Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Liquid crystalline dimers with bent-core mesogenic units

Remko Achten[a]; Arie Koudijs[a]; Marcel Giesbers[a]; Antonius T. M. Marcelis[a]; Ernst J. R. Sudhölter[a]; Martin W. Schroeder[b]; Wolfgang Weissflog[b]
[a] Laboratory of Organic Chemistry, Wageningen University, 6703 HB Wageningen, The Netherlands [b] Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, D-06108 Halle, Germany

To cite this Article Achten, Remko , Koudijs, Arie , Giesbers, Marcel , Marcelis, Antonius T. M. , Sudhölter, Ernst J. R. , Schroeder, Martin W. and Weissflog, Wolfgang(2007) 'Liquid crystalline dimers with bent-core mesogenic units', Liquid Crystals, 34: 1, 59 — 64

To link to this Article: DOI: 10.1080/02678290601061330

URL: http://dx.doi.org/10.1080/02678290601061330

Liquid Crystals, Vol. 34, No. 1, January 2007, 59–64

Taylor & Francis
Taylor & Francis Group

Liquid crystalline dimers with bent-core mesogenic units

REMKO ACHTEN†, ARIE KOUDIJS†, MARCEL GIESBERS†, ANTONIUS T. M. MARCELIS*†,
ERNST J. R. SUDHÖLTER†, MARTIN W. SCHROEDER‡ and WOLFGANG WEISSFLOG‡

†Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands
‡Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany

(*Received 15 May 2006; in final form 28 August 2006; accepted 28 August 2006*)

Two series of dimers, in which two identical aromatic bent core mesogenic units are connected via an organosiloxane or an alkylene spacer, have been investigated. The dimers with a spacer consisting of a trisiloxane central group and relatively long alkylene groups show an intercalated tilted smectic structure. The layer spacings appear to be very weakly dependent on the terminal chain lengths. In these dimers the smectic phase is stabilized for the compounds with a short terminal chain. Dimers with an aliphatic alkylene spacer are liquid crystalline only when the spacer is relatively short and the terminal chains are long. For these dimers a monolayer tilted smectic phase is observed.

1. Introduction

Bent-core mesogens have attracted considerable interest in recent years because they are able to form new smectic mesophases with a polar structure [1, 2]. The restricted rotation around the molecular long axis gives rise to a macroscopic polarization in the smectic layers. Furthermore, in tilted smectic phases formed by these bent-core molecules the combination of polar order and director tilt leads to a chiral structure of the layers without the presence of chiral molecules [3]. The application of an alternating external electric field can induce ferroelectric or antiferroelectric switching. In the ferroelectric phases the polarization is uniform in adjacent layers, whereas in antiferroelectric phases the polarization alternates from layer to layer. To avoid bulk polarization, an antiferroelectric ground state occurs in most polar SmC phases of bent-core molecules. However, ferroelectric phases have also been observed, most notably when F-substituents are present on the positions on the aromatic groups close to the aliphatic tails, or when the interlayer fluctuations are disturbed by the presence of a siloxane sublayer [4–7]. The formation of two-dimensional modulated structures or columnar-like blocks is another way to avoid bulk polarization.

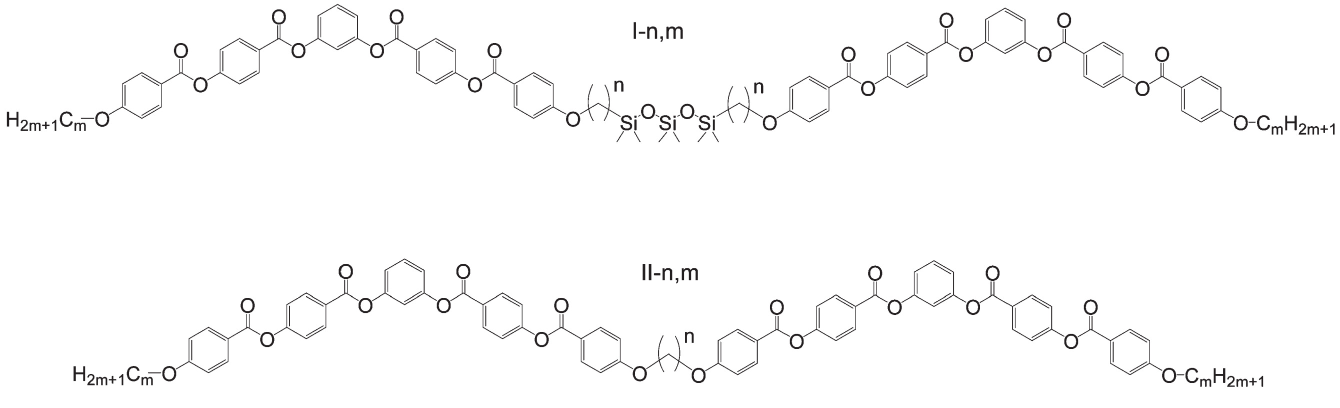
Several modifications of bent-core mesogens have been investigated [1, 2, 5, 8]. For example, the effects of the number of aromatic groups, the nature of the bending unit and small substituents on the aromatic groups have been investigated. An important factor that determines the liquid crystalline properties is the length of the aliphatic tails of the molecules [6, 8, 9]. A phase sequence that is often found on increasing the tail length in bent-core molecules is SmC$_c$–Col$_r$–SmCP [2]. In this sequence the organization changes from intercalated to monolayer. Changes in smectic ordering as a function of terminal chain length are also often observed in calamitic dimer liquid crystals in which two mesogenic units are connected through a flexible chain [10–12]. In these molecules the organization in smectic layers is dependent on spacer and terminal chain length, the ratio of both, and also on the dipole moment of the mesogenic groups. Furthermore, the liquid crystalline properties often strongly depend on the parity of the spacer. For compounds with even spacers the transition temperatures and transition enthalpies are usually considerably higher than for compounds with an odd spacer.

In the literature only a small number of dimer and oligomer liquid crystalline molecules with bent-core groups have been described. A few dimers have been described that contain only one bent-core unit [13, 14]. These give, besides SmA or Col phases, also nematic phases with unusual properties. Dimeric molecules with two identical bent-core mesogens connected by a siloxane-containing spacer have been investigated recently [15, 16]. Depending on the number of siloxane units in the spacer, either a ferroelectric or antiferroelectric intercalated SmCP phase was found. Dimers

---

*Corresponding author. Email: Ton.marcelis@wur.nl

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601061330



Scheme 1. Structures of the compounds of series **I-*n*,*m*** and **II-*n*,*m***

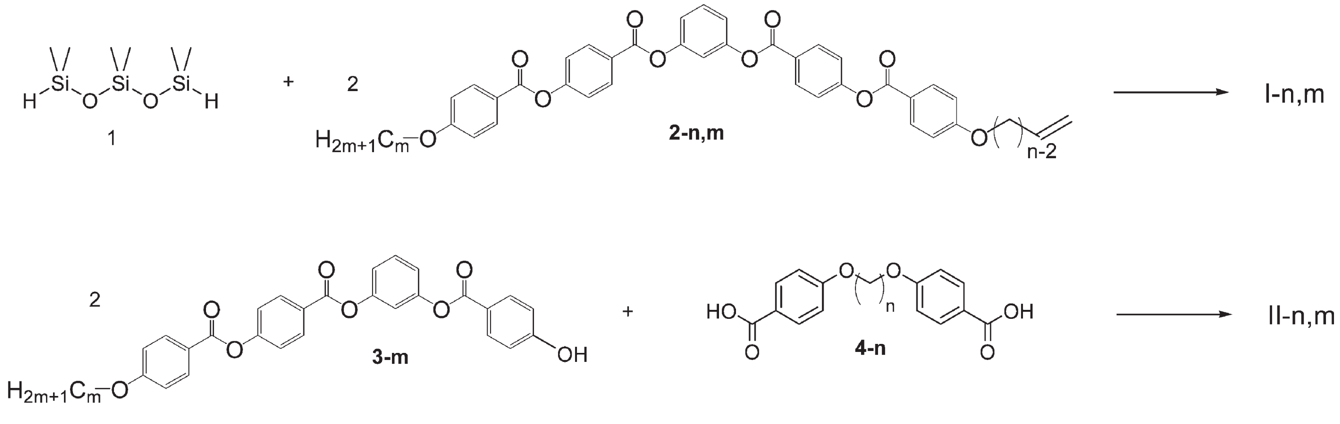
with an alkylene spacer have recently been described for which columnar phases were found [15, 17]. These molecules contain spacers and terminal chains with similar alkyl lengths. In this paper we describe two series of dimer liquid crystals with two bent-core mesogenic units (see scheme 1). As spacers we use relatively short alkylene spacers and relatively long terminal chains. We also investigate dimers with a trisiloxane-containing spacer to study the effect of terminal chain lengths on the liquid crystalline properties.

2. Experimental

2.1. *Synthesis*

The siloxane dimers **I-*n*,*m*** were prepared by a hydrosilylation reaction of monovinyl-terminated bent-core molecules **2-*n*,*m*** [18] with 1,1,3,3,5,5-hexamethyltrisiloxane **1** in toluene using platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt reagent) as catalyst. The dimers **II-*n*,*m*** with an alkyl spacer were prepared by condensation of phenols **3-*m*** [9] with biscarboxylic acids **4-*n*** [19] (scheme 2). The syntheses of two representative examples are given below.

2.1.1. I-11,8. A mixture of 150 mg (0.18 mmol) of **2–11,8** and 18 µl (0.07 mmol) of 1,1,3,3,5,5-hexamethyltrisiloxane **1** was dissolved in 10 ml of dry toluene under N_2. Then 4 µl of Karstedt reagent in xylenes (0.1M) was added and the mixture heated at 60°C for 8 h. After evaporation of the solvent the residue was purified by column chromatography on silica gel with dichloromethane containing 0.75% methanol as eluant, and recrystallization from petroleum ether 40–60/dichloromethane; yield 100 mg (70%). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.22 (d, 8H), 8.09 (d, 8H), 7.43 (t, 2H), 7.36 (d, 8H), 7.14 (s, 2H), 7.12 (d, 4H), 6.92 (d, 8H), 3.99 (t, 8H, $-OCH_2$), 1.77 (m, 8H), 1.6–1.1 (52H, $-CH_2-$), 0.84 (t, 6H, $-CH_3$), 0.47 (m, 4H, $-CH_2-Si$), (0.00 (18H, CH_3-Si). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 164.3, 164.1, 163.8, 155.5, 151.4, 132.5, 131.9, 129.9, 126.6, 122.2, 120.9, 119.3, 115.8, 114.4, 68.4, 33.5, 31.8, 29.6, 29.4, 29.3, 29.2, 29.1, 26.0, 23.3, 22.7, 18.3, 14.1, 1.3, 0.3.



Scheme 2. Syntheses of the dimers **I-*n*,*m*** and **II-*n*,*m***

Table 1. Thermotropic properties (°C) and layer spacings (*d*) of twins in series **I-*n*,*m***. ΔH in kJ mol^{-1} in square brackets.

Compound	Thermotropic properties	*d*/Å
I-11,**8**	Cr 90 [33] SmCP$_F$ 132 [40] I	40.1
I-11,**12**[15]	Cr 85 [31] SmCP$_F$ 136 [48] I	40.8
I-11,**16**	Cr 84 [21] SmCP$_F$ 134 [48] I	41.8
I-10,**8**	Cr 82 [22] SmCP$_F$ 132 [42] I	38.1

2.1.2. II-6,18.

Diacid **4–6** (83 mg) was heated under reflux in 5 ml thionyl chloride for 1 h. After evaporation of the excess thionylchloride the acid chloride was dissolved in 12 ml of dry THF, and 410 mg of phenol **3–18** and 112 mg DMAP were added. This mixture was stirred at room temperature for 2 days. After removal of the solvent, dichloromethane was added and the solution was washed twice with 1M HCl and with $NaHCO_3$ solutions. After drying with Na_2SO_4 and evaporation of solvent the residue was purified by column chromatography (0.5% methanol in dichloromethane) and recrystallization from ethanol/chloroform; yield 215 mg (52%). A final purification was performed by preparative thin layer chromatography on silica gel using 1% methanol in dichloromethane as eluant. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.20 (d, 8H), 8.08 (d, 8H), 7.42 (t, 2H), 7.30 (d, 8H), 7.11 (6H), 6.91 (d, 8H), 4.02 (m, 8H, $-OCH_2$), 1.76 (m, 8H), 1.53–1.39 (m, 64H, $-CH_2-$), 0.81 (t, 6H, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 164.7, 164.5, 164.2, 164.1, 155.9, 151.8, 132.8, 132.3, 130.3, 127.0, 122.5, 121.5, 121.3, 119.7, 116.2, 114.8, 68.8, 68.5, 32.3, 30.1, 30.0, 29.9, 29.8, 29.5, 29.4, 26.4, 26.2, 26.0, 25.7, 23.1, 14.5.

2.2. *Measurements*

The thermal behaviour was investigated using a Perkin-Elmer DSC-7 instrument. The optical textures and 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 non-oriented samples were carried out using a Panalytical X'pert Pro MRD, equipped with an Anton Paar temperature controller. X-ray investigations on oriented samples were performed 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 method was used to study the switching current response.

3. Results and discussion

The thermotropic properties of the dimers with the oligosiloxane central segment, series **I-*n*,*m***, are summarized in table 1. All four dimers in this series show many similarities with the dimers described by Dantlgraber *et al.* [16] and Weissflog *et al.* [15]. The melting points and isotropization temperatures of all four dimers are rather similar. The properties of compound **I-11**,**12** were reported before [15] and the transition properties agree well. The polarization microscopy textures of the dimers all appear almost optically isotropic. By decrossing the polarizers domains of opposite handedness could be observed (see figure 1). This points to a chiral superstructure. The ferroelectric ground state for **I-11**,**12** was proven by one current peak per half period of a triangular voltage [15]. The ferroelectric ground state is promoted by the microphase separation of the siloxane units which disturbs the interlayer correlation that causes the antiferroelectric ground state in most SmCP phases of bent core molecules [16, 20].

The XRD patterns for all four dimers are also quite similar and suggest a well defined layered structure with liquid-like ordering within the layers. The *d*-spacings are

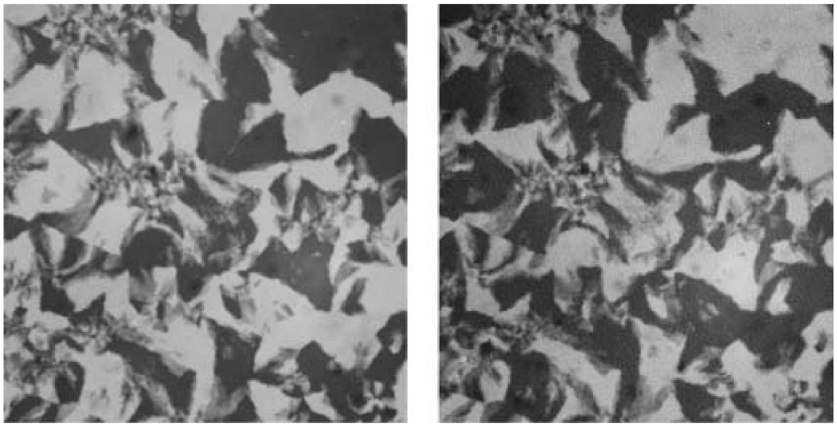


Figure 1. Optical polarization micrographs of **I-11**,**8** at 130°C; one obtained upon slightly decrossing the polarizer to the left and the other to the right.

summarized in table 1. Figure 2 shows the layer spacing of the dimers and of their monomeric precursors as a function of terminal chain length *m*. The *d*-spacings of the corresponding monomeric precursors with a $\mathrm{SmCP_A}$ phase, **2–11**,**12** and **2–11**,**16**, are 35.4 and 38.1 Å, respectively. This indicates that the dimer molecules are intercalated, because the lengths of the molecules have become more than twice as large, whereas the layer spacing has increased only slightly. This was also concluded previously [15]. Interestingly, the three dimeric compounds with a $C_{11}H_{22}$ spacer, **I-11**,**m**, all have a rather similar layer thickness. Apparently, the length of the terminal chains does not influence the layer spacing strongly. Upon increasing the length *m* of the monomeric precursor **2–11**,**12** with four C-atoms (to compound **2–11**,**16**) the thickness of the smectic layers increases by 2.7 Å, whereas the layer spacing in the corresponding siloxane dimers increases by only 1.0 Å. When the tail *m* is longer than one aliphatic spacer fragment *n*, the last part of the tail mixes in with the siloxane sublayer. Comparison of **I-10**,**8** and **I-11**,**8** shows that the *d*-spacings are more strongly dependent on *n*. A similar dependence of the layer spacings on *n* and *m* was recently observed in oligomeric siloxanes with side chain bent-core mesogens [21] and siloxane-terminated bent-core molecules [7].

Another interesting phenomenon is that the monomeric compounds with the shortest terminal (i.e. octyloxy) groups give a $\mathrm{Col_r}$ phase, while as a dimer they exhibit the $\mathrm{SmCP_F}$ phase. This indicates that the smectic ordering is stabilized in the dimers, probably due to the strong tendency for microphase separation of the siloxane groups. Something similar is seen for siloxane-terminated bent-core molecules where even very short spacers also give $\mathrm{SmCP_F}$ phases [7].

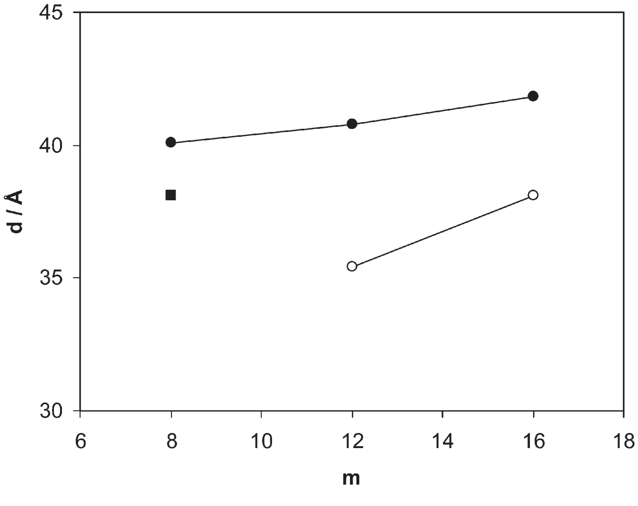


Figure 2. Layer spacings *d* (Å) of the siloxane containing dimers **I-*n*,*m*** as a function of *m* (-●-: *n*=11; ■:*n*=10) and of the corresponding monomeric alkenes **2-*n*,*m*** (-○-).

Until very recently, dimer bent-core molecules with an alkylene spacer had not been described in the literature. The few compounds that have been described and that have liquid crystalline properties have columnar or nematic phases [15, 17]. We prepared several compounds in which both the spacer and the terminal chain lengths were varied. The compound with a decamethylene spacer and decyloxy tails **II-10**,**10** showed a relatively high melting point and no mesogenic properties. Similar results were recently obtained by Weissflog *et al.*, who investigated dimers with four different bent-core mesogenic units with dodecyloxy tails linked by a decamethylene spacer. For these compounds no liquid crystalline phases were observed [15]. The compound with a shorter pentamethylene spacer **II-5**,**10** was also not liquid crystalline. When dimer liquid crystals with relatively short spacers and long terminal chains were investigated, liquid crystalline phases were observed. The results are shown in table 2. Only compound **II-5**,**18** is enantiotropic; the compounds with a hexamethylene **II-6**,**18** or decamethylene spacer **II-10**,**18** are monotropic liquid crystalline.

A photomicrograph obtained for compound **II-5**,**18** on cooling from the isotropic phase is shown in figure 3. The texture indicates that a smectic mesophase might be present although certain circular domains are reminiscent of a columnar phase. However, X-ray diffraction measurements of the mesophases show in all cases up to third or fourth order reflections in the small angle region. This suggests a smectic ordering of the layers. X-ray work on oriented samples also indicates a smectic ordering (figure 4). A scan through the maxima at constant Bragg angle yields a tilt angle ß of the molecules with respect to the layer normal of 53°+/−3°.

An estimation of the length of the molecule in the fully stretched configuration yields a value *L* of ~10.5 nm. This value agrees very well with the value calculated for the length of the building unit of the layer, if only the experimentally obtained values of ß and *d* are used. This result unambiguously proves that

Table 2. Thermotropic properties (°C) and layer spacings (*d*) of twins in series **II-*n*,*m***. Δ*H* in kJ mol^{-1} in square brackets.

Compound	Thermotropic properties	*d*/Å
II-5,**10**	Cr 180 [90] I	
II-10,**10**	Cr 163 [82] I	
II-5,**18**	Cr 164 [28] $\mathrm{Sm}C_X$ 188 [35] I	57.7
II-6,**18**	Cr 174 [67] ($\mathrm{Sm}C_X$ 172 [25]) I	56.7
II-10,**18**	Cr 161 [67] ($\mathrm{Sm}C_X$ 158 [a]) I	59.0

[a] Could not be obtained due to crystallization.

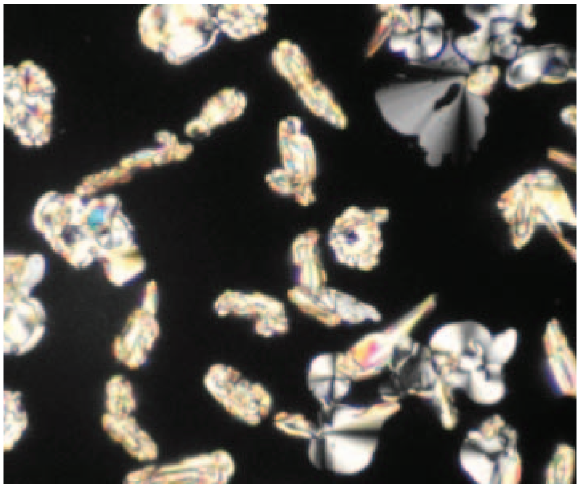


Figure 3. Optical photomicrograph of compound **II-5,18** on cooling from the isotropic state.

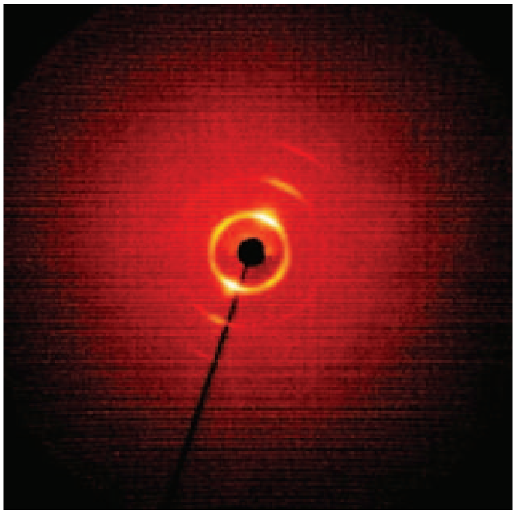


Figure 4. X-ray pattern of an aligned sample of **II-6,18** on cooling just below the isotropic state.

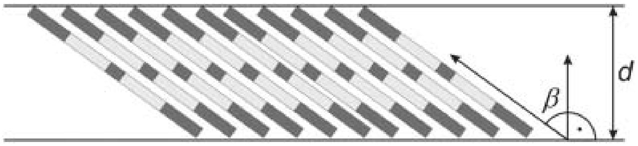


Figure 5. Structural model for the smectic ordering of the dimers **II-*n*,*m***.

the layer structure is built up by the whole dimer, as sketched in figure 5.

Clearly, the molecular structure—with the long aliphatic chains and relatively short spacer between the bent-core moieties—prevents an interdigitation of the molecules of adjacent layers. This is a clear difference from the behaviour of the siloxane-containing dimers. The results compare well with other non-bent-core dimers with short spacers and long terminal chains for which a monolayer structure is usually observed in the smectic phases [10–12].

The three liquid crystalline compounds in series **II-*n*,*m*** all show DSC traces with multiple transitions. As shown, the high temperature phase is liquid crystalline and the same textures are seen for all three compounds, whereas the other phases are probably different crystal modifications.

Electro-optical investigations on both compounds **II-5,18** and **II-6,18** were carried out in commercial EHC cells with 6 µm thickness. By application of a relatively high voltage (+/−200 V/6 µm) a very slight change of the birefringence could be observed, but an unambiguous proof of ferroelectric or antiferroelectric switching was not possible. Unfortunately, due to the beginning of decomposition of the samples at the high temperatures where the liquid crystalline phase is present and a too high conductivity, switching current experiments were not possible. Therefore, a more detailed assignment of the $\mathrm{SmC_X}$ phase was not possible.

4. Conclusions

In contrast to the olefinic monomeric precursors, all compounds in the series with a central trisiloxane group show $\mathrm{SmCP_F}$ phases with ferroelectric switching properties. This confirms the suggestion that decoupling of the layers by the siloxane units suppresses the antiferroelectric ground state of the banana-shaped monomeric precursors. Incorporation of the monomeric precursors in a siloxane-containing dimer stabilizes a smectic ordering. Moreover, the thickness of the smectic layers in this series is only very weakly dependent on the length of the terminal chains. The dimeric compounds with an aliphatic alkylene spacer are only liquid crystalline if the terminal chains are relatively long. These compounds show a strongly tilted monolayer smectic phase with relatively high transition temperatures.

Acknowledgements

This research was financially supported by the Dutch Technology Foundation (grant WPC5325).

References

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

[2] R. Amaranatha Reddy, C. Tschierske. *J. mater. Chem.*, **16**, 907 (2006).

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

[4] C. Tschierske, G. Dantlgraber. *Pramana*, **61**, 455 (2003).

[5] R. Amaranatha Reddy, B.K. Sadashiva. *Liq. Cryst.*, **30**, 1031 (2003).

[6] R. Amaranatha Reddy, V.A. Raghunathan, B.K. Sadashiva. *Chem. Mater.*, **17**, 274 (2005).

[7] C. Keith, R. Amaranatha Reddy, A. Hauser, U. Baumeister, C. Tschierske. *J. Am. chem. Soc.*, **128**, 3051 (2006).

[8] D. Shen, A. Pegenau, S. Diele, I. Wirth, C. Tschierske. *J. Am. chem. Soc.*, **122**, 1593 (2000).

[9] R. Achten, R. Cuypers, M. Giesbers, A. Koudijs, A.T.M. Marcelis, E.J.R. Sudhölter. *Liq. Cryst.*, **31**, 1167 (2004).

[10] C.T. Imrie. *Struct. Bonding*, **95**, 150 (1999).

[11] C.T. Imrie, P.A. Henderson. *Curr. Opin. colloid interface Sci.*, **7**, 298 (2002).

[12] A.T.M. Marcelis, A. Koudijs, Z. Karczmarzyk, E.J.R. Sudhölter. *Liq. Cryst.*, **30**, 1357 (2003).

[13] C.V. Yelamaggad, S. Krishna Prasad, G.G. Nair, I.S. Shashikala, D.S. Shankar Rao, C.V. Lobo, S. Chandrasekhar. *Angew. Chem. int. Ed.*, **43**, 3429 (2004).

[14] M.G. Tamba, B. Kosata, K. Pelz, S. Diele, G. Pelzl, Z. Vakhovskaya, H. Kresse, W. Weissflog. *Soft Matter*, **2**, 60 (2006).

[15] 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, W. Weissflog. *Chem. Mater.*, **18**, 691 (2006).

[16] G. Dantlgraber, S. Diele, C. Tschierske. *Chem. Commun.*, 2768 (2002).

[17] S. Umadevi, B.K. Sadashiva, H.N. Shreenivasa Murthy, V.A. Raghunathan. *Soft Matter*, **2**, 210 (2006).

[18] R. Achten, A. Koudijs, M. Giesbers, A.T.M. Marcelis, E.J.R. Sudhölter. *Liq. Cryst.*, **32**, 277 (2005).

[19] A.H. Khant, J.E. McIntyre, A.H. Milburn. *Polymer*, **24**, 1610 (1983).

[20] G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl, C. Tschierske. *Angew. Chem. int. Ed.*, **41**, 2408 (2002).

[21] R. Achten, A. Koudijs, M. Giesbers, R. Amaranatha Reddy, T. Verhulst, C. Tschierske, A.T.M. Marcelis, E.J.R. Sudhölter. *Liq. Cryst.*, **33**, 681 (2006).