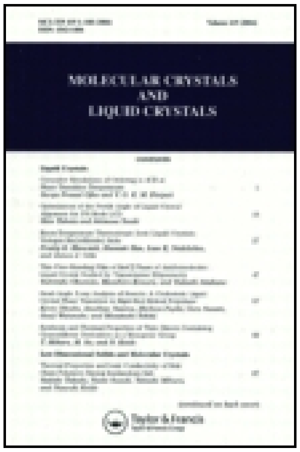


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Bulky End Groups and Mesomorphism Study of Mesogenic Stilbenes with Chlorosilyl Groups

G. Subramaniam [a]

[a] Department of Chemistry, Penn State University, Hazleton, PA, 18201

Version of record first published: 04 Oct 2006

To cite this article: G. Subramaniam (1997): Bulky End Groups and Mesomorphism Study of Mesogenic Stilbenes with Chlorosilyl Groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 308:1, 121-132

To link to this article: http://dx.doi.org/10.1080/10587259708045100

Mol. Cryst. Liq. Cryst., 1997, Vol. 308, pp. 121–132
Reprints available directly from the publisher
Photocopying permitted by license only

Bulky End Groups and Mesomorphism Study of Mesogenic Stilbenes with Chlorosilyl Groups

G. SUBRAMANIAM

Department of Chemistry, Penn State University, Hazleton, PA 18201

(Received 6 November 1996)

Liquid crystalline alkoxy stilbenes with chlorosilyl end groups were synthesized for the first time. The chlorosilyl end groups, even though bulky, tend to promote smectic mesophase due to their high polarity. The long range dipole–dipole intermolecular attractive forces overpower repulsive steric interactions. Theoretical calculations show the dimers from these chlorosilyl precursors to prefer bent conformation over extended one and thus they prove to be good models for side chain polysiloxanes.

Keywords: Mesomorphism; chlorosilyl groups; stilbenes; smectic; bulky end groups

INTRODUCTION

Traditionally, liquid crystalline, side chain polysiloxanes have been synthesized by the direct hydrosilylation of polydimethylhydrogen siloxane, PDMHS. An alternate route is via direct condensation of dichloroalkylsilyl mesogens. We decided to explore the viability of this method over the traditional route; this task involved the syntheses of chlorosilyl recursors. In spite of the growing interest in the field of liquid crystalline polysiloxanes, it is surprising to note that no systematic study was attempted to date, on liquid crystal monomers with chlorosilyl moiety. In fact, this work may be the first and the only one to explore the mesogenic properties of chlorosilyl compounds. The lack of the initiative may be partly due to the hydrolytic instability of chlorosilyl compounds.

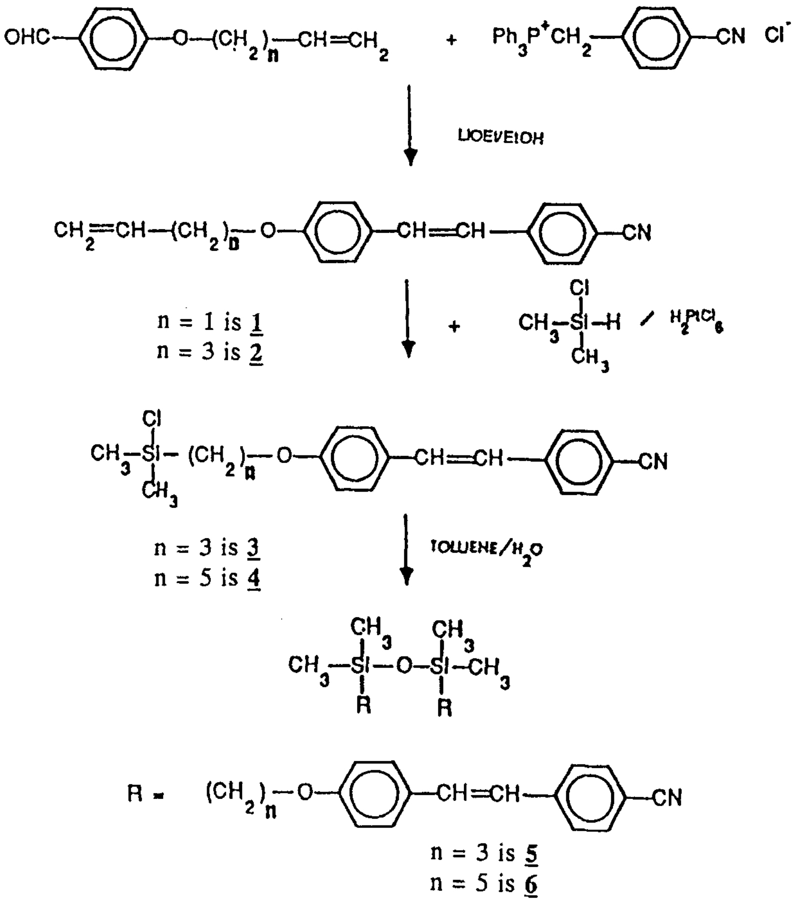
However there are numerous reports on the study of liquid crystals with methylsilyl groups. For e.g. Young and Haller [1] had studied three series of Schiff's bases in which a trimethyl silyl and a pentamethyl–disiloxyl group were attached to the aromatic core directly or by an intervening oxygen atom. They did not attempt to study the effect of these bulky groups as they are moved away from the aromatic core. Similarly, attempts were made by Griffin *et al.* [2] to prepare twin dimers with symmetrical bismethylene tetramethyldisiloxane spacers as possible models for (Rigid-flexible) mesogenic polymers. Tetramers have also been synthesized for the same purpose. None of the reported works [2–4] on dimers with siloxane spacer analyzed the effect of silyl end groups on liquid crystallinity. There has been no systematic study on liquid crystals with chlorosilyl end groups, to the best of our knowledge.

This paper describes the successful synthesis of dimeric liquid crystal with oligomethylenetetramethyldisiloxane spacers and their chlorosilyl precursors. It also deals with structure-mesomorphic correlation, in particular, the effect of introducing the bulky chloromethylsilyl group on the alkoxy end of 4′-cyano-4-alkoxystillbenes.

RESULTS AND DISCUSSION

The cyano precursors, 4-cyano-4-alkoxybenzaldehydes were prepared by reported method [5]. Wittig reaction was used to prepare the E-isomers of stilbenes **1** and **2** (Scheme I). Both of these vinylic precursors are nematic liquid crystals with crystal to nematic transitions onset at 121.5° and 93.7° respectively. In addition, **2** shows a crystal to crystal transition at 73.4°. The transitions temperatures along with heats of transition from DSC are summarized in Table I. There is close agreement between the microscopic and DSC data of these transitions. Comparison of the thermal transitions of vinylic stilbenes with saturated analogues shows that the terminal double bond has little influence on the melting and clearing temperatures [6]. This observations is consistent with those of Petrzilka *et al.* who systematically studied the effect of position of double bond on the mesogenic properties [7].

Platinum (VI) catalyzed hydrochlorosilylation of **1** and **2** yielded the respective monomers **3** and **4** (Scheme I). DSC of 3 shows four phase transitions occurring at 111.9°, 125.3°, 131.9° and 144.1°. These transitions are observable by microscopy and are indicated by texture changes during heating cycle. However, During cooling, microscopy reveals some biphasic regions (spherulites and smectic texture) in **3**; this is very likely due to some dimerization that might have occurred during microscopic examination.



SCHEME I

TABLE I Transition temperatures of compounds 1–6

1	C	121.5	N	142.2	I				
2	C	73.4	C	93.7	N	125.1	I		
3	C	111.9	S	125.2	S	131.9	N	144.1	I
4	C	61.5	S	90.6	I				
5	C	137.0	S	152.1	I				
6	C	116.1	S	137.6	I				

Temp. in°C.

DSC of **4** shows only two transitions, one at 61.5° and another at 90.6°. The first transition occurs with very little change in the mobility and shows a polygonal texture characteristic of smectic mesophase. On cooling from isotropic phase, a texture consisting of concentric circles, with very little fluidity is obtained and thus differs from the nematic droplets (Fig. 1).

The occurrence of smectic phases in these compounds is quite surprising in view of the observation by Young *et al.* that addition of a bulky substituent precludes liquid crystallinity in Schiff's bases. The Schiff's bases studied by them were the aza analogs of the stilbenes and are almost identical in length, as far as the aromatic cores are concerned. They had trimethylsilyl or pentamethyldisiloxy groups end groups either directly attached or by an oxygen to the core. None of them exhibited mesophases. They were able to observe mesophase formation only when the aromatic core was extended by another phenyl ring. They measured a higher clearing and transition temperatures for Schiff's bases with different bulky polar gorups and noted that the size of the bulky end groups did not have any effect on the clearing temperatures. They proposed several close packing arrangements to account for the observed data (Fig. 2). On the contrary, we observed decreased transition and clearing temperatures in stilbenes **3** and **4**, with bulky polar end groups, relative to their vinylic precursors. The occurrence of smectic phases with lower onset temperatures in these compounds suggests the following facts: (i) bulky polar end groups did not preclude mesophase formation (ii) Rather, they help either to increase the lateral attractive forces or to decrease end–end intermolecular attractions – the ideal factors to favor the formation of smectic phase – by some mechanism.

One would expect the bulky chlorosilyl end groups to prevent the molecular close packing due to steric repulsion and thus decrease the lateral

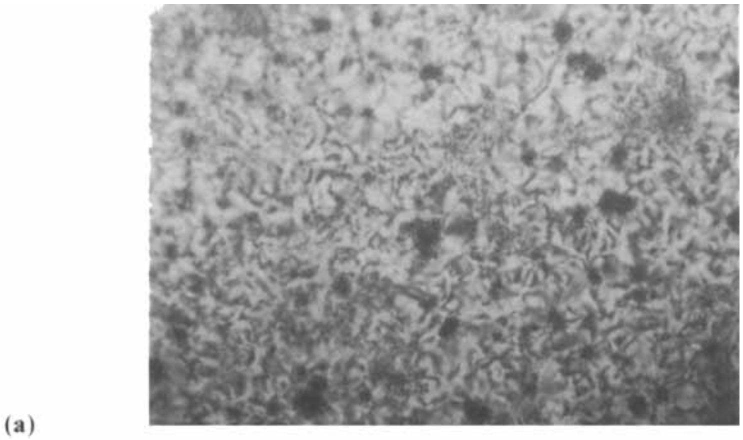


FIGURE 1 Optical Micrographs of Chlorosilylstilbenes: (a) Smectic Texture of 3; (b) Smectic Texture of 4. (See Color Plate VI).

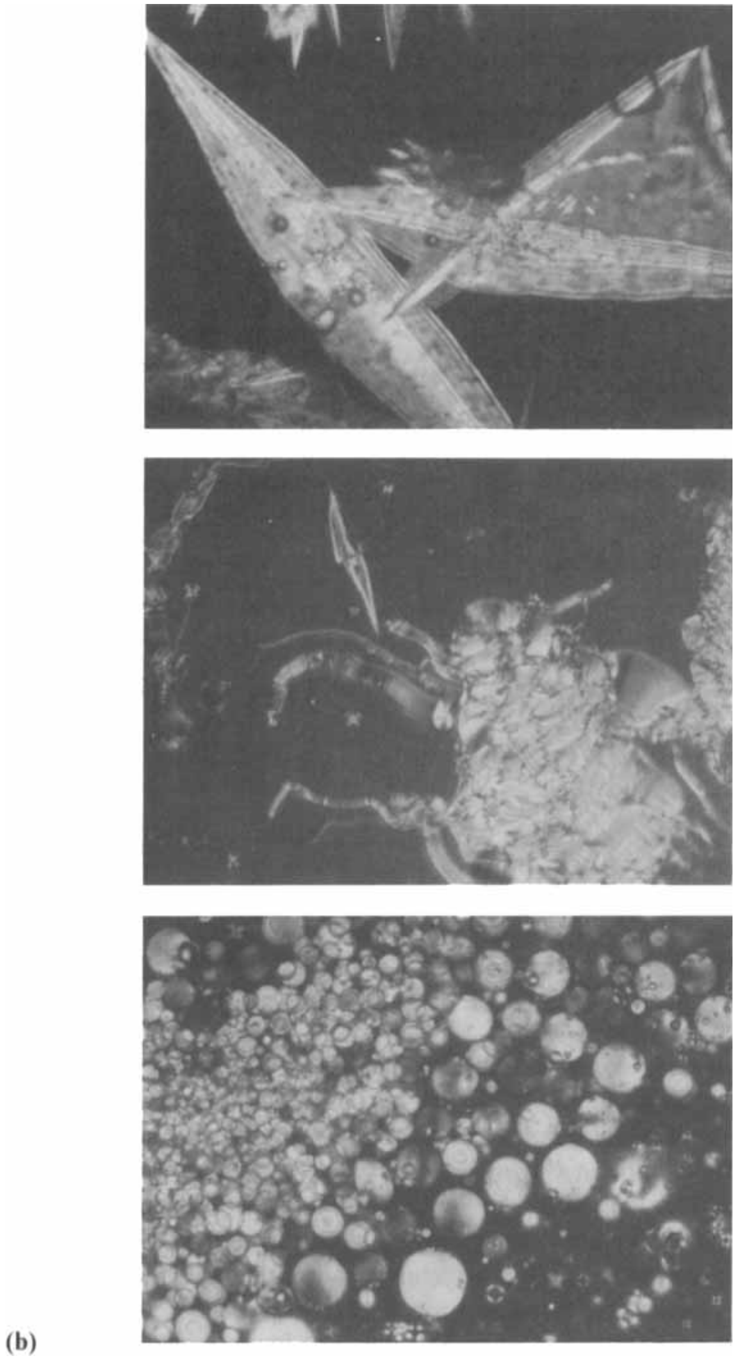


FIGURE 1 (Continued).

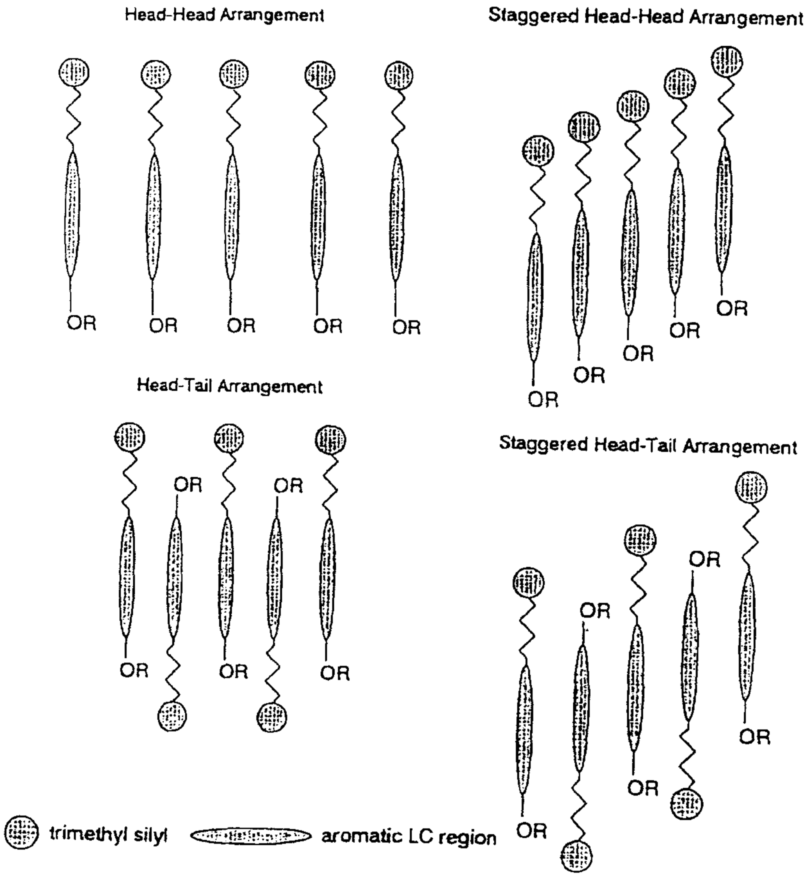


FIGURE 2 Possible Head–Head and Head–Tail Arrangements for Compounds with Bulky End Groups in Smectic Mesophase.

attractive force, necessary for smectic mesophase formation. It is very likely that the polar Si–Cl bond contributes to a much stronger dipole moment and thereby to stronger dipole–dipole intermolecular attractions; these forces being electrostatic in origin can act over a long range unlike van der waals' forces. This long range dipolar cohesive force between the molecules, in spite of being counteracted by steric repulsive forces, must be strong enough to maintain a layered structure against thermal fluctuations. It appears that the critical factor to form a smectic phase is a layered structure, but not necessarily a close packed one. The lower transition temperatures as well as clearing temperatures of these chlorosilyl compounds can be thus attributed to the increased intermolecular distance in the crystal and smectic phases. We propose the partial bilayer structure (Fig. 3) to be a very likely arrangement for molecules with bulky polar ends (**3**, **4**). The reasons for this proposal is discussed latter in this section.

The dimers **5** and **6** were prepared as shown in Scheme I. Only one prominent peak was seen in the DSC of **5**; the transition observed at around 137° in microscopy is not clearly seen in DSC (Fig. 4). It may be due to low enthalpy changes associated with smectic transitions [12]. The two transitions observed for **6** in DSC are also seen under microscope. Both of them show smectic phases in contrast to the dimeric systems of A. C. Griffin *et al.* with siloxane spacers. They did not show any mesomorphism; the alternating bond angles, 0-C-Si and Si-0-Si, preventing the two aromatic cores in adopting either a collinear or parallel arrangement were cited as possible reasons [8–9]. Introduction of the methylene spacers in **5** and **6** increases the length and internal flexibility of the molecules and allows the aromatic ring to adopt, very likely, a parallel arrangement. Recent X-ray diffraction work by Hardouin *et al.* [10] on smectic oligo- and polysiloxanes showed a partial bilayer arrangement of molecules in smectic mesophases; they observed the same layer spacing of smectic phases in dimeric- oligo- and poly-siloxanes suggesting a similar arrangement of

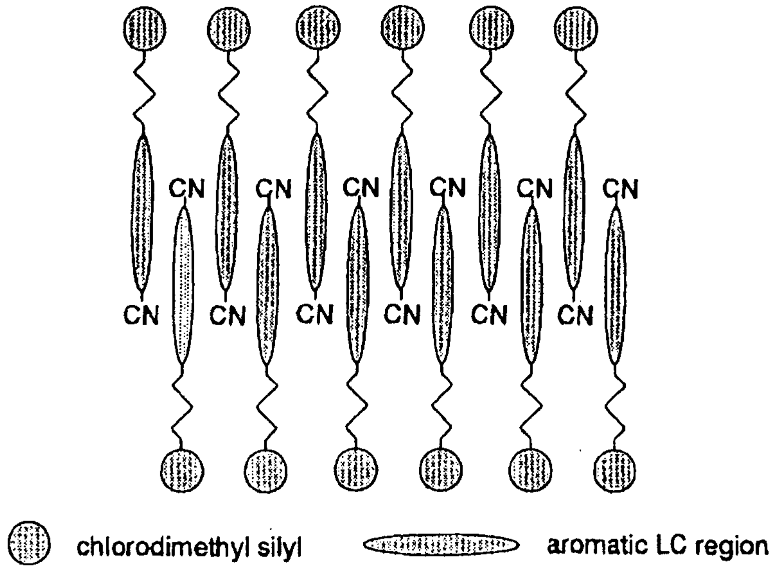


FIGURE 3 Proposed Packing for Compounds with Polar Bulky End Groups in Smectic Mesophase.

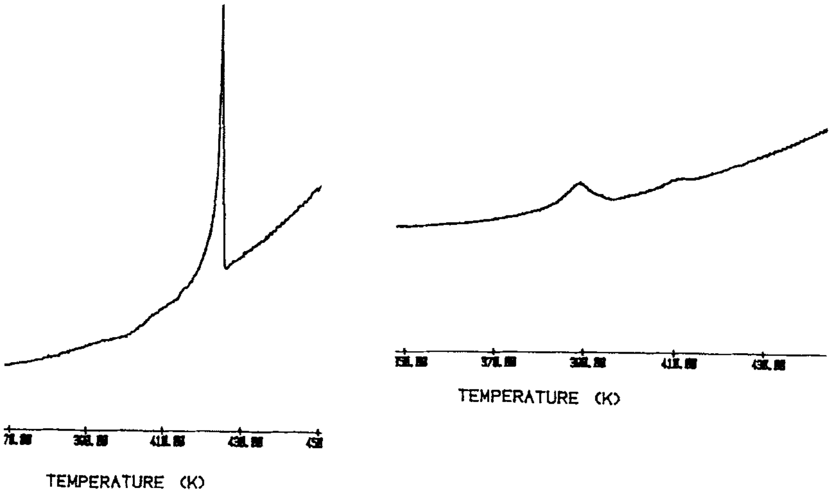


FIGURE 4 DSC curve of dimers 5 & 6.

mesogenic groups inside these partial bilayers. The layer spacing data strongly suggest that the extended conformation of these molecules do not exist, at least, in the smectic phase, but favor some bent conformation with very likely parallel alignment of aromatic cores. Geometry and energy optimizations of the extended and bent conformers by MMX method support that these molecules prefer the lower energy bent conformations. MMX calculations were done using Pcmodel; dihedral angle constraint was used during the optimization of the bent conformation. Calculated heats of formation and the optimized geometries are shown in Figure 5.

Considering the similarity of chlorosilyl and siloxy groups, one would expect the chlorosilyl monomers to act in the same fashion forming a partial bilayer. Basically the chlorosilylmethylene units in the monomer or the siloxymethylene units in the dimer or in the polymer act like fences around the locked-in mesogenic units in the partial bilayer. This idea is illustrated for the dimer in Figure 6.

Thus the chlorosilyl monomers or the dimeric siloxanes may very well be taken as a good model for side chain polysiloxanes. They are not good models for rigid-flexible-rigid polymers, since they are not as constrained as polymer [11] due to the motional freedom of the extremely flexible siloxane spacers. This work suggests that there is a high probability that bulky, non-polar end groups will preclude mesomorphic behavior due to steric repulsions; however, polar bulky groups, due to long range electrostatic

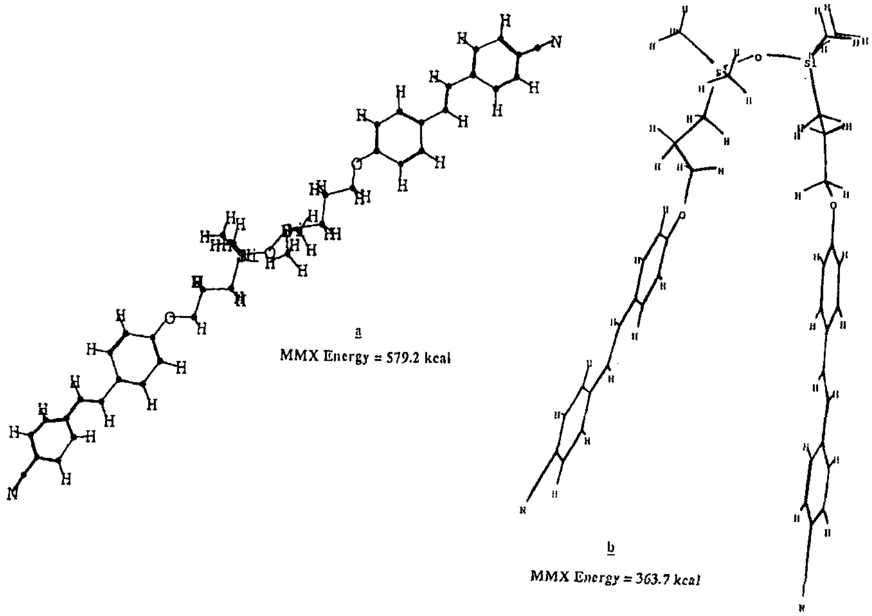


FIGURE 5 Optimized Geometries of 5: (a) Extended Conformer (b) Two views of bent conformer.

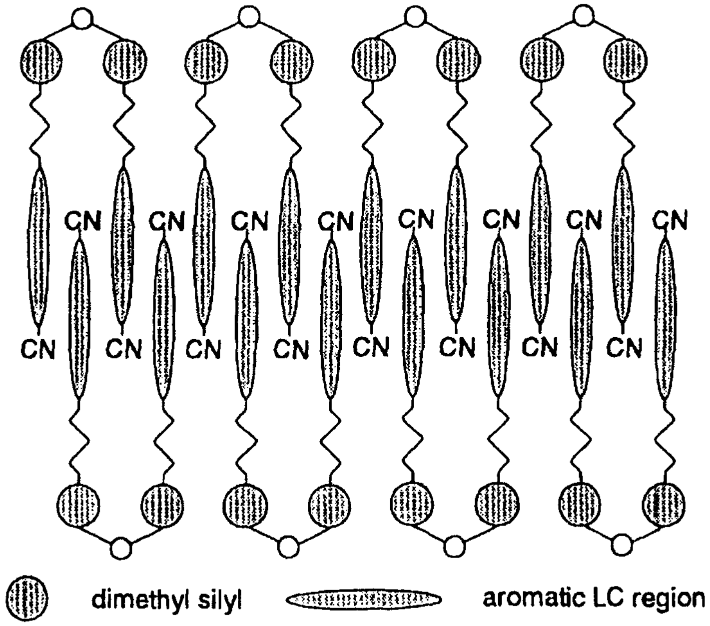


FIGURE 6 Proposed Packing for Dimeric Compounds 5 and 6 in Smectic Mesophase.

forces overpower repulsive steric interactions and tend to favor smectic mesophases. This fact can be exploited to tailor smectic liquid crystals to the specific needs of the applications or devices. If this hypothesis is correct, analogous molecules with non-polar bulky *t*-butyl groups should fail to form smectic mesophases. Immediate proof comes from the schiff's bases synthesized by Young *et al.* Currently synthesis of *t*-butyl analogs of **2** and **4** are being undertaken to see whether it holds good even in stilbenes with alkyl spacers and thus to confirm its generality.

Acknowledgement

The author thanks Professor Gilpin for use of instrumentation facility, samples and for constructive suggestions and Dr. Tittelbach for the art work.

EXPERIMENTAL SECTION

Materials and Techniques

Most chemicals needed for synthesis were purchased from Aldrich Chemicals Company (Milwaukee, WI) and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric GN-300 Spectrometer. Infrared spectra were recorded on an IBM model IR/32 F-IR spectrometer. The microscopic studies were made in triplicate at heating rate of 2°C or 10°C/min. using a Leitz-Wetzler Ortholux polarizing microscope fitted with a modified Mettler FP-2 heating stage. Photographs were taken using a Leitz microscopic 35 mm camera and Kodak Ektachrome film (160 ASA). The DSC scans were recorded using a Perkin-Elmer model DSC-2 differential scanning colorimeter with a scan rate of 2.5°/min. under nitrogen.

Synthesis

4′-cyano-4-alkyloxystilbene 1

Absolute ethanol (25 mL) solutions of 4-cyanobenzyltriphenylphosphonium chloride (14 g, 0.034 m) and 4-allyloxybenzaldehyde (5.68, 0.034 mol) were mixed with lithium ethoxide (0.2 M, 170 mL). The solution was stirred for 3 days at RT and water was added (140 mL). The precipitated stilbene was filtered, washed with absolute ethanol, dried and purified from a mixture of toluene and petroleum ether. mp (cp) 143.4° Yield. 16.9%; IR (Diffused Reflectance): 1600, 1510, 1460, 1410, 1250, 1180, 1120, 925, 830, 725, 565, 525 cm; ^{1}H NMR ($CDCl_3$) δ: 7.58–7.43 (m, 6H, aromatic), 7.17–7.12 (d, 1H, —CH=), 6.95–6.9 (m, 3H, aromatic), 6.15–6.0, 5.5–5.25 (m, 3H, —CH_2=CH), 4.56 (t, 2H, —$0CH_2$); ^{13}C NMR ($CDCl_3$) δ: 159.03, 142.15, 132.92, 132.39, 131.87, 129.15, 128.21, 126.51, 124.56, 119.10, 117.85, 115.04, 109.99, 68.79.

4′-cyano-4-pentenoxystilbene 2

It is prepared by the same procedure as described under **1**. Yield 20%, mp (cp) 123–125°; IR (Diffused Reflectance) (solid); 2200, 1600, 1500, 1450, 1160, 1100, 975, 925, 830, 650, 585, 550, 475 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 7.51–7.41 (m, 6H, Aromatic) 7.14–7.09 (d, 1H, —CH=), 6.9–6.86 (m 3H aromatic), 5.82, 5.03 (m, ABX, vinylic), 3.96 (t, 2H, —$0CH_2$), 2.24, 1.87 (m, 4H, —CH_2 CH_2); ^{13}C NMR ($CDCl_3$) δ: 159.40, 142.08, 132.54, 132.25, 131.84, 128.77, 128.13, 126.38, 124.23, 119.01, 115.15, 109.81, 67.13, 29.94, 28.24.

4′-cyano-4-(3-chlorodimethylsilyl) propyloxystilbene 3

A mixture of **1** (1.04 g, 0.001, mol), chloroplatinic acid (THF soln, 0.122 M, 3 mL), toluene (5 mL) and chlorodimethylsilance (0.38 g, 0.004 mol) was heated at ≈40–50°C for 16 h. The hot reaction mixture was filtered (under N2) and allowed to crystallize. Yield. 97%, ^{1}H NMR ($CDCl_3$) δ: 8.17–7.98, 7.8–7.7, 7.5–7.44 (m, Aromatic and olefinic), 4.5 (m, 2H, —OCH_2), 2.45 (m, 2H, —CH_2), 1.22 (m, —CH_2), 0.67 (s, 6H, —$SiCH_3$); ^{13}C NMR ($CDCl_3$) δ: 159.58, 142.18, 1232.39, 121.94, 128.22, 126.48, 123.50, 119.11, 117.86, 113.78, 109.93, 70.00, 22.89, 14.13, 0.1.

4′-cyano-4-(5-chlorodimethylsilyl)-pentyloxystilbene, 4

It is prepared using the same procedure as described under **3**. Yield 76.9% ^{1}H NMR ($CDCl_3$) δ: 7.52–7.36 (m, 6H, Aromatic) 7.1–7.04 (d, 1H, —CH=), 6.87–6.81 (m, 3H, aromatic), 3.9 (t, 2H, —$0CH_2$), 173 (m, 2H, —CH_2), 1.45 (m, 4H, —CH_2 CH_2), 0.78 (m, 2H, —CH_2), 0.35 (s, 6H, —$SiCl_3$) ^{13}C NMR ($CDCl_3$) δ: 159.49, 142.11, 132.27, 131.66, 128.73, 128.15, 126.40, 124.22, 119.03, 116.70, 109.80, 67.78, 29.19, 28.14, 22.11, 18.78, 1.56.

Dimer of 3, 5

A mixture of **3** (0.8899, 0.0025 mol) and toluene saturated with water (5 mL) was refluxed for 24 h and cooled. The white jelly-like solid was filtered, recrystallized from a mix of toluene and petroleum ether. Yield 58.5%, mp (cp) 151.6°C; IR (neat-solid): 2924, 2222, 1597, 1512, 1252, 1174, 1064–1037, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.61–7.46, 7.14, 6.92 (m, Aromatic and olefinic), 3.97 (m, 2H, $—OCH_2$), 1.86 (m, 2H, $—CH_2$), 0.68 (m, $—CH_2$), 0.14, 0.04 (s, 6H, $—SiCH_3$); ^{13}C NMR ($CDCl_3$) δ: 159.52, 142.14, 1232.31, 131.10, 128.71, 128.14, 126.40, 124.23, 118.99, 115.74, 114.73, 70.39, 23.08, 14.13, 0.21.

Dimer of 4, 6

It is prepared by the same procedure described under **5**. Yield 50.2% mp (cp) 137.6°C; IR (neat solid): 2924, 2222, 1597, 1502, 1252, 1174, 1064–1037, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.61–7.32 (m, Aromatic) 7.4, 7.17, 6.90 (m, aromatic and olefinic), 3.97 (t, 2H, $—0CH_2$), 1.77 (m, 2H, $—CH_2$), 1.49 (m, 4H, $—CH_2CH_2$), 0.57 (m, 2H, $—CH_2$), 0.05 (s, 6H, $—SiCH_3$); ^{13}C NMR ($CDCl_3$) δ: 159.54, 142.11, 132.33, 131.01, 128.86, 128.72, 128.33, 124.23, 119.05, 114.68, 109.86, 61.76, 29.59, 28.87, 23.03, 18.23, 0.31.

References

[1] W. R. Young, T. Haller and D. C. Green, *Mol. Cryst. Liq. Cryst.*, **13**, 305 (1971).
[2] D. Creed, J. R. D. Gross, S. L. Sullivan, A. C. Griffin and C. E. Hoyle, *Mol. Cryst. Liq. Cryst.*, **149**, 185 (1987).
[3] C. Aguilera and L. Bernal, *Poym. Bull.*, **12**, 383 (1984).
[4] Y. Oscaryir, Y. Lai, J. Ratio and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **185**, 75 (1990).
[5] G. Subramaniam and R. K. Gilpin, *Macromolecules*, **23**, 693 (1990).
[6] B. Grant, N. J. Clecak and R. J. Cox, *Mol. Cryst. Liq. Cryst.*, **51**, 209 (1979).
[7] M. Petrzilka, R. Buchecber, S. Leeschmiederer, M. Schadt and A. Germann, *Mol. Cryst. Liq. Cryst.*, **148**, 123 (1987).
[8] J. W. Ensley, G. R. Luckhurst and G. N. Shilstone, *Mol. Phys.*, **53**, 1023 (1984).
[9] J. A. Buglione, A. Roviello and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, **106**, 169 (1984).
[10] F. Hardouin, H. Richard and H. F. Achard, *Liquid Crystals*, **14**, 971 (1993)
[11] A. C. Griffin and E. T. Samulski, *J. Am. Chem. Soc.*, **197**, 2975 (1985).
[12] G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals, Textures and Structures*, Leonard Hill, Glasgow and London, 1984, p. 66.