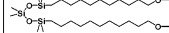
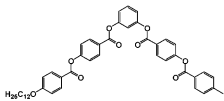
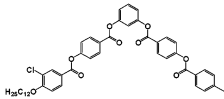
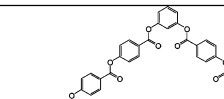
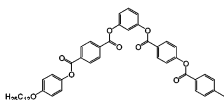
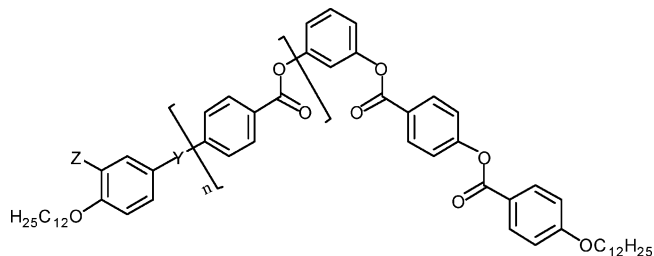
mesogenic unit \ spacer -O-X-O-	spacer -O-X-O-		
			
	1a Cr 165 [65.9] I	2a Cr 131 [12.6] Col 149 [23.4] I	3a Cr 82 [5.0] SmCP _F 139 [24.3] I
	1b Cr 167 [51.6] I	2b Cr 124 [15.2] Col 149 [23.8] I	3b Cr 106 [11.8] SmCP _F 141 [20.5] I
	1c Cr 205 [47.6] I	2c Cr 157 [17.5] Col 196 [24.3] I	3c Cr 115 [17.2] SmCP _F 178 [21.6] I
	1d Cr 185 [66.0] I	2d Cr 137 [12.8] Col 164 [26.3] I	3d Cr 107 [23.3] SmCP _F 154 [23.6] I

Table 2. Transition Temperatures (°C) and Enthalpies (J/g) of the Bent-Core Mesogens 4a–d



4

no.	n	Y	Z	mesophase behavior
4a ²⁹	1	COO	H	Cr 109 [41.9] SmCP _A 119 [22.5] I
4b	1	COO	Cl	Cr 108 [19.8] SmCP _A 121 [22.6] I
4c	2	COO	H	Cr 124 [41.0] SmCP _A 154 [21.4] I
4d ²⁹	1	OOC	H	Cr 110 [25.0] SmCP _A 133 [23.0] I

and bright domains can be distinguished. If this polarizer is rotated in the opposite direction, the dark domains become bright and vice versa (see Figure 5).

This finding gives evidence for the existence of domains of opposite handedness. Such a texture was also reported by Dantlgraber et al.²⁵ for a siloxane-linked dimer composed of bent monomers, but it is also described for some five-ring bent-core mesogens.^{34–37} If an electric field (~ 15 V/ μ m)

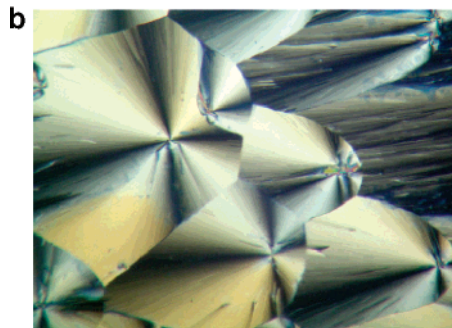
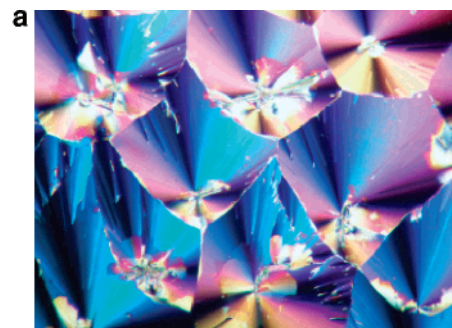


Figure 2. Textures of the columnar phases (a) of compound 2a and (b) of compound 2b.

is applied, the dark texture transforms into a grainy texture. When the field is removed, the texture relaxes into a weakly birefringent texture.

If the isotropic liquid is cooled in the presence of an electric field (~ 15 V/ μ m), also a birefringent texture arises which contains sometimes a few circular domains with extinction crosses. If the polarity of the field is reversed,

(34) Thisayukta, J.; Nakayama, Y.; Kawauchi, S.; Takezoe, H.; Watanabe, J. *J. Am. Chem. Soc.* **2000**, *122*, 7441.

(35) Shreenivasa Murthy, H. N.; Sadashiva, B. K. *Liq. Cryst.* **2002**, *29*, 1223.

(36) Dantlgraber, G.; Eremin, A.; Diele, S.; Hauser, A.; Kresse, H.; Pelzl, G.; Tschierske, C. *Angew. Chem.* **2002**, *41*, 2404.

(37) Schröder, M. W.; Pelzl, G.; Dunemann, U.; Weissflog, W. *Liq. Cryst.* **2004**, *31*, 633.

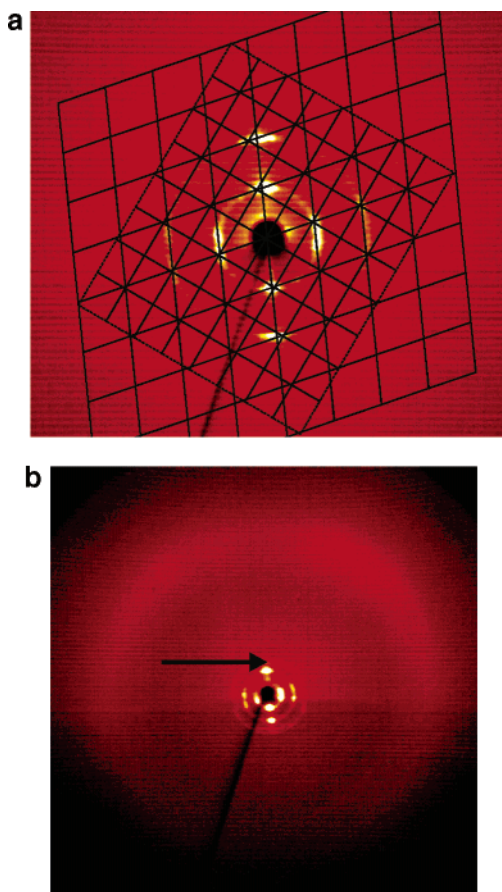


Figure 3. X-ray scattering of a partially aligned sample of compound **2b**: (a) small-angle range showing possible two-dimensional lattices (full lines correspond to the interpretation of an oblique lattice, dashed lines would correspond to an interpretation of a rectangular lattice); (b) full scattering range. The arrow indicates the position of a weak incommensurable reflection.

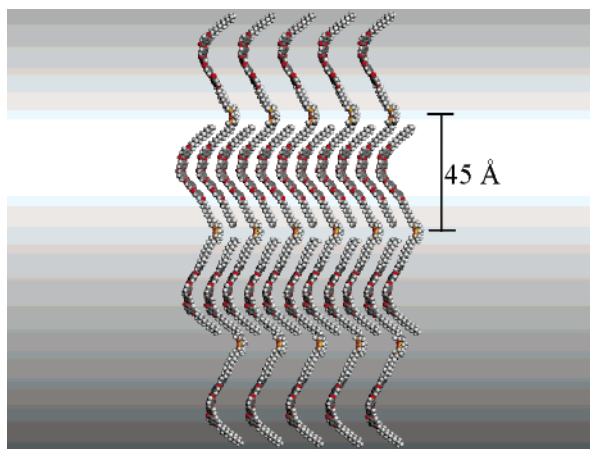


Figure 4. Structure model of the SmCP_F phase formed by the dimers **3a**–**3d** with a siloxane-containing spacer.

the texture (also the extinction crosses) do not change, although a switching is clear visible. Surprisingly, the removal of the field does not lead to a noticeable change of the texture. On the other hand, the current response to a triangular voltage shows only one peak per half period, indicating a ferroelectric ground state (Figure 6). Therefore, this phase can be classified as a ferroelectric polar SmC (SmCP_F) phase. As shown in ref 25 for comparable compounds the odd-numbered siloxane spacer stabilizes the

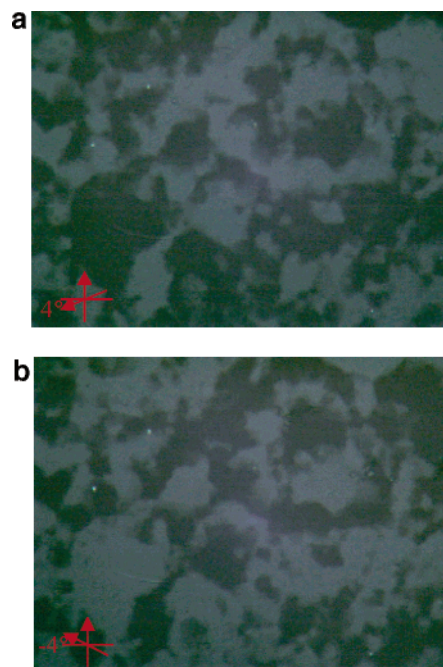


Figure 5. Texture of the SmCP_F phase of compound **3a** on cooling the isotropic liquid. One polarizer is rotated by 10° (a) clockwise and (b) counterclockwise from the crossed polarizer position.

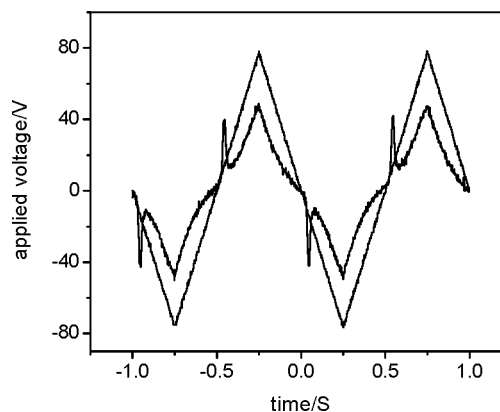


Figure 6. Switching-current response in the SmCP_F phase of compound **3a** on applying a triangular voltage.

anticlinic interlayer correlation which favors the ferroelectric structure.

The unusual optical appearance of the field-induced switching is obviously the result of an unusual mechanism, which takes place through a collective rotation of the molecules around their long axis. This mechanism of polar switching was observed for some B₁ phases³⁸ as well as for SmCP phases.^{39–43} It is of interest to learn that the connection of two bent-core mesogens does not hinder this rotation process around the long molecular axis.

(38) Szydłowska, J.; Mieczkowski, J.; Maraszek, J.; Bruce, D. W.; Gorecka, E.; Pocięcha, D.; Guillon, D. *Phys. Rev. E* **2003**, *67*, 31702.

(39) Schroeder, M. W.; Diele, S.; Pelzl, G.; Weissflog, W. *ChemPhysChem* **2004**, *5*, 99.

(40) Bedel, J. P.; Rouillon, J. C.; Marcerou, J. P.; Nguyen, H. T.; Achard, M. F. *Phys. Rev. E* **2004**, *69*, 61702.

(41) Nakata, M.; Shao, R.-F.; Weissflog, W.; Takezoe, H.; Clark, N. A. Ferroelectric Liquid Crystal Conference, Dublin, 2003, poster.

(42) Amaranatha Reddy, R.; Schroeder, M. W.; Bodyagin, M.; Kresse, H.; Diele, S.; Pelzl, G.; Weissflog, W. *Angew. Chem.* **2005**, *117*, 784.

(43) Weissflog, W.; Dunemann, U.; Schröder, M. W.; Diele, S.; Pelzl, G.; Kresse, H.; Grande, S. *J. Mater. Chem.* **2005**, *15*, 939.

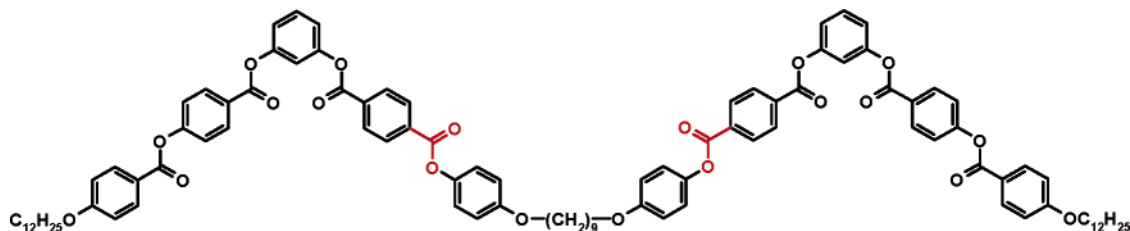


Figure 7. Compound **1e**: Cr 151 [24.5] Col 163 [23.3] I.

The switching polarization P_S derived from the current response is nearly temperature-independent and varies between 350 and 830 nC/cm² for the compounds **3a–d**. (P_S values: **3a**, 700; **3b**, 830; **3c**, 600; **3d**, 350 nC/cm²). We found interesting behavior above the clearing temperature in all dimers **3a–d** with a siloxane spacer. If a sufficiently high electric field (20–40 V/ μ m) is applied to the isotropic melt, the SmCP_F phase can be induced. In this way the clearing temperature can be enhanced up to 2 K. This effect can be explained by the existence of ferroelectric clusters in the short-range order region already in the isotropic liquid.^{44,45}

In compounds **1d**, **2d**, and **3d** the outer ester groups are reversed in comparison with the isomeric reference compounds **1a**, **2a**, and **3a**. This minor structure modification has no influence on the phase behavior. That means, compound **1d** does not exhibit a mesophase, compound **2d** forms a columnar phase, and compound **3d** forms a SmCP_F phase, whereby the clearing temperatures of the compounds **2d** and **3d** are clearly higher than those of the reference substances. On the other hand, when the ester groups between the “inner” rings near the alkylene spacer have an opposite direction, the phase behavior is clearly changed. Whereas compounds **1a** and **1d** do not show a mesophase, compound **1e** (Figure 7) forms a columnar phase.

The columnar phase has an oblique lattice, which is clearly proved by the pattern of an aligned sample (Figure 8a). The lattice parameters are $a = 57.5$ Å, $b = 24.5$ Å, and $\gamma = 100^\circ$. Since the outer diffuse scattering provides a tilt angle of about 45° with respect to the b -axis of the two-dimensional unit cell, the structural model illustrated in Figure 8b is proposed: Blocks of molecules are stacked with liquidlike order in columns perpendicular to the drawing plane. Within the plane, these blocks are arranged in a two-dimensional oblique lattice with the molecular long axes tilted by about 45° with respect to the b -axis. This model requires an overall molecular length for the dimer of about 82 Å, which is in satisfactory agreement with the length of the dimer obtained by CPK models (91 Å), and about three molecules should be in the cross section of the unit cell, i.e., in the building block.

The mesogenic unit of the dimer **5** (Figure 9) is a five-ring bent-core monomer derived from 4-cyanoresorcinol as the central ring. We used this monomer because 4-cyano-substituted five-ring bent-core mesogens exhibit an unusual polymorphism SmCP_A–SmC–SmA,⁴⁶ hoping that also the

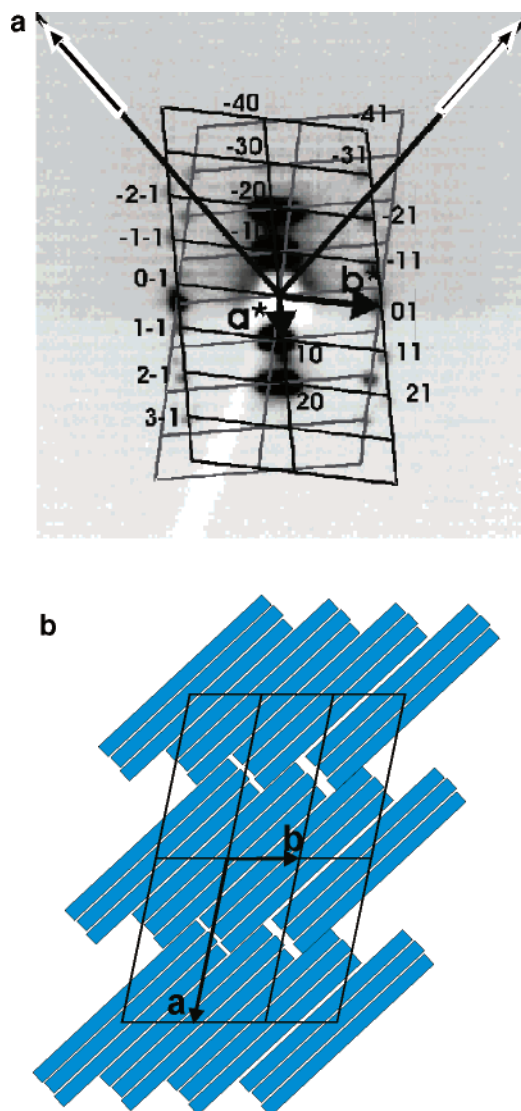


Figure 8. (a) X-ray pattern of an aligned sample of compound **1e** showing the indexing for a two-dimensional oblique lattice for one domain and the approximate directions of the maximum outer scattering. (b) Structural model for the dimer **1e** based on the X-ray pattern. The dimer is sketched by one rod.

dimer could show such interesting phase sequence. But we found a nematic phase only, which was proved by X-ray studies and the characteristic texture. This could be the consequence of the relatively short terminal chains.

We used the bent-core compound **6** (Figure 10) having a carbon–carbon double bond in one ω -position to prepare a side-chain polymer as well as a dendrimer. Compound **6** shows liquid-crystalline behavior itself. On cooling of the isotropic liquid, this monomer forms a mesophase which exhibits a weakly birefringent texture with domains of opposite handedness such as compounds **3a–d**. The X-ray

(44) Bourny, V.; Lorman, V.; Pavel, J.; Mettout, B.; Nguyen, H. T. *Ferroelectrics* **2003**, *276*, 127.

(45) Weissflog, W.; Schröder, M. W.; Diele, S.; Pelzl, G. *Adv. Mater.* **2003**, *15*, 630.

(46) Wirth, I.; Diele, S.; Eremin, A.; Pelzl, G.; Grande, S.; Kovalenko, L.; Pancenko, N.; Weissflog, W. *J. Mater. Chem.* **2001**, *11*, 1642.

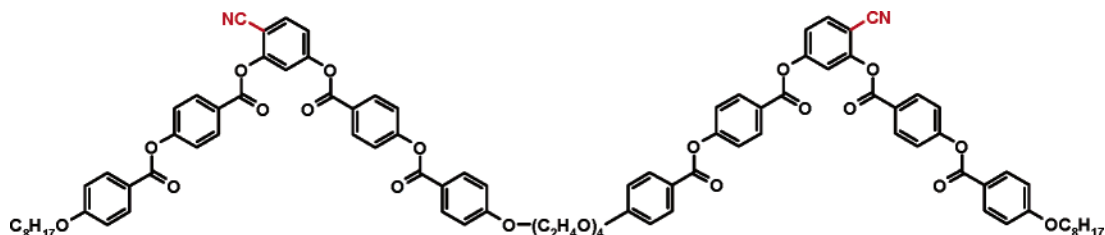


Figure 9. Compound 5: Cr 99 [19.1] N 141 [0.7] I.

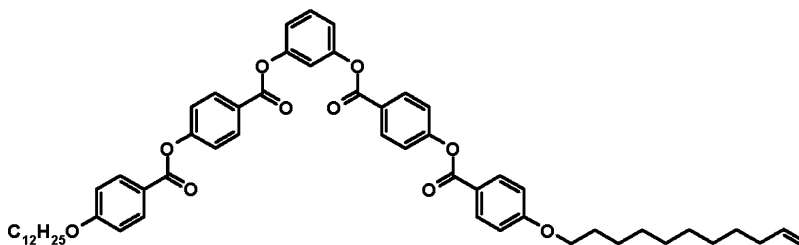


Figure 10. Compound 6: Cr 101 [40.1] SmCP_A 113 [22.9] I.

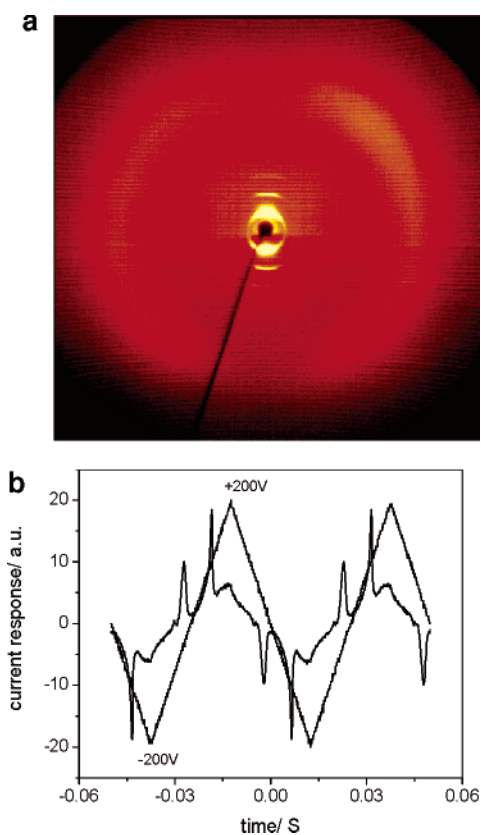


Figure 11. (a) X-ray pattern of an aligned sample of compound 6 at 106 °C on cooling. (b) Current response to a triangle voltage (20 V/μm, 20 Hz, sample thickness 10 μm, temperature 98 °C).

pattern of an oriented sample displays 3 orders of a layer reflection on the meridian in the small-angle region and diffuse scattering maxima out of the equator in the wide-angle region which give evidence for a tilted smectic phase with a tilt angle of 45° (Figure 11a). The layer spacing was found to be 35 Å whereas the molecular length is about 55 Å. If an electric field is applied, the weakly birefringent texture transforms into a stronger birefringent texture, which is independent of the polarity of the field. The current response to a triangular voltage shows two peaks per half period, which indicates an antiferroelectric ground state; that

means, this smectic phase can be assigned as a SmCP_A phase (Figure 11b).

If compound 6 is linked to a siloxane main chain, the resulting polymer 7 forms a viscous mesophase, which can be supercooled up to room temperature. We observed broad phase transition ranges (about 10 K). From DSC the transition temperatures Cr 114 SmX 143 I can be given. This SmX phase shows a nonspecific weakly birefringent texture. It follows from X-ray investigations on a powder-like sample that the mesophase possesses a simple layer structure without in-plane order. As in the case of compound 6, the layer spacing d (39 Å) was found to be clearly smaller than the length L of the monomer (55 Å), which points again to a tilted smectic phase. Since we did not find a clear electro-optical response, we cannot decide if this smectic phase is a polar one.

The dendrimer 8 contains eight bent-core units derived from compound 6. The mesophase of the dendrimer (Cr 75 [5.1] SmA 143 [20.1] I) appears as an optically uniaxial homeotropic texture. The X-ray diffraction pattern shows layer reflections up to the third order in the small-angle region and a diffuse scattering maximum in the wide-angle region which indicates a layered structure with liquidlike order within the layers. The layer thickness (45.4 Å at 140 °C) is significantly greater than this of the polymer but again smaller than the length of the monomeric unit. Nevertheless, we assign this smectic phase as a SmA phase because of the uniaxial texture. The difference between d and L can be explained by an intercalation of the terminal chains. On application of an electric field, a current response could not be detected.

Up to now, only few high-molecular compounds containing bent-core mesogens have been reported; none of them exhibited polar phases.^{47–50} The first corresponding side-

(47) Demel, S.; Slugovc, C.; Stelzer, F.; Fodor-Csorba, K.; Galli, G. *Macromol. Rapid Commun.* **2003**, *24*, 636.

(48) Sentman, A. C.; Gin, D. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 1815.

(49) Choi, E.-J.; Ahn, J.-C.; Chien, L.-C.; Lee, C.-K.; Zin, W.-C.; Kim, D.-C.; Shin, S.-T. *Macromolecules* **2004**, *37*, 71.

(50) Barbera, J.; Gimeno, N.; Monreal, L.; Pinol, R.; Ros, M. B.; Serrano, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 7190.

chain polymer was prepared by Keith et al.⁵¹ derived from a diluted polysiloxane. The ratio between non-mesogenic dimethylsiloxane units and bent-core moieties amounts to ca. 15:1. In such a polymer the chain is more flexible and able to form a polar SmCP_A phase. In the polymer compound **7** every silicon atom is substituted by mesogenic units, which seems to be a disadvantage for the formation of polar mesophases.

Dendrimers represent another type of high-molecular compounds that are more homogeneous and defined in their structure. To obtain dendrimeric compounds having liquid-crystalline properties, calamitic or discotic mesogens have been attached to the dendritic core in most cases. Recently, Kardas et al.⁵² reported on DAB-derived dendrimers bearing four and eight banana-shaped mesogenic units, respectively. These compounds exhibit a columnar and smectic phase, respectively. The assignment of the smectic phase, which does not show polar switching, was not conclusive. That means, including the results of dendrimer **8**, there is no concept up to now of a design of dendritic molecules which show polar smectic phases typical for banana-shaped liquid crystals.

Summary

Symmetric twin molecules were prepared by linking two bent-core moieties. The question arises if the mesophase behavior of the monomeric mesogens is significantly changed by the dimerization via a flexible spacer. It is seen from Table 1 that the formation of mesophases mainly depends on the

structure and length of the spacer. This finding is supported by a comparison with the corresponding single-unit compounds **4a–d** (Table 2). That means if the spacer is sufficiently flexible such as a siloxane spacer the mesogenic units are largely decoupled. Therefore, it is plausible that the siloxane-linked dimers **3** form SmCP phases such as the five-ring monomers. But this type of spacer leads to a modification of the phase structure. As seen from Figure 4, the siloxane fragments form a strongly disordered sublayer and enable an anticlinic layer interface, giving rise to the formation of a ferroelectric structure (in contrast to the monomers **4**). In the case of the dimers **2** the flexibility of the spacer is reduced by ethylene glycol units, but the tendency for microsegregation is changed, too, and so the formation of columnar phases is favored. The columnar phases possess a 2D lattice, which is not unusual for bent-core mesogens. In dimers with alkylene spacers (compounds **1**) mesophases could not be observed. The clearly higher melting points in comparison to compounds **2** and **3** could be a reason for this because in particular the supercooling of the isotropic liquid is less pronounced. By reverse direction of the ester groups between the “inner” rings (compound **1e**), the melting temperature becomes lower and a columnar phase occurs such as in compounds **2**.

For a given spacer the variation of the bent-core mesogenic units results in the same tendency concerning the change of the mesophase behavior, as proved on comparison of all compounds listed in Tables 1 and 2.

Supporting Information Available: Experimental details of synthesis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM051918Y

-
- (51) Keith, C.; Amaranatha Reddy, R.; Tschierske, C. *Chem. Commun.* **2005**, 871.
(52) Kardas, D.; Prehm, M.; Baumeister, U.; Pocięcha, D.; Amaranatha Reddy, R.; Mehl, G. H.; Tschierske, C. *J. Mater. Chem.* **2005**, *15*, 1722.