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Molecular Design of Nonchiral Bent-Core Liquid Crystals with Antiferroelectric Properties

Dong Shen,[†] Annegret Pegenau,[†] Siegmar Diele,[‡] Ina Wirth,[‡] and Carsten Tschierske*,[†]

Contribution from the Institute of Organic Chemistry, Martin-Luther University Halle-Wittenberg,
Kurt-Mothes Strasse 2, D-06120 Halle, Germany, and Institute of Physical Chemistry,
Martin-Luther University Halle-Wittenberg, Mühlpforte 1, D-06108 Halle (Saale), Germany

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Abstract: Novel bent-core (banana-shaped) liquid crystals without Schiff-base units have been synthesized and investigated by polarized light optical microscopy, differential scanning calorimetry, X-ray scattering, and electrooptical investigations. These molecules are 4-(4-alkylbenzoyloxy)benzoates and 4-(4-alkoxybenzoyloxy)benzoates of resorcinol, 3,4′-dihydroxybiphenyl, and 4,4″-dihydroxy-1,1′:3′,1″-terphenyl. Three different mesophases were found depending on the molecular structure and the length of the terminal alkyl chains: a rectangular columnar phase, a highly ordered low-temperature mesophase, and an antiferroelectric switchable fluid smectic mesophase designated as $SmCP_A$. The influence of the molecular structure on the occurrence of the $SmCP_A$ phase was investigated. The spontaneous polarization of these molecules is quite high ($P_S = 500-700$ nC cm^{-2}) and specially those molecules with long alkyl chains and short bent-core structures have low melting points and broad regions of this switchable mesophase. Furthermore, first examples of antiferroelectric switchable bent-core molecules with semifluorinated terminal chains will be described.

Introduction

Ferroelectrics are materials with a macroscopic electric polarization, switchable between two polarized states. They have a variety of useful properties, such as piezo- and pyroelectricity and second-order nonlinear optical activity (NLO). This macroscopic polarization can occur when permanent electric dipole moments of molecules are aligned parallel or when ions are organized in a noncentrosymmetric structure. Ferroelectricity was first detected in noncentrosymmetric crystals.[1] Meyer reported that ferroelectricity can also occur in fluid, liquid crystalline phases which are formed by a tilted arrangement of enantiomerically enriched chiral molecules in layers (e.g. SmC* phases).[2] Because of the fluidity of these ferroelectrics novel technical applications are possible, as for example, in fast-switching electrooptical devices. Therefore, ferroelectric and also antiferroelectric liquid crystals have attracted considerable interest.[3,4] Although it was already predicted by theory that ferroelectricity in liquid crystals is also possible without molecular chirality,[5] for a long time ferroelectric properties were only found in SmC* phases of chiral molecules in practice. In recent years great efforts were made to obtain ferroelectric liquid crystals with achiral molecules. For example, polyphilic molecules[6] and bowl-shaped molecules[7,8] have been designed to obtain nonchiral ferroelectric fluids.

In 1996 Niori et al. reported on ferroelectricity in a smectic phase formed by banana-shaped Schiff-base derivatives (see Figure 1),[9] first synthesized by Matsunaga et al.[10] The distinct molecular structure, the unconventional mesomorphic properties, the occurrence of a spontaneous symmetry breaking in some cases, and the special switching behavior of some of their mesophases immediately attracted great interest.[11,12] One of the liquid crystalline phases, which was first designated as B2,[13] revealed an antiferroelectric switching process. It was shown that the liquidlike smectic layers of these molecules have a polar structure provided by the dense packing of the bent-core molecules.[14,15,16] For these antiferroelectric switchable phases

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* Address correspondence to this author. Fax: +49 (0) 345 55 27030. E-mail: Tschierske@Chemie.Uni-Halle.de.

[†] Institute of Organic Chemistry.

[‡] Institute of Physical Chemistry.

(1) Valasek, J. *Phys. Rev.* **1920**, *15*, 537.

(2) Meyer, R. B.; Liebert, L.; Strzelecki L.; Keller, P. *J. Phys.* **1975**, *36*, L-69.

(3) (a) Goodby, J. W. *J. Mater. Chem.* **1991**, *1*, 307. (b) Lagerwall, S. T. *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, p 515.

(4) Miyachi, K.; Fukuda, A. *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, p 665.

(5) (a) Saupe, A. *Mol. Cryst. Liq. Cryst*. **1969**, *7*, 59. (b) Prost J.; Barois, P. *J. Chim. Phys*. **1983**, *80*, 65. (c) Petschek R. G.; Wiefling, K. M. *Phys. Rev. Lett*. **1987**, *59*, 343. (d) Tredgold, R. H. *J. Phys. D* **1990**, *23*, 119. (e) Blinov, L. M. *Liq. Cryst.* **1998**, *24*, 143.

(6) Tournilhac, F.; Blinov, L. M.; Simon J.; Yablonski, S. V. *Nature* **1992**, *359*, 621.

(7) Lei, L. *Mol. Cryst. Liq. Cryst*. **1983**, *91*, 77.

(8) Swager, T. M.; Serrette, A. G.; Knawby, D. B.; Zeng, H. *Int. Liq. Cryst. Conf. 15th* **1994**, *2*, 771.

(9) (a) Niori, T.; Sekine, F.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231. (b) Niori, T.; Sekine, F.; Watanabe, J.; Furukawa T.; Takezoe, H. *Mol. Cryst. Liq. Cryst.* **1997**, *301*, 337. (c) Sekine, F.; Takanashi, Y.; Niori, T.; Watanabe, J.; Takezoe, H. *Jpn. J. Appl. Phys.* **1997**, *36*, L 1201. (d) Sekine, F.; Niori, T.; Watanabe, J.; Furukawa, T.; Chol, S. W.; Takezoe, H. *J. Mater. Chem.* **1997**, *7*, 1307.

(10) (a) Matsunaga, Y.; Miyamoto, S. *Mol. Cryst. Liq. Cryst*. **1993**, *237*, 311. (b) Akutagawa, T.; Matsunaga, Y.; Yashahura, K. *Liq. Cryst*. **1994**, *17*, 659.

(11) Heppke, G.; Moro, D. *Science* **1998**, *279*, 1872.

(12) Recent review: Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater*. **1999**, *11*, 707.

(13) The nomenclature of the mesophases of the banana-shaped molecules as B1, B2, etc. was recommended at the Workshop “Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules”, Dec. 1997, Berlin, see also ref 12. Their use is recommended as long as the precise structure of these mesophases is uncertain.

(14) (a) Jakli, A.; Rauch, S.; Lötzsch, D.; Heppke, G. *Phys. Rev. E* **1998**, *57*, 6737. (b) Diele, S.; Grande, S.; Kruth, H.; Lischka, C.; Pelzl, G.; Weissflog W.; Wirth, I. *Ferroelectrics* **1998**, *212*, 169.

(15) Link, D. R.; Natale, G.; Shao, R.; Maclennan, J. E.; Körblova, N. A.; Walba, D. M. *Science* **1997**, *278*, 1924.

10.1021/ja993572w CCC: $19.00

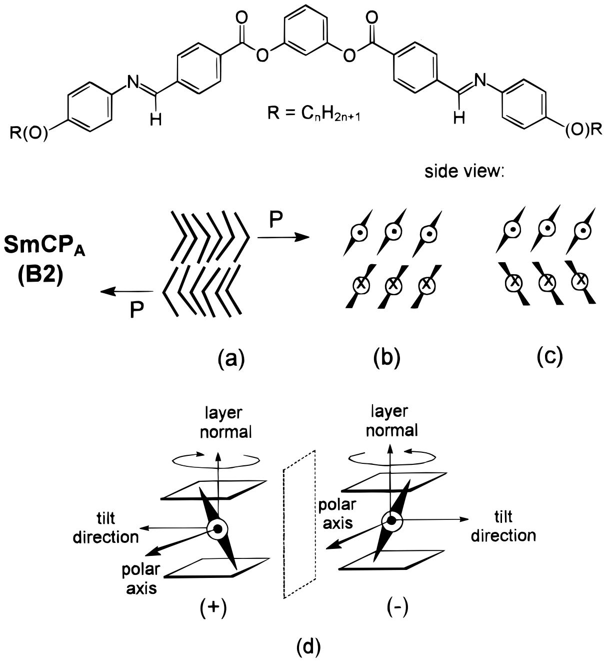
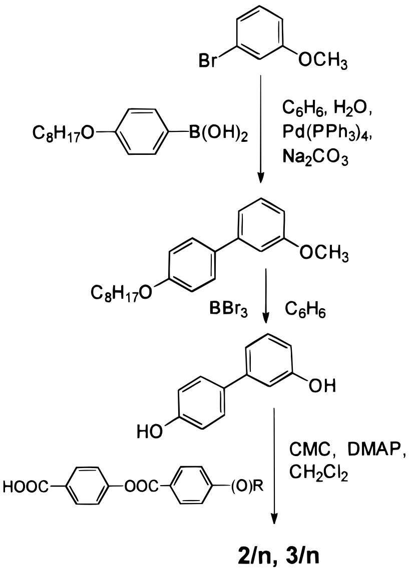


Figure 1. Structure of a typical bent-core molecule and organization of the molecules in the antiferroelectric switchable mesophase. Owing to the bent-core each molecule possesses a dipole moment in the molecular plane and perpendicular to the long axis of the molecules. (a) The molecules are arranged in layers whereby the polar direction changes from layer to layer (antiferroelectric order). The side views show that the molecules can be tilted either (b) with synclinic ($\mathrm{SmC_SP_A}$) or (c) with anticlinic interlayer correlation ($\mathrm{SmC_AP_A}$). (d) Schematic representation of one polar chiral layer consisting of achiral bent-core molecules (only one molecule is shown). In the picture at the left-hand side the layer normal, tilt direction, and the polar axis define a right-handed coordinate system (+), whereas in the mirror image these vectors define a left-handed system (−).

it was proposed that the molecules arrange in layers whereby the layer polarization alternates from layer to layer (antiferroelectric structure). The resulting smectic phase is biaxial whereby one optical axis is tilted relative to the layer normal (see Figure 1).[15] Therefore, this mesophase can be more precisely described as $\mathrm{SmCP_A}$, a tilted smectic phase (SmC) with a polar order of the molecules (P) within the layers and an antiferroelectric interlayer correlation (A).[15] By applying an electric field the molecules can be switched into a ferroelectric, *i.e.* noncentrosymmetric structure ($\mathrm{SmCP_F}$). Recently, very large second-order NLO effects have been measured for these ferroelectric states.[17] Hence, an interesting application of such materials could be in switchable nonlinear optical devices. Typically, bent-core molecules with antiferroelectric switchable $\mathrm{SmCP_A}$ phases incorporate at least one Schiff-base unit. Therefore, a major drawback of these compounds is their limited thermal, hydrolytic, and photochemical stability. Furthermore, in most cases, these special mesophases occur at rather high temperatures. Therefore, the design of novel stable and low-melting bent-core liquid crystals without sensitive Schiff-base units is a topical subject in liquid crystal research.

For simplicity, these special molecules can be considered as built up by three distinct parts, a bent central unit **Z**, two linear rigid cores **M**, and two terminal chains. The central unit **Z** is in most cases an 1,3-substituted benzene ring or an aromatic ring system, but it can also be an odd-numbered alkylene chain.[18] In previous work we have described several different bent-core molecules incorporating non-Schiff-base rigid cores, such as 2-phenylpyrimidines, 2-phenyl-1,3,4-thiadiazoles, biphenyls, and phenylbenzoates.[19] However, none of these compounds exhibited an antiferroelectric switchable mesophase as known from the Schiff-base derivatives. At this stage it seemed that the Schiff-base unit was necessary to obtain these special mesophases.

Scheme 1. Syntheses of the Compounds **2/*n*** and **3/*n***



A significant break-through has now been achieved by combination of the angular 3,4′-disubstituted biphenyl central unit with two phenyl benzoate rigid cores via ester linkages which is described in this paper (compounds **2** and **3**).[20] Additionally, the sizes of the bent central unit and of the terminal chains were changed systematically (compounds **1**, **4**−**6**), which allows us to tailor the mesomorphic properties and to provide some general rules for the design of $\mathrm{SmCP_A}$ materials. Furthermore, first examples of bent-core molecules with semifluorinated terminal chains and broad regions of $\mathrm{SmCP_A}$ phases will be reported.[21]

Results and Discussion

A. Syntheses. The compounds were obtained by esterification of 4-[4-alkyl(oxy)benzoyloxy]benzoic acids or semifluorinated 4-(4-alkyloxybenzoyloxy)benzoic acids with appropriate bent-core dihydroxy compounds using the carbodiimide method.[22] 3,4′-Dihydroxybiphenyl and compounds **2** and **3** were obtained according to the synthetic route shown in Scheme 1. The first step was the Pd°-catalyzed Suzuki cross-coupling[23] of 3-bromoanisole with 4-octyloxyphenylboronic acid. The obtained

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(16) There are several other possibilities for the packing arrangement of such molecules in fluid phases, but most of them are unexplored: Brand, H. R.; Cladis, P. E.; Pleiner, H. *Eur. J. Phys. B* **1998**, *6*, 347.

(17) (a) Kentischer, F.; MacDonald, R.; Warnick, P.; Heppke, G. *Liq. Cryst.* **1998**, *25*, 341. (b) Araoka, F.; Park, B.; Kinoshita, Y.; Ishikawa, K.; Takezoe, H.; Thisayukta, J.; Watanabe, J. *Jpn. J. Appl. Phys.* **1999**, *38*, 3526.

(18) Watanabe, J.; Niori, T.; Choi, S.-W.; Takanishi, Y.; Takezoe, H. *Jpn. J. Appl. Phys.* **1998**, *37*, L401.

(19) Shen, D.; Diele, S.; Pelzl, G.; Wirth, I.; Tschierske, C. *J. Mater. Chem.* **1999**, *9*, 661.

(20) Preliminary communication: Shen, D.; Diele, S.; Wirth, I.; Tschierske, C. *J. Chem. Soc., Chem. Commun.* **1998**, 2573.

(21) Recently, some bent core molecules with perfluorinated chains have been reported, but exclusively SmA phases have been found for these compounds: Kovalenko, L.; Lose, D.; Pelzl, G.; Weissflog, W. *Proc. 26. Freiburger Arbeitstagung Flüssigkristalle* **1999**, P40.

(22) (a) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem.* **1978**, *90*, 602. (b) Tschierske C.; Zaschke, H. *J. Prakt. Chem.* **1989**, *331*, 365.

diether was then cleaved with BBr_3 in benzene.[24] Resorcinol is commercially available and the synthesis of the other aromatic dihydroxy compounds has recently been described in detail.[19] The 4-[4-alkyl(oxy)benzoyloxy]benzoic acids were obtained by esterification of 4-alkyl(oxy)benzoyl chlorides with 4-hydroxybenzaldehyde[25] followed by CrO_3 oxidation in aqueous acetic acid.[26] The related semifluorinated 4-(4-alkyloxybenzoyloxy)-benzoic acids were obtained in the same way starting with semifluorinated 4-alkoxybenzoic acids.[27] The synthesis of compound **7** will be reported in a separate paper together with other molecules incorporating different mesogenic units **M**.

The purification of the final compounds was done by means of column chromatography followed by recrystallization from ethyl acetate. The purity and structure was confirmed by thin-layer chromatography, elemental analysis, and ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectroscopy.

B. Mesomorphic Properties of the Biphenyl Derivatives 2. The mesomorphic properties of the obtained compounds were investigated by polarized light optical microscopy on a hot stage (Mettler FP 82 HT) and by differential scanning calorimetry (DSC, Perkin-Elmer DSC-7, heating and cooling scans with 10 deg K per min). The transition temperatures and corresponding enthalpy values of all synthesized compounds are summarized in Table 1. In Figure 3 the dependence of the mesomorphic properties of the homologous series of the alkyl substituted compounds **2/*n*** ($n = 4$, 6−14) on the chain length is shown schematically. Three different mesophases were found. The short-chain molecules **2/4** to **2/7** exhibit only one mesophase. On cooling from the isotropic liquid state the mesophase can be detected by the formation of small batonnets which coalesce into a mosaic-like texture. Sometimes also spherulitic domains can be observed (see Figure 4a). The same texture was found for **2/9** with nonyl side chains and for the high-temperature mesophases of **2/8** and **2/10**. This texture is identical with those of B1-phases[13] of short-chain Schiff-base bent-core molecules for which a rectangular columnar structure was proposed.[28]

The X-ray diagrams of compounds **2/4** to **2/9** show two reflections in the small-angle region in addition to a diffuse wide-angle scattering (Table 2). The pattern of an oriented sample of compound **2/4** displays Bragg-spots out of the meridian as well as Bragg-spots at the meridian, which point to the existence of a two-dimensional rectangular cell (Figure 5). It supposes to index the first reflection of the powder-like pattern by (11) and the second one by (02). The calculated lattice constants are given in Table 3. The outer diffuse scattering is splitted off, too, and is arranged symmetrically to the equator. It yields an angle of $\alpha = 126°$, which can be attributed to the bending angle of the two halves of the molecules.

Using this bending angle the molecular lengths of compounds **2/*n*** were calculated according to $L = (L_1^2 + L_2^2 - 2L_1L_2 \cos\alpha)^{0.5}$ whereby L_1 and L_2 correspond to the lengths of the two different halves determined using CPK models and assuming all-trans conformations of the alkyl chains. In the case of compound **2/4**, the calculated length L agrees very well with the periodicity c. Obviously, this long axis is within the $a-c$ plane and is directed parallel to the c-axis, *i.e.* the molecules are nontilted. With increasing chain length the difference between L and c increases. The differences to the c parameter can be explained by the

Table 1. Transition Temperatures (T/°C) and Corresponding Enthalpy Values (lower lines in italics), ΔH/kJ mol^{-1}, of Compounds **1**−**7** As Obtained by DSC (peak temperatures in the first heating cycle, heating rate: 10 K min^{-1})[a]

Comp.	Phase transitions
1/10	Cr$_1$ 84 Cr$_2$ 101 Cr$_3$ 110 (SmCP$_A$ 108) Iso *13.7 4.8 34.5 (17.1)*
1/10[b]	Iso 108 Col$_r$ 107 SmCP$_A$ 89 Cr
1/12	Cr$_1$ 70 Cr$_2$ 105 SmCP$_A$ 117 Iso *6.8 36.2 21.3*
1/14	Cr$_1$ 78 Cr$_2$ 105 SmCP$_A$ 119 Iso *11.8 44.8 22.2*
1/6F4	Cr 133 SmCP$_A$ 164 Iso *39.8 22.4*
1/4F6	Cr$_1$ 63 Cr$_2$ 134 SmCP$_A$ 201 Iso *5.9 19.9 27.0*
2/4	Cr$_1$ 82 Cr$_2$ 161 (Col$_r$ 157) Iso *12.3 34.1 (11.7)*
2/6	Cr 119 Col$_r$ 158 Iso *12.4 14.6*
2/7	Cr$_1$ 89 Cr$_2$ 129 Col$_r$ 167 Iso *8.7 21.1 18.8*
2/8	Cr$_1$ 68 Cr$_2$ 85 SmX 86 SmCP$_A$ 152 Iso *2.8 9.2 (6.3) 19.6*
2/8[b]	Iso 152 Col$_r$ 147 SmCP$_A$ 86 SmX *-16.2 -3.4 -6.3*[c]
2/9	Cr 99 Col$_r$ 158 Iso *18.5 19.1*
2/10	SmX 79 SmCP$_A$ 148 Iso *6.8 18.4*
2/10[b]	Iso 148 Col$_r$ 147 SmCP$_A$ 79 SmX
2/11	Cr$_1$ 67 Cr$_2$ 88 (SmX 87) SmCP$_A$ 157 Iso *5.2 10.3 (6.7) 21.6*
2/12	Cr$_1$ 68 Cr$_2$ 89 (SmX 78) SmCP$_A$ 156 Iso *6.8 3.5 (6.3) 20.7*
3/8	Cr$_1$ 97 Cr$_2$ 131 Col$_r$ 172 Iso *25.7 21.3 21.0*
3/9	Cr$_1$ 89 Cr$_2$ 99 Cr$_3$ 116 Col$_r$ 169 Iso *3.5 25.4 2.9 18.6*
3/10	Cr 119 Col$_r$ 166 Iso *37.7 20.4*
3/11	Cr$_1$ 77 Cr$_2$ 85 Col$_r$ 154 Iso *30.4*[c] *20.2*
3/12	Cr$_1$ 82 Cr$_2$ 106 SmCP$_A$ 159 Iso *28.2 19.3 23.1*
3/13	Cr 86 SmCP$_A$ 161 Iso *40.6 24.2*
3/14	Cr 85 SmCP$_A$ 162 Iso *39.5 24.8*
3/6F4	Cr$_1$ 90 Cr$_2$ 127 SmCP$_A$ 213 Iso *12.7 17.1 23.5*
3/4F6	Cr$_1$ 122 Cr$_2$ 150 SmCP$_A$ 252 Iso *5.5 19.0 26.9*
4/12	Cr$_1$ 120 Cr$_2$ 165 Col$_r$ 203 Iso *15.5 34.9 21.5*
4/14	Cr$_1$ 137 Cr$_2$ 158 SmCP$_A$ 202 Iso *5.7 22.7 22.9*
4/4F6	Cr 211 SmCP$_A$ 309 Iso *40.2 31.6*
5/14	Cr$_1$ 107 Cr$_2$ 137 Col$_r$ 203 Iso *23.8 18.3 24.3*
6/14	Cr$_1$ 106 Cr$_2$ 136 Col$_r$ 204 Iso *17.9 38.8 17.7*
7	Cr 135 SmCP$_A$ 211 Iso *37.1 25.9*

[a] Abbreviations: Cr$_1$, Cr$_2$, Cr$_3$ = different crystalline modifications; Col$_r$ = rectangular columnar mesophase (B1-phase),[13] SmCP$_A$ = tilted smectic phase with polar antiferroelectric order of the molecules (B2-phase),[13] SmX = highly ordered smectic mesophase of unknown precise structure, Iso = isotropic liquid state; phase assignments in parentheses refer to monotropic (metastable) mesophases, their transitions were determined in a second heating scan. [b] Phase sequence obtained on cooling; these transition temperatures were determined by polarized light microscopy. [c] Determined from the cooling scan.

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(23) (a) Miyaura, N.; Yanagi T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (b) Hird, M.; Gray, G. W.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1991**, *206*, 187.

(24) McOmie, J. F. W.; West, D. E. *Organic Syntheses; Wiley: New York*, 1973; Collect. Vol. V, p 412.

(25) Tschierske, C.; Zaschke, H. *J. Prakt. Chem.* **1988**, *330*, 1.

(26) Wiberg, K. B.; Mill, T. *J. Am. Chem. Soc.* **1958**, *80*, 3022.

(27) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855.

(28) Watanabe, J.; Niori, T.; Sekine, F.; Furukawa T.; Takezoe, H. *Jpn. J. Appl. Phys.* **1998**, *37*, L 139.

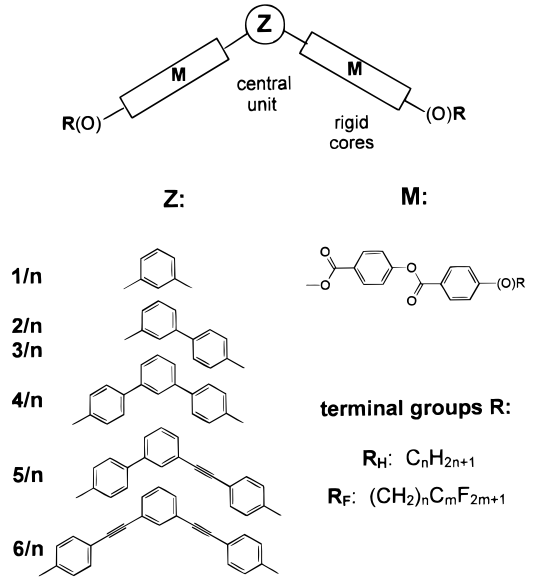

Figure 2. General structure of bent-core liquid crystals and structures of the molecules under investigation.

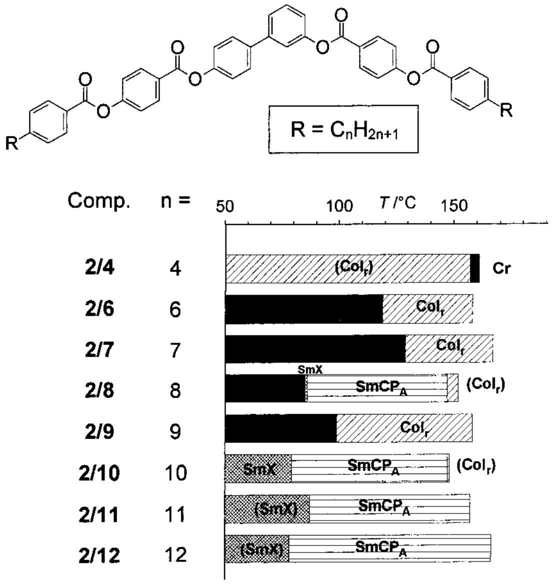

Figure 3. Transition temperatures of the homologous series of compounds **2/n**; for the abbreviations see Table 1; black parts of the columns represent crystalline phases (Cr); phase assignments in parentheses refer to monotropic (metastable) mesophases, which can only be observed on cooling from the isotropic liquid state; the crystalline phases of compounds **2/11** and **2/12** are not shown.

deviation of the alkyl chains from the all-trans conformation, which becomes more pronounced on elongation of the chains. Thus, this mesophase is a rectangular columnar mesophase (Col_r) built up of ribbons of parallel aligned bent-core molecules. The bending direction of the molecules of neighboring ribbons is antiparallel. In this way the dipoles cancel out from ribbon to ribbon, and the system can escape from a macroscopic polar order (see Figure 6a).

The parameter *a* is related to the number of molecules arranged side by side in the lateral diameter of each ribbon. Unexpectedly, this parameter has an especially strong increase on elongation of the alkyl chains, which means that the number of molecules also depends on the chain length. It rises from a value between two and three molecules for compound **2/4** to a value of about four molecules in the case of compound **2/8**.

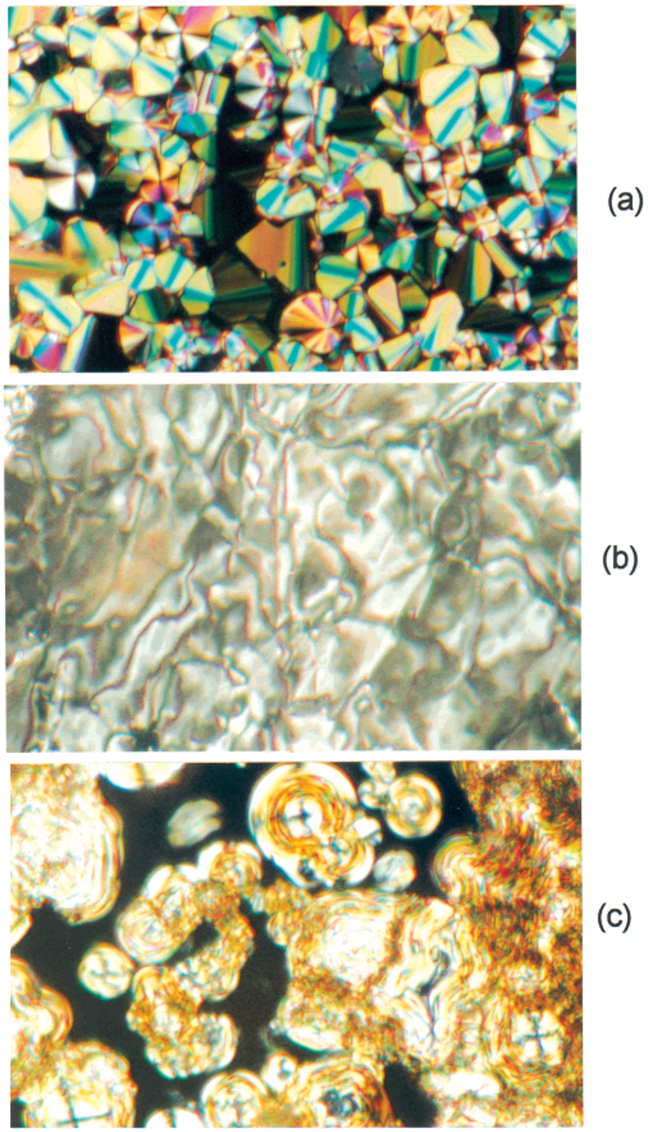

Figure 4. Optical photomicrographs (crossed polarizers): (a) Col_r phase of compound **2/8** as obtained by cooling from the isotropic liquid at 152 °C; (b) schlieren texture of the $SmCP_A$ phase at 120 °C; and (c) $SmCP_A$ phase of compound **2/12** as obtained by cooling from the isotropic liquid at 156 °C.

Table 2. Scattering Vectors of Compounds **2/4** to **2/12**'

	Col_r		$SmCP_A$
compd	d_1/nm	d_2/nm	*d*/nm
2/4	2.19	1.93	
2/6	2.49	2.10	
2/7	2.64	2.17	
2/8	3.18	2.34	3.70
2/9	3.04	2.32	
2/10			3.72
2/11			3.82
2/12			3.96

This observation can be explained on the basis of the ribbon model of this columnar phase. In the borderline regions between the ribbons, the aromatic cores and the aliphatic chains have to overlap (see Figure 6). These unfavorable chain−core interactions become increasingly more important with longer terminal alkyl chains. It seems that on increasing the chain length the system tries to reduce the number of these borderline regions by increasing the size of the individual ribbons (increase in the

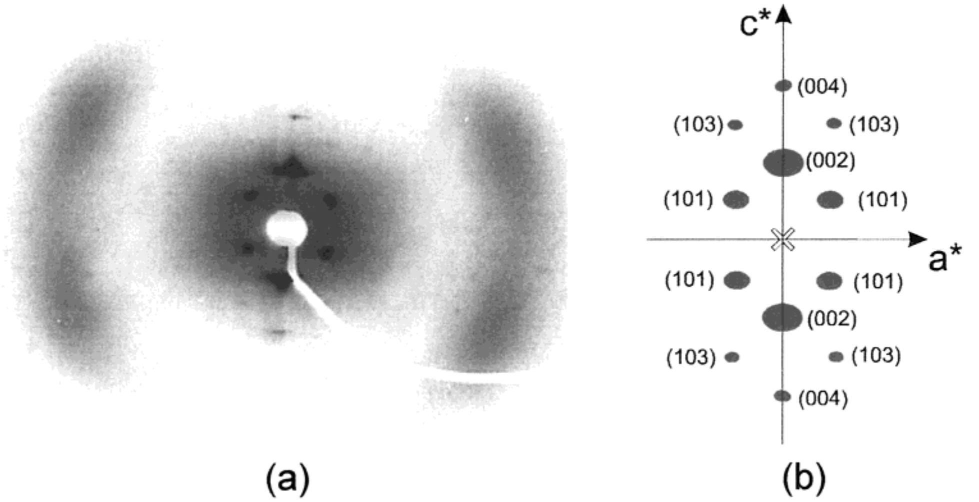

Figure 5. (a) X-ray pattern of a monodomain of the $\mathrm{Col_r}$ phase of compound **2/4** at 120 °C (supercooled state); (b) schematic sketch of the small angle pattern, together with the Millers indices.

Table 3. Comparison of the Molecular Length (*L*) the Lattice Parameter of the $\mathrm{Col_r}$ Phase (*a*, *c*) and the Layer Distance in the $\mathrm{SmCP_A}$ Phases (*d*)

		$\mathrm{Col_r}$		$\mathrm{SmCP_A}$
compd	*L*/nm	*a*/nm	*c*/nm	*d*/nm
2/4	3.9	2.66	3.86	
2/6	4.3	3.09	4.20	
2/7	4.6	3.33	4.34	
2/8	4.9	4.33	4.68	3.70
2/9	5.1	4.02	4.64	
2/10	5.3			3.72
2/11	5.5			3.82
2/12	5.7			3.96
3/9	5.3	3.46	4.75	
3/11	5.7	6.38	4.78	

parameter *a*). On further elongation of the chains, however, the ribbon phase becomes unstable. Hence, the columnar phase is lost or it can only be observed over a small temperature range (compounds **2/8** and **2/10**).

The lattice parameters *a* and *c* of compounds with odd-numbered chains are unusually small in comparison to those of their neighboring homologues with even-numbered chains which is especially evident if one compares compounds **2/8** and **2/9**. This should be attributed to an odd−even effect. Interestingly, compounds **2/7** and **2/9** which exclusively form the columnar phase have reduced diameters of their ribbons in comparison to **2/8**, which has only a small existence region of the columnar phase. Hence, the odd−even effect of parameter *a* is in line with the alternation of the mesophase type.

The homologues **2/8** and **2/10** show a rather complicated polymorphism (see Table 1 and Figure 3). On cooling from the isotropic liquid state the typical mosaic texture of the columnar phase occurs (see Figure 4a), but on further cooling a transition to another phase which has a schlieren texture can be found (see Figure 4b). This mesophase always shows a distinct birefringence and no pseudoisotropic regions can be obtained by shearing, indicating a biaxial structure. Furthermore, it has a rather low viscosity, comparable to conventional SmA and SmC phases. On heating the samples, this mesophase directly turns into the isotropic liquid phase without passing the columnar mesophase. However, the columnar phase is obtained again by cooling. It seems that the 2D lattice of the columnar phase can only be formed by cooling from the isotropic liquid state.[29]

On further cooling of compound **2/8**, at 86 °C the schlieren texture turns into a mosaic-like texture with a significant increase of the viscosity. This mesophase is designated as SmX. Compound **2/8**, which forms all three mesophases, was investigated in more detail by X-ray diffraction. Here the changes of the diffraction pattern depending on the phase type can be studied. The X-ray diagram (Figure 7) is changed on cooling the sample from the columnar phase. Now the first and second order of a layer reflection can be seen beside the diffuse wide angle scattering, which is characteristic for fluid smectic phases. Such a pattern is also obtained for compounds **2/8** and **2/10** to **2/12.** The layer periods are listed in Table 3. Compound **2/8** also offers the possibility of comparing the molecular length with the periods in both phases. As mentioned above, the *c* parameter in the columnar phase corresponds with the length of the molecule. The period in the fluid smectic phase however is significantly lower. With both values a tilt of the molecular long axis with respect to the layer normal of 38° can be estimated. This means that in this smectic phase, the banana-shaped molecules are inclined with respect to the layer normal (see Figure 1). As the electrooptical investigations (see below) reveal an antiferroelectric switching behavior, we can assign this fluid smectic phase as the $\mathrm{SmCP_A}$ phase.

Cooling down the $\mathrm{SmCP_A}$ phases of compounds **2/8** and **2/10** to **2/12** the transition into the SmX phase takes place. The X-ray pattern of the nonoriented sample is only scarcely changed in the small angle region but the wide angle region contains several reflections, which resemble a highly ordered layer structure, such as G or H. This pattern is maintained down to room temperature. Remarkably no crystallization can be observed after the first melting of compounds **2/8** and **2/10** to **2/12** even over prolonged storage at room temperature.

Exclusively the fluid smectic phase and the SmX phases were found for compounds **2/10** to **2/12.** The typical texture of the $\mathrm{SmCP_A}$ phase as obtained on cooling the isotropic liquid state of **2/12** is shown in Figure 4c. The enthalpies of the transitions from the liquid crystalline to the isotropic phase increase in this homologous series with the chain length ranging from 11.7 kJ $\mathrm{mol^{-1}}$ for compound **2/4** to 21.6 kJ $\mathrm{mol^{-1}}$ for compound **2/11** (see Table 1). The enthalpy of the transition between the $\mathrm{Col_r}$ phase and the $\mathrm{SmCP_A}$ phase is significantly lower and amounts to 3.4 kJ $\mathrm{mol^{-1}}$ (compound **2/8**). For the transitions between

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(29) The $\mathrm{Col_r}$-$\mathrm{SmCP_A}$ dimorphism of **1/10** is related to that of compounds **2/8** and **2/10** as a small region of the columnar phase can be observed in the cooling cycle, whereas on heating only the direct transition to the $\mathrm{SmCP_A}$ phase is found, see Table 1.

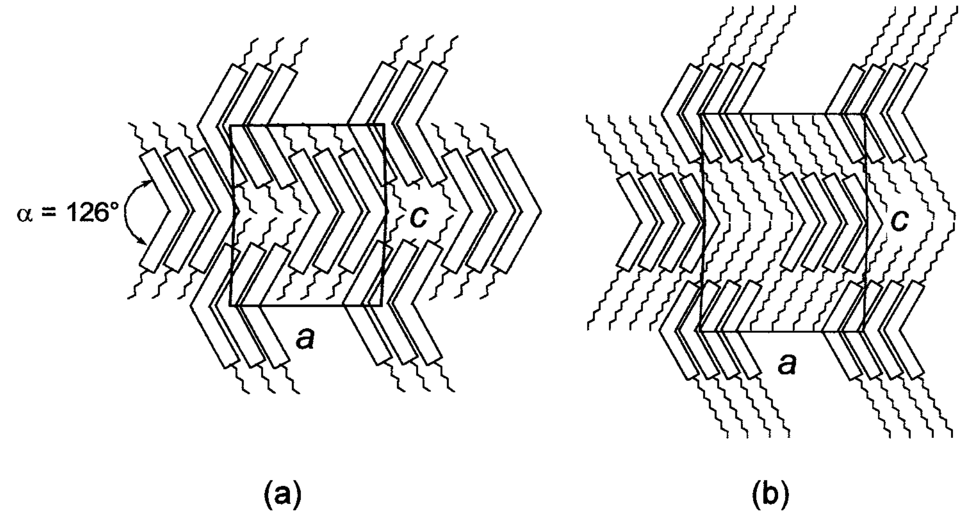

Figure 6. Structure model of the Col_r phase: (a) stable Col_r phase of molecules with short chains or with large bent rigid cores; (b) the same arrangement of molecules with long chains and small bent cores is unstable.

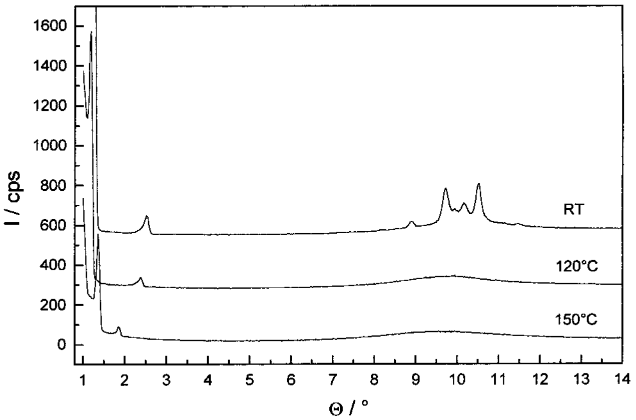

Figure 7. Scattering diagrams of a nonoriented sample of compound **2/8** in the Col_r phase (150 °C), in the $SmCP_A$ phase (120 °C), and in the SmX phase (room temperature 25 °C).

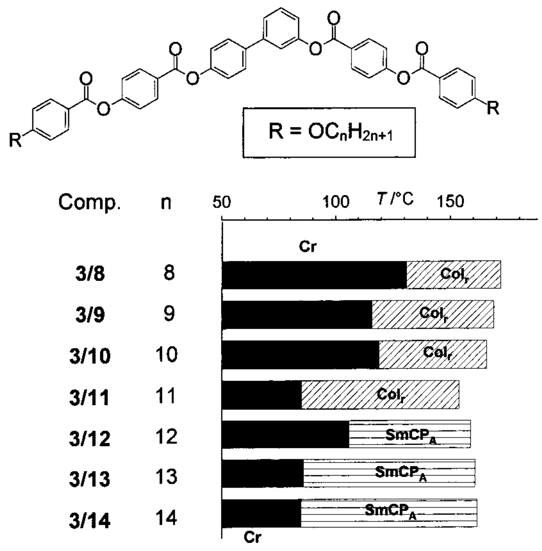

Figure 8. Transition temperatures of the homologous series of compounds **3/*n***.

the $SmCP_A$ phases and the SmX phases enthalpies of about 6.5 kJ mol^{-1} were determined.

C. Mesomorphic Properties of the Alkoxy-Substituted Compounds 3. The dependence of the mesomorphic properties of the homologous series of 4-(4-alkoxybenzoyloxy)benzoates **3/8** to **3/14** on the chain length is shown in Figure 8. Again, the homologues with short chains have the columnar phase whereas the homologues with long chains display the $SmCP_A$ phase. However, the length of the alkyl chains which is necessary to obtain the $SmCP_A$ phase ($n = 12$) is significantly larger than in the series of the alkyl-substituted compounds **2** ($n = 8$). Another interesting difference between these two homologous series is the following. For the molecules with alkyloxy chains the columnar phases suddenly disappear when the terminal chains are longer than C_{11} whereas in the series of alkyl-substituted compounds this occurs over a certain chain length range (C_7-C_{11}) with a pronounced odd−even effect. Additionally the alkoxy-substituted compounds do more readily crystallize and no additional low-temperature mesophase could be detected.

X-ray investigations of the columnar mesophases of **3/9** and **3/11** indicate again centered rectangular cells. The lattice parameter are included in Table 3. The *c* values are in good agreement with the molecular lengths. Also the parameter *a* of compound **3/9** is in the same order as those of the alkyl-substituted compounds **2** whereas compound **3/11** has an unusual large value ($a = 6.38$ nm). It corresponds to approximately six molecules in the diameter of the ribbons. It seems that the critical diameter of the ribbons depends not only on the chain length but also on the precise molecular structure. Obviously, in the case of alkoxy-substituted bent rigid cores an increased stability of the ribbons is provided. This effect of the oxygen atoms could be due to their polarity or to changes of the molecular conformation.[30] Additionally, the ether oxygen atoms could increase the effective length of the rigid parts of the bent-cores because of the enhanced rotational barrier around the C(ar)−O bond due to the conjugation of the oxygen lone pairs with the aromatic π-system.

D. Influence of the Core Structure. We asked if the stability of the ribbon arrangement could be related to the size of the bent rigid cores. Therefore, we have investigated the molecules **1/*n*** to **6/*n*** with $n = 10$, 12, and 14, incorporating bent-core units **Z** with the same bending angle, but with a different size. This comparison (Figure 9) shows that the alkyl chain length,

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[30] Kleinpeter, E.; Köhler, H.; Lunow, A.; Tschierske, C.; Zaschke, H. *Tetrahedron* **1988**, *44*, 1609.

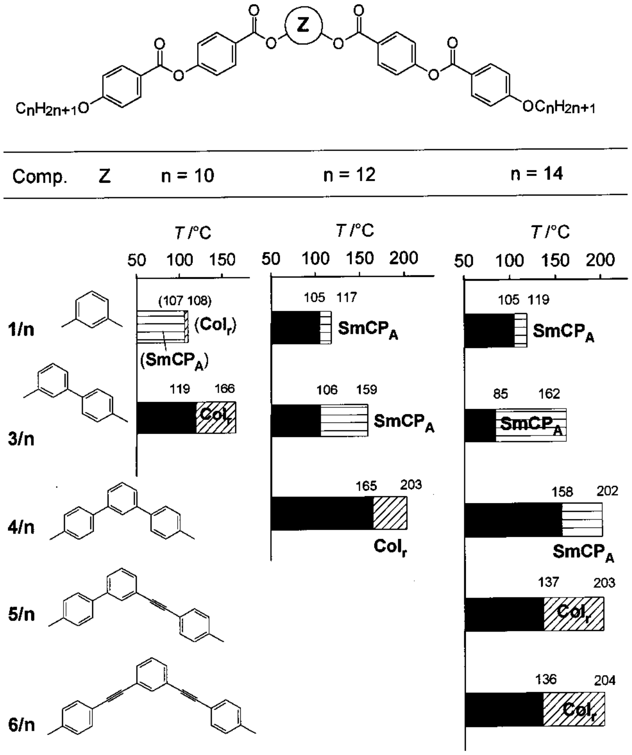

Figure 9. Comparison of mesophases and transition temperatures of the compounds **1/*n***, **3/*n***, **4/*n***, **5/*n***, and **6/*n*** depending on the alkyl chain length (*n* = 10, 12, 14); the mesophases of compound **1/10** are monotropic,[29] but its crystalline phase (see Table 1) is not shown for clarity.

necessary to replace the columnar phase by the SmCP$_A$ phase, increases on enlargement of the bent rigid core. For molecules with very large central units **Z** (e.g. **5/*n*** and **6/*n***) even a tetradecyloxy chain (*n* = 14) is not sufficient to replace the columnar phase by the SmCP$_A$ phase. Interestingly, the columnar phase disappears if the chain length reaches the length of the rigid aromatic halves attached to the central 1,3-disubstituted benzene ring (respectively the average length for compounds **2**, **3**, and **5** with different halves). Therefore, it seems that the columnar phase is only stable if a partial overlap of the aromatic cores of the antiparallel arranged molecules at the ribbon interfaces is possible. Hence, the ribbon structure is stabilized by core–core interaction in the borderline regions between neighboring ribbons (see Figure 6a). These core–core interactions should be especially effective for molecules with extended rigid cores and they can be reduced or lost on increasing the chain length (see Figure 6b). In conclusion, SmCP$_A$ phases can only be obtained if sufficiently long and flexible chains are chosen, which can suppress the formation of frustrated layer structures. Thereby, the critical chain length necessary to obtain SmCP$_A$ phases strongly rises with the size of the rigid aromatic molecular parts (**Z** + **M**).

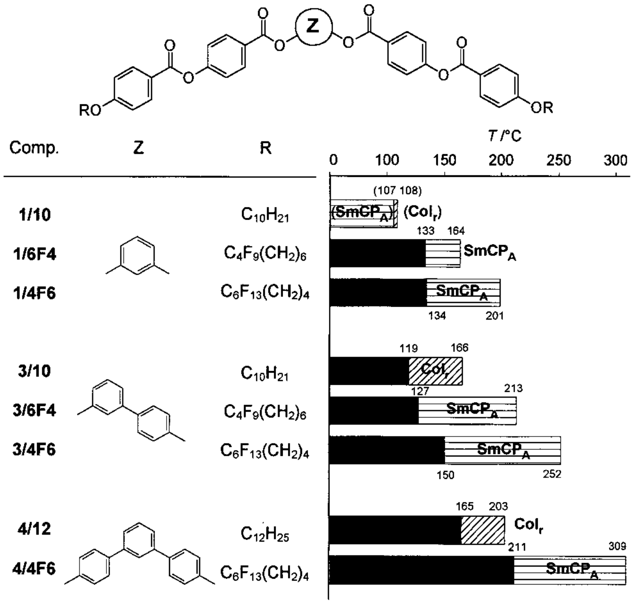

Figure 10. Comparison of mesophases and transition temperatures of semifluorinated and related hydrocarbon compounds. The crystalline phase of compound **1/10** is not shown.[29]

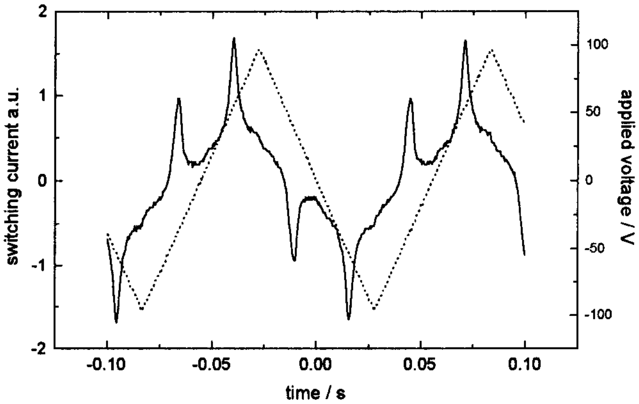

Figure 11. Switching current response in the SmCP$_A$ phase of compound **2/12** obtained by applying a triangular voltage (V_{pp} = 192 V, f = 9 Hz, T = 100 °C).

E. Semifluorination as Designing Principle. As shown above, the separation of aliphatic and aromatic regions is an important factor determining the mesophase structure of such molecules.[31,32] We asked if it would be possible to stabilize the SmCP$_A$ phases by using the fluorophobic effect, *i.e.* the inherent incompatibility of perfluorinated alkyl chains with aliphatic chains, aromatic hydrocarbons, and polar groups.[33,34] Indeed as shown in Figure 10, the mesophases of banana-shaped molecules can be efficiently stabilized by replacing the alkyl chains by semifluorinated chains and, even more interestingly, SmCP$_A$ phases can be induced for molecules which have Col$_r$ phases as hydrocarbon analogues. The stability of the mesophases rises with increasing degree of fluorination, which can be achieved by elongation of the fluorinated segments, or alternatively, by

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(31) Review on the importance of segregation effects in liquid crystals: Tschierske, C. *J. Mater. Chem*. **1998**, *8*, 1485.

(32) Segregation of aliphatic chains and rigid cores is also important for alkylene-bridged dimers (ref 18) and main chain polymers: Watanabe, J.; Nakata, Y.; Simizu, K. *J. Phys. II Fr.* **1994**, *4*, 581.

(33) Smart, B. E. *Organofluorine Chemistry– Principles and Commercial Applications*; Banks, R. E., Smart B. E., Tatlow J. C., Eds.; Plenum Press, New York, 1994; p 57.

(34) Examples for the stabilization of liquid crystalline phases by perfluorinated chains: (a) Viney, C.; Twieg, R, J.; Russell, T. P.; Depero, L. E. *Liq. Cryst*. **1989**, *5*, 1783. (b) Doi, T.; Sakurai, Y.; Tamatani, A.; Takenaka, S.; Kusabashi, S.; Nishihata, Y.; Terauchi, H. *J. Mater. Chem.* **1991**, *1*, 169. (c) Nguyen, H. T.; Sigaud, G.; Achard, M. F.; Hardouin, F.; Twieg, R. J.; Betterton, K. *Liq. Cryst.* **1991**, *10*, 389. (d) Pensec, S.; Tournilhac, F.-G.; Bassoul, P. *J. Phys. II Fr.* **1996**, *6*, 1597. (e) Arehart, S. V.; Pugh, C. *J. Am. Chem. Soc.* **1997**, *119*, 3027. (f) Takenaka, S. *J. Chem. Soc., Chem. Commun*. **1992**, 1748. (g) Johansson, G.; Percec, V.; Ungar, G.; Smith, K. *Chem. Mater.* **1997**, *9*, 164. (h) Dahn, U.; Erdelen, C.; Ringsdorf, H.; Festag, R.; Wendorff, J. H.; Heiney, P. A.: Maliszewskyj, N. C. *Liq. Cryst.* **1995**, *19*, 759. (i) Percec, V.; Schlueter, D.; Kwon, Y. K.; Blackwell, J.; Möller, M.; Slangen, P. J. *Macromolecules* **1995**, *28*, 8807. (j) Reference 27. (k) Pegenau, A.; Cheng, X. H.; Tschierske, C.; Göring, P.; Diele, S. *New J. Chem.* **1999**, *23*, 465. (l) Cheng, X. H.; Diele, S.; Tschierske, C. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 592.

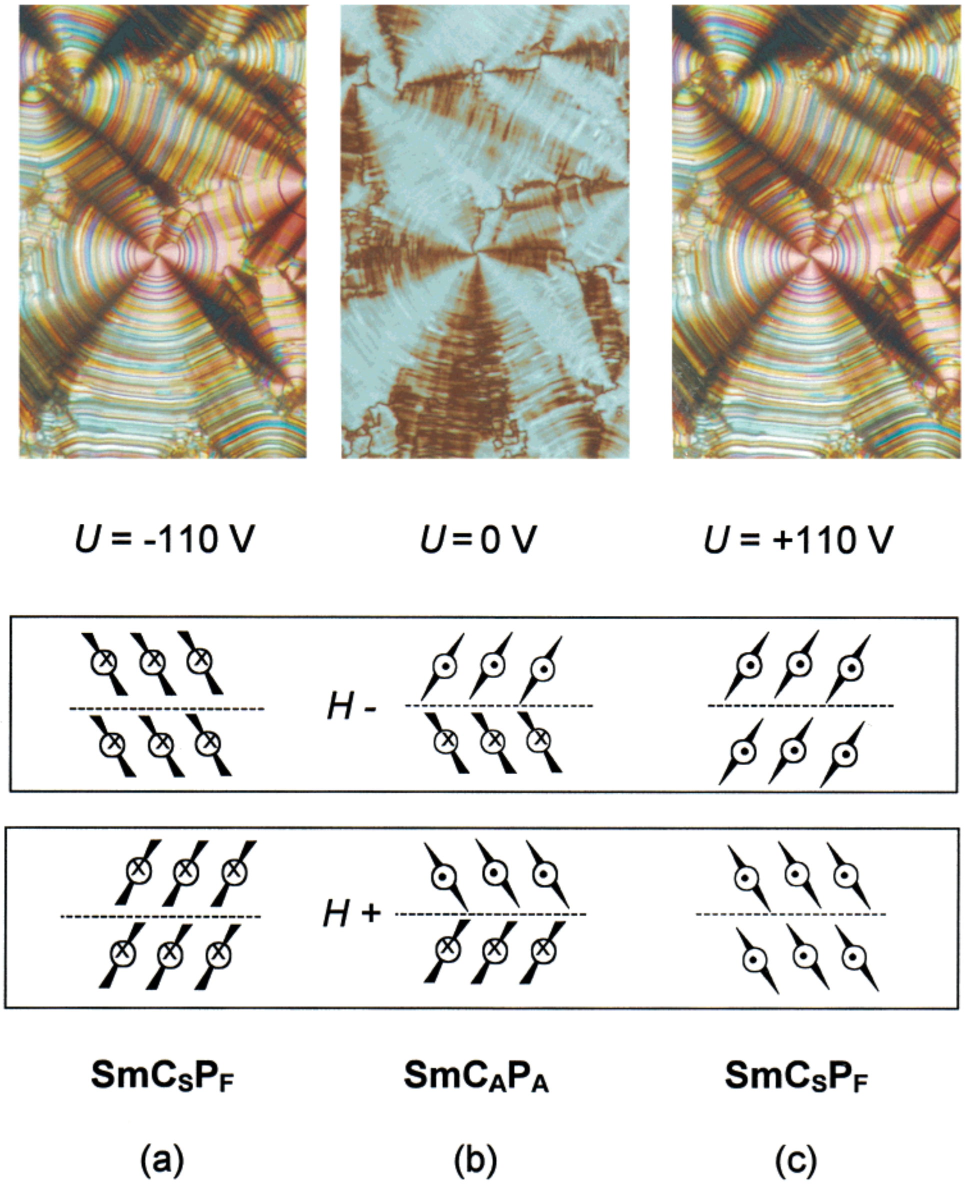
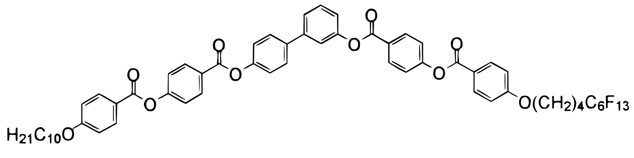


Figure 12. Rotation of an extinction cross in the $SmCP_A$ phase of compound **2/12** on applying an electric field (polyimide coated ITO cell, sample thickness 6 μm, $T = 125$ °C) and proposed organization of the molecules in the different states; $H+$, $H-$ = homochiral states of opposite handedness. The brightness of each image was separately scaled, which means that in reality the birefringence of part b is significantly lower than those of parts a and c.

increasing the number of fluorinated chains (see compound **7**).[35] The mesophase stabilization amounts to ca. 50 °C per C_6F_{13} segment.



7: Cr 135 $SmCP_A$ 211 Iso

F. Electrooptical Investigations. The electrooptical behavior of the $SmCP_A$ phases of all compounds with the exception of **3/4F6** and **4/4F6** was studied in 6 μm thick polyimide-coated ITO cells (measuring area 100 mm^2) by applying a triangular voltage. Only the mesophases of compounds **3/4F6** and **4/4F6** could not be investigated because of their high clearing temperatures which did not allow the filling of the ITO cells without damage. Figure 11 shows the electric response of compound **2/12** under a triangular wave voltage with a peak-to-peak voltage of 192 V and a frequency of 9 Hz at $T = 100$ °C. Two sharp peaks were recorded during a half period indicating an antiferroelectric switching behavior.[36] The spontaneous polarization determined by integration of the switching current peaks amounts to 700 nC cm^{-2}.

The switching process was also observed between crossed polarizers. On slowly cooling a cell filled with **2/12** from the isotrop liquid state (−0.5 deg K per min), without applied voltage, exclusively a schlieren texture was obtained, which means that the smectic layers are predominately oriented parallel

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(35) X-ray investigations indicate a layer distance corresponding to a single-layer arrangement, *i.e.* no hint on the segregation of the fluorinated and the nonfluorinated chains could be observed, which should lead to a bilayer arrangement.

(36) Only one sharp current peak can be detected by applying a peak to peak voltage below 92 V which would suggest a ferroelectric switching (see ref 20). On increasing the peak-to peak voltage a broad second peak occurs which becomes sharper on increasing the triangular voltage.

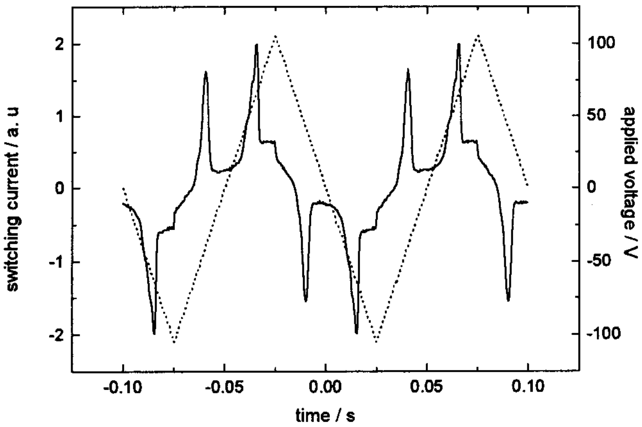

Figure 13. Switching current response in the $SmCP_A$ phase of compound **1/6F4** by applying a triangular voltage (6 μm polyimide coated ITO-cell, $V_{pp} = 212$ V, $f = 10$ Hz, $T = 140$ °C).

to the surfaces. A focal conic texture with parallel stripes is obtained by slow cooling (−0.3 deg K per min) in an electric field of at least 30 V. On increasing the voltage the number of stripes increases and at a voltage of 46 V the stripes suddenly become significantly brighter and colored, indicating that the birefringence increases. On further rising the voltage no further changes of the stripe pattern take place.

The textures of a sample of compound **2/12** are shown in Figure 12, after switching off the voltage (b) and after applying a voltage of −110 (a) and +110 V (c). The images of the two switched states are nearly identical, independent of the sign of the applied field. Furthermore, the orthogonal extinction brushes rotate clockwise, respectively anticlockwise with inversion of the polarization of the electric field. Brushes of different domains can rotate in the same direction or in opposite directions.

The field-induced rotation of extinction brushes was first analyzed by Link et al.[15] The tilt direction of the molecules and the direction of the polar order of the bent molecules are two independent symmetry breaking factors which cause the chirality of the smectic layers (see Figure 1d).[15] Changing one of them changes their handedness. Accordingly, there are two possible equilibrium structures which both have an antiferroelectric switching behavior: (a) In the racemic state (*R*) the tilt of the molecules is uniform (synclinic interlayer correlation, see Figure 1b) whereas the polar direction alternates in sign from layer to layer (antiferroelectric order). Thus the handedness changes from layer to layer. The texture of the ground state is characterized by parallel stripes. On applying an electric field the stripes disappear and the extinction brushes do not rotate when the sign of the field is reversed. (b) In the homogeneous chiral ground state (*H*) the tilt direction and also the polar axis alternate from layer to layer (anticlinic and antiferroelectric, see Figure 1c). Here the handedness of the layers is uniform. In this case the extinction crosses of flowerlike domains rotate in opposite directions depending on the polarity of the field.

Under our experimental conditions the extinction brushes rotate in different directions on reversing the sign of the field, which points to a predominately homogeneous chiral ground state. As the rotation directions can be different in different domains, separate regions of opposite handedness (*H*+ and *H*−) should coexist in the samples. The angle between the extinction crosses amounts to ca. 86°. Provided that the smectic layers are arranged perpendicular to the substrate (book-shelf geometry) the average optical axis should be tilted about 43° with respect to the layer normal. The increase in birefringence upon field application should be the result of the loss of the tilt alternation at zero field to give uniformly tilted chiral domains (ferroelectric order) with synclinic interlayer correlation (SmC_SP_F, see Figure 12a,c). Hence, in the predominate ground state the polar axes of the molecules alternate from layer to layer and the interlayer correlation is anticlinic (SmC_AP_A phase, see Figure 12b).

In respect to the stripe pattern these novel materials behave different from some Schiff-base materials for which SmA-like fan textures without stripes were obtained above a certain saturation voltage.[37] In our case the stripes do not disappear on further increase of the voltage. It seems that this stripe pattern results from the interruption of the predominating homogeneous chiral regions by small regions with opposite handedness.

Antiferroelectric switching behavior was also proven for the SmC_A phases of all other investigated compounds**.** Also the switching process observed between crossed polarizers is identical with that of **2/12**. However, in the Col_r phases and in the SmX phases no antiferroelectric switching can be detected.

As an example for a semifluorinated molecule, the electric response of **1/6F4** is shown in Figure 13. Here, the spontaneous polarization amounts to 500 nC cm^{-2} at 145 °C.

Conclusions

A wide variety of novel bent-core molecules without the unstable Schiff-base structural unit have been synthesized. Depending on the precise molecular structure they can form antiferroelectric switchable $SmCP_A$ phases or rectangular columnar phases (and a highly ordered smectic low-temperature mesophase). The rectangular columnar mesophase obviously enables the most efficient escape from the macroscopic polarization of the molecular dipole moments provided by the special shape of these molecules. However, this arrangement is accompanied by a partial loss of the segregation of incompatible molecular parts. Therefore, structural variation which increases the segregation of rigid bent cores and flexible terminal chains destabilizes the columnar phase leading to the $SmCP_A$ phase in which the polarization cancels out from layer to layer. Therefore, short rigid core units, long alkyl chains, and especially semifluorinated chains suppress columnar phases and favor the occurrence of the $SmCP_A$ phases. In some cases especially broad regions of $SmCP_A$ phases with remarkably low melting points (some of the compounds do not crystallize at all) and high values of spontaneous polarization have been obtained. Under our experimental conditions the $SmCP_A$ phases of the investigated compounds have a predominately homogeneous chiral ground state (SmC_AP_A). In this respect they are different from the classical Schiff-base molecules for which the racemic ground state (SmC_SP_A) is dominating.[15] It seems that the $SmCP_A$ phases of these compounds have an enhanced tendency for the achiral symmetry breaking. Hence, these novel and stable materials should be of interest for various future applications.

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Supporting Information Available: Experimental procedures, ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra, a table with the elemental analyses data, and schemes describing the synthesis of the aromatic dihydroxy compounds (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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[37] Pelzl, G.; Diele, S.; Grande, S.; Jakli, A.; Lischka, C.; Kresse, H.; Schmalfuss, H.; Wirth, I. *Liq. Cryst.* **1999**, *26*, 401.