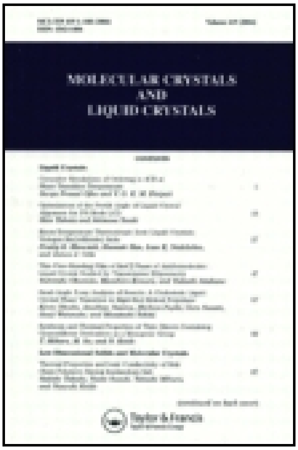


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Dimer Biphenyl Liquid Crystals with Trisiloxane-Containing Spacers

Remko Achten [a] , Arie Koudijs [a] , Marcel Giesbers [a] , Antonius T. M. Marcelis [a] & Ernst J. R. Sudhölter [a]

[a] Laboratory of Organic Chemistry, Wageningen University, Wageningen, The Netherlands

Version of record first published: 22 Sep 2010

To cite this article: Remko Achten, Arie Koudijs, Marcel Giesbers, Antonius T. M. Marcelis & Ernst J. R. Sudhölter (2007): Dimer Biphenyl Liquid Crystals with Trisiloxane-Containing Spacers, Molecular Crystals and Liquid Crystals, 477:1, 169/[663]-176/[670]

To link to this article: http://dx.doi.org/10.1080/15421400701734098

Mol. Cryst. Liq. Cryst., Vol. 477, pp. 169/[663]–176/[670], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701734098

Dimer Biphenyl Liquid Crystals with Trisiloxane-Containing Spacers

Remko Achten
Arie Koudijs
Marcel Giesbers
Antonius T. M. Marcelis
Ernst J. R. Sudhölter[1]
Laboratory of Organic Chemistry, Wageningen University,
Wageningen, The Netherlands

Dimeric biphenyl liquid crystals with trisiloxane containing spacers were studied. Both the tail lengths and the spacer lengths to a central hexamethyltrisiloxane group were varied. In most cases a SmC-phase was found with an anticlinic interlayer relation. One of the compounds appears to have a SmA-phase, which could be a de Vries SmA-phase. A few other compounds show liquid crystalline polymorphism. X-ray diffraction experiments show that the smectic layers are strongly interdigitated. The thickness of the layers is mainly dependent on the length of the spacers. The length of the terminal alkyl chains hardly influences the smectic layer thickness.

Keywords: anticlinic; de Vries smectic; interdigitation; layer spacing

INTRODUCTION

Siloxane containing liquid crystals form an interesting class of liquid crystals. The polyphilic nature of these molecules results in a strong tendency of the siloxane groups to microsegregate into layers and thus strongly promote smectic phases. Usually these smectic layers are tilted, SmC-like, because the cross sectional area occupied by one

---

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

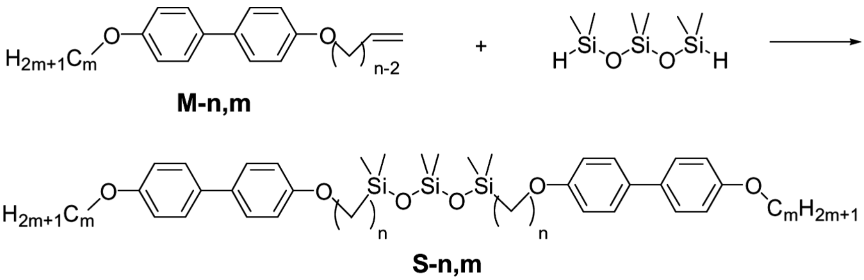
[1] Present address: Department of Chemical Technology DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.

Address correspondence to Antonius T. M. Marcelis, Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, Wageningen, 6703 HB, The Netherlands. E-mail: Ton.Marcelis@wur.nl

siloxane group is significantly larger than the cross sectional area of classical mesogenic moieties [1]. This phenomenon is found for siloxane-terminated liquid crystals [2–5], side-chain liquid crystalline siloxane polymers [6] and dimers containing a central siloxane group [1,3–5, 7–10]. This mismatch in cross-section often results in interdigitation of the mesogenic moieties.

Chiral dimer liquid crystals with a trisiloxane group in the spacer have been investigated in detail, since they often form chiral SmC phases with antiferroelectric switching properties [1,3–5,7–10]. This can be attributed to the anticlinic layer correlation that exists in these SmC_a-phases. This behaviour has been found for many dimers with an odd number and not for those with an even number of siloxane groups [3,5,8]. It was also not found for liquid crystals with one siloxane end-cap [2–5]. Initially, the anticlinic ordering was thought to result from the bent shape of the odd-numbered siloxane group. In this respect this behaviour shows similarities with the preference of bent-core molecules to form antiferroelectric phases [11]. Interestingly, bent-core molecules with siloxane groups (both dimers [12] and siloxane-end capped molecules [13]) usually show ferroelectric behaviour. However, there is still some controversy about the conformation of the trisiloxane unit. A linear conformation can probably not be excluded due to the very small energy differences between the conformations [1]. Also a hairpin conformation cannot be excluded based on a crystal structure of a siloxane group containing dimer [14]. It has also been suggested that all conformations exist together in the actual liquid crystalline phase [4].

In this paper a series of achiral dimesogenic organosiloxanes with biphenyl groups as mesogenic moieties are presented (Scheme 1). The length of the spacers *n* to the central trisiloxane unit and the terminal chains *m* was varied. The liquid crystalline phase behaviour and especially the dependence of the smectic layer thickness on *n* and *m* was studied.



SCHEME 1 Synthesis of the compounds.

MATERIALS

The compounds were synthesized as given in the scheme. The alkenes **M-n,m** were prepared as described before [15]. A representative example of the synthesis of the dimers is given for **S-8,6**. The other dimers were prepared similarly.

Synthesis of S-8,6

To a solution of 0.5 g of **M-8,6** (1.32 mmol) and 1,1,3,3,5,5-hexamethyltrisiloxane (0.53 mmol; 0.109 g; 133 μl) in 20 mL of toluene was added 5 μl of Karstedt reagent (0.1 M platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution in xylenes). The mixture was heated at 65°C for 4 h. The reaction mixture was concentrated and chromatographed on a silica gel column with CH_2Cl_2/petroleum ether 40–60 1:2 as eluent. Recrystallization from hexane gave 360 mg (56 %) of pure product.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.45 (d, 8H, Ar), 6.93 (d, 8H, Ar), 3.98 (t, 8H. OCH_2), 1.80 (m, 8H, OCH_2CH_2), 1.6–1.2 (m, 32H, CH_2), 0.91 (t, 6H, CH_3), 0.50 (m, 4H, $SiCH_2$), 0.04 (m, 18H, $SiCH_3$). Anal: calcd for $C_{58}H_{92}O_6Si_3$: (969.62) C 71.85, H 9.56; found C 71.60, H 9.76%.

RESULTS AND DISCUSSION

Several starting compounds **M-n,m** have been prepared before [15]. The others were prepared similarly. Although most of the compounds are not liquid crystalline there are some that are. They have a very narrow liquid crystalline range and usually are SmA. One compound, **M-8,12**, also exhibits a SmC-phase. The transition temperatures, phase behaviour, *d*-spacings and calculated length L of the compounds are given in Table 1. It seems that the tails have to be sufficiently long for liquid crystallinity and that asymmetry in the tail lengths is also important. The *d*-spacings correspond quite well with the calculated length L of the molecules, although they are a little bit shorter. Below the SmA-SmC transition of **M-8,12** the layer spacing decreases as expected, due to the tilting of the molecules.

The trisiloxane dimers **S-n,m** were prepared by a hydrosilylation reaction between 1,1,3,3,5,5-hexamethyltrisiloxane and alkenes **M-n,m** in toluene with a platinum complex (Karstedt reagent) as catalyst. The thermotropic properties, phase transition temperatures and corresponding enthalpy values, and the *d*-spacings of the compounds from series **S-n,m** are summarized in Table 2. The length of the

TABLE 1 Transition Temperatures, Phases, *d*-Spacings and Calculated Length (L) of Biphenyl Monomers **M-n,m**

Compound	Liquid crystalline properties	*d*(Å)	L(Å)
M-3,4	Cr 147 I		
M-3,6	Cr 129 I		
M-3,12	Cr 118 I		
M-5,6	Cr 126 I		
M-5,9[15]	Cr 109 I		
M-5,12	Cr 110 SmA 114 I	30.3	32
M-8,4	Cr 115 I		
M-8,6[15]	Cr 111 I		
M-8,9	Cr 104 I		
M-8,12	Cr 100 SmC 102 SmA 103 I	31.6 (SmA)	36
M-10,12	Cr 105 I		
M-11,3[15]	Cr 107 I		
M-11,4[15]	Cr 108 I		
M-11,6[15]	Cr 101 SmA 104 I	31.2	32
M-11,9[15]	Cr 98 SmA 99 I	33.8	36

spacer *n* was varied from very short ($n = 3$) to relatively long ($n = 11$). The number of carbon atoms in the terminal chains *m* was varied from 3 to 12.

TABLE 2 Transition Temperatures, Corresponding Enthalpies [kJ/mol], Phases, *d*-spacings and Calculated Length (L) of Trisiloxane Dimers **S-n,m**

Compound	Mesophase properties	*d*(Å)	L(Å)
S-3,4	Cr 138 [67.5] (SmC$_{\mathrm{a}}$ 119.5) [#]) I	23.6	46
S-3,6	Cr 109 [57.6] (SmC$_{\mathrm{a}}$ 105) [21.0]) I	23.6	50
S-3,12	Cr 87 [60.3] (SmC$_{\mathrm{a}}$ 82.5) [17.5] I	#	
S-5,6	Cr 111.5 [17.7] SmC$_{\mathrm{a}}$ 117.5 [23.9] I	27.1	56
S-5,9	Cr 89 [16.9] SmC$_{\mathrm{a}}$ 102 [21.8] I	27.4	62
S-5,12	Cr 86 [17.9] SmC$_{\mathrm{a}}$ 99.5 [23.7] I	28.2	70
S-8,4	Cr 130 [46.3] I	–	
S-8,6	Cr 118 [23.2] SmC$_{\mathrm{a}}$ 121 [23.2] I	31.6	62
S-8,9	Cr 92 [12.3] SmC$_{\mathrm{a}}$ 110 [24.1] I	31.9	69
S-8,12	Cr 80 [8.1] SmC$_{\mathrm{a}}$ 86 [2.5] SmC$_{\mathrm{X}}$ 105 [#] M$^{*}_{\mathrm{X}}$ 107.5 [23.9] I	32.5 (SmC$_{\mathrm{a}}$)	77
S-10,12	Cr 100 [6.9] SmC$_{\mathrm{a}}$ 104 [3.2] SmC$_{\mathrm{X}}$ 112 [#] M$^{*}_{\mathrm{X}}$ 114 [25.2] I	34.8 (SmC$_{\mathrm{a}}$)	83
S-11,3	Cr 123 [44.6] I	–	63
S-11,4	Cr 126 [24] SmA 127 [20] I	36.2	66
S-11,6	Cr 118.5 [15.6] SmC$_{\mathrm{a}}$ 123.5 [26.5] I	35.5	70
S-11,9	Cr 114.5 [16.9] SmC$_{\mathrm{a}}$118 [28.8] I	35.9	78

[#]Could not be determined; [*]Unidentified liquid crystalline phase.

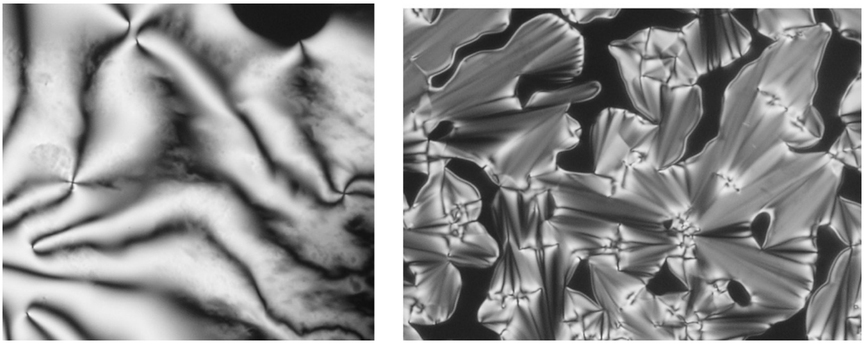


FIGURE 1 Textures of **S-5,6** at 116°C a) homeotropic texture showing both two- and four-point brushes. b) focal conic texture.

Two compounds with short tails and long spacers **S-8,4** and **S-11,3** are not liquid crystalline. Most compounds that are liquid crystalline have a SmC phase with an anticlinic layer correlation, denoted as $\mathrm{SmC_a}$. This is deduced from the observation by polarization microscopy of both two-point and four-point brushes in homeotropic textures of these compounds (Fig. 1) [16,17]. An anticlinic interlayer correlation is often observed for liquid crystalline siloxane dimers with chiral endgroups [1,3-5,7-10]. One compound, **S-11,4**, shows a different behaviour by polarization microscopy (Fig. 2). Under homeotropic conditions a rather dark texture is seen without Schlieren. Upon cooling from the isotropic state the formation of large circular domains is seen. These observations indicate a SmA ordering for this phase. A change from $\mathrm{SmC_a}$ to SmA has been observed before for siloxane-containing dimers upon increasing the spacer length [4,18].

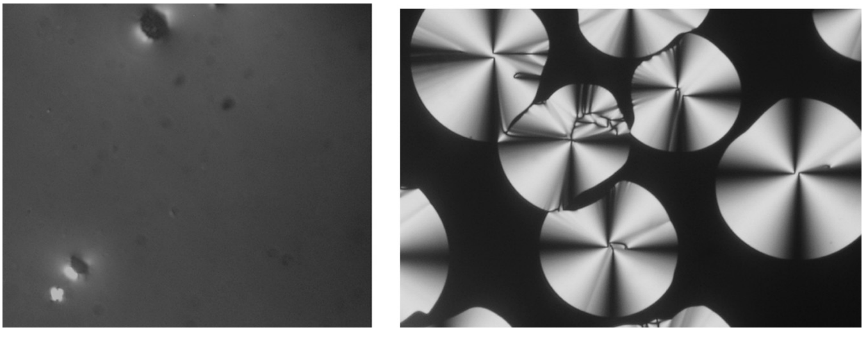


FIGURE 2 Textures of **S-11,4** at 127°C a) homeotropic texture. b) non-homeotropic texture upon cooling from the isotropic state.

Two other compounds **S-8,12** and **S-10,12** show three liquid crystalline phases. The highest temperature phase which exists in a small temperature range shows a texture that could be a nematic phase. It was not detected by DSC, but was clearly seen with polarization microscopy. The lower temperature phases are SmC, denoted as $\mathrm{SmC_X}$. At least the lowest temperature phase is anticlinic as can be deduced from the two-point brushes that are observed.

The layer thicknesses of the smectic phases are plotted in Figure 3. Generally, the layer spacing is about half the estimated length of the dimers. This is a strong indication for an interdigitated structure with separate siloxane sublayers. It is seen that the spacing is dependent on the spacer length *n* and hardly on the tail length *m*. A linear correlation between spacer length and *d*-spacing for similar (chiral) dimers has been found before [9]. Recently, studies on siloxane containing oligomers [19] with bent-shaped mesogenic units and bent-shaped mesogens end-capped with siloxane groups [13] have shown similar results. The smectic layer thickness is determined by the length of the spacer to the siloxane unit and not by the tail length. If the tails are longer than the spacer, the remaining part of the tail mixes in with the siloxane layer.

This also means that for compound **S-11,4** the tails are not long enough to reach the siloxane sublayer when the spacer is fully extended. Compared to the estimated length of the molecule (L), this compound has a *d*/L ratio of about 0.55, which is the highest of this series of compounds. It could mean that this compound is the least interdigitated. It could also be the reason for the SmA-phase of this compound. On the other hand, when we compare the *d*-spacings of this compound with those of the other compounds **S-11,n** in the

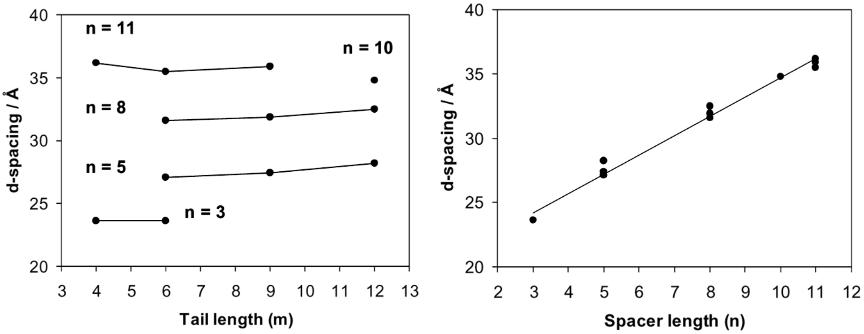


FIGURE 3 *d*-Spacings (in Å) of compounds **S-n,m** plotted as function of the tail lengths (left) and spacer length (right).

series, it is only marginally larger. This means that the tilt angle of the SmC compounds is small or that the SmA-phase of this compound is of the de Vries type. In these phases the mesogenic units are tilted but the correlation length is so small that it does not result in optical anisotropy. De Vries SmA-phases have been found for other chiral trisiloxane monomers and dimers with relatively short tails and long spacers [20,21]. Two compounds with relatively long spacers **S-8,12** and **S-10,12** show more than one liquid crystalline phase. The d-spacing of the high temperature smectic phase is given in Table 2. The lower temperature smectic phase has a d-spacing that is $\sim 1.0\,\text{Å}$ longer. These compounds have a rather low d/L value of about 0.42 and it is suggested that the alkyl tails become mixed with the siloxane sublayers. At higher temperatures this ordering could be preceded by a less ordered phase like a nematic phase.

The compounds with the C_{11}-spacers and long tails **S-11,6** and **S-11,9** exhibit two to three Cr–Cr transitions just below the Cr-SmC_a transition as revealed by DSC, XRD and polarization microscopy.

CONCLUSIONS

Most dimers investigated here that have a central trisiloxane unit and biphenylyl mesogenic groups exhibit a SmC-phase with an anticlinic layer correlation. Some compounds however, show slightly different behaviour. One compound with a long spacer and short tails shows a SmA-phase that is probably of the de Vries type. Two compounds with relatively long tails show more liquid crystalline phases and also smectic mesomorphism. Interestingly, the smectic layer spacings are almost independent on the tail length and increase almost linearly with the spacer length.

REFERENCES

[1] Guillon, D., Osipov, M. A., Méry, S., Siffert, M., Nicoud, J.-F., Bourgogne, C., & Sebastião, P. (2001). *J. Mater. Chem.*, *11*, 2700.

[2] Naciri, J., Ruth, J., Crawford, G., Shashidhar, R., & Ratna, B. R. (1995). *Chem. Mater.*, *7*, 1397.

[3] Robinson, W. K., Carboni, C., Kloess, P., Perkins, S. P., & Coles, H. J. (1998). *Liq. Cryst.*, *25*, 301.

[4] Olsson, N., Helgee, B., Andersson, G., & Komitov, L. (2005). *Liq. Cryst.*, *32*, 1139.

[5] Corsellis, E., Guillon, D., Kloess, P., & Coles, H. (1997). *Liq. Cryst.*, *23*, 235.

[6] Helgee, B., Hjertberg, T., Skarp, K., Andersson, G., & Gouda, F. (1995). *Liq. Cryst.*, *18*, 871.

[7] Robinson, W. K., Kloess, P. S., Carboni, C., & Coles, H. J. (1997). *Liq. Cryst.*, *23*, 309.

[8] Lehmann, P., Robinson, W. K., & Coles, H. J. (1999). *Mol. Cryst. Liq. Cryst.*, *328*, 221.

[9] Kaeding, A. & Zugenmaier, P. (1998). *Liq. Cryst.*, *25*, 449.

[10] Robinson, W. K., Lehmann, P., & Coles, H. J. (1999). *Mol. Cryst. Liq. Cryst.*, *328*, 229.

[11] Reddy, R. A. & Tschierske, C. (2006). *J. Mater. Chem.*, *16*, 907.

[12] Kosata, B., Tamba, G.-M., Baumeister, U., Pelz, K., Diele, S., Pelzl, G., Galli, G., Samaritani, S., Agina, E. V., Boiko, N. I., Shibaev, V. P., & Weissflog, W. (2006). *Chem. Mater.*, *18*, 691.

[13] Keith, C., Reddy, R. A., Hauser, A., Baumeister, U., & Tschierske, C. (2006). *J. Am., Chem. Soc.*, *128*, 3051.

[14] Zugenmaier, P. (2002). *Liq. Cryst.*, *29*, 613.

[15] Nieuwhof, R. P., Marcelis, A. T. M., Sudhölter, E. J. R., Picken, S. J., & de Jeu, W. H. (1999). *Macromolecules*, *32*, 1398.

[16] Takanishi, Y., Takezoe, H., Fukuda, A., Komura, H., & Watanabe, J. (1992). *J. Mater. Chem.*, *2*, 71.

[17] Nishiyama, I., Yamamoto, T., Yamamoto, J., Goodby, J. W., & Yokoyama, H. (2003). *J. Mater. Chem.*, *13*, 1868.

[18] Olsson, N., Andersson, G., Helgee, B., & Komitov, L. (2005). *Liq. Cryst.*, *32*, 1125.

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

[20] Panarina, O. E., Panarin, Y. P., Antonelli, F., Vij, J. K., Reihmann, M., & Galli, G. (2006). *J. Mater. Chem.*, *16*, 842.

[21] Panarina, O. E., Panarin, Y. P., Vij, J. K., Spector, M. S., and Shashidhar, R. (2003). *Phys. Review E.*, *67*, 051709.