# Liquid Crystals

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

# Phase transitions in novel disulphide-bridged alkoxycyanobiphenyl dimers

Santanu Kumar Pal[a]; V. A. Raghunathan[a]; Sandeep Kumar[a]
[a] Raman Research Institute, Bangalore - 560 080, India

**To cite this Article** Pal, Santanu Kumar , Raghunathan, V. A. and Kumar, Sandeep(2007) 'Phase transitions in novel disulphide-bridged alkoxycyanobiphenyl dimers', Liquid Crystals, 34: 2, 135 — 141

**To link to this Article: DOI:** 10.1080/02678290601061280

**URL:** http://dx.doi.org/10.1080/02678290601061280

*Liquid Crystals*, Vol. 34, No. 2, February 2007, 135–141

# Phase transitions in novel disulphide-bridged alkoxycyanobiphenyl dimers

SANTANU KUMAR PAL, V. A. RAGHUNATHAN and SANDEEP KUMAR*
Raman Research Institute, C.V. Raman Avenue, Bangalore - 560 080, India

(*Received 27 April 2006; in final form 28 July 2006; accepted 10 August 2006*)

The synthesis, characterization and mesomorphic properties of the first examples of novel disulphide-bridged alkoxycyanobiphenyl dimers are reported. The thermal behaviour of these mesogens was investigated by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. The dimers with a shorter spacer exhibit only the nematic phase while dimers with a longer spacer display nematic as well as smectic phases. X-ray diffraction experiments reveal the intercalated structure of the SmA phase of these dimers and the presence of short range SmA-like order in the N phase (cybotactic nematic) of all the compounds, except the one with the shortest spacer.

## 1. Introduction

Although the first examples of liquid crystalline dimers were reported by Vorlander in 1927 [1], they attracted particular attention during the 1980s. Griffin and Britt showed that a liquid crystalline dimer, a precursor to main chain polymeric liquid crystals, can be prepared by coupling two mesogenic units with an aliphatic spacer [2]. Subsequently, several classes of dimeric liquid crystals have been prepared and studied extensively [3]. The interest in these materials stems not only from their ability to act as model compounds for semi-flexible main chain liquid crystalline polymers but also from their properties which are quite different from those of conventional low molar mass mesogens [3].

Dimers containing two calamitic units show interesting mesomorphic behaviour depending on the length of the spacer and structure of the linking group. For example, dimesogenic compounds containing an oligosiloxyl group form smectic mesophases regardless of the nature of the terminal substituent, whereas the same type of compounds having a methylene spacer form only nematic phases [4, 5]. An ether linkage between the mesogenic unit and the central polymethylene spacer usually produces nematogens, whereas an ester linkage induces smectogenic properties in the system [5].

The effects of methylene, ethylene oxide and siloxane spacers on the mesomorphic properties of symmetrical and unsymmetrical liquid crystalline dimers containing alkoxycyanobiphenyl have been studied by Creed *et al.* [6]. It is generally observed that the nematic–isotropic transition temperatures are higher for compounds with an alkoxy chain than for an alkyl chain with the same total number of atoms. This difference is attributed to the higher anisotropy of the molecular polarizability expected for an ether linkage in comparison with a methylene group. Using a molecular field theory for flexible molecules, Emerson and Luckhurst showed that the difference in behaviour between the alkoxy- and alkyl-cyanobiphenyl-based monomers and dimers can be attributed entirely to difference in the geometry [7].

The formation of self-assembled monolayers (SAMs) by thiols, disulphides and thioethers on metals, particularly on gold, is well documented. SAMs provide a convenient, flexible and simple system for studies in nanoscience and nanotechnology. A variety of thiols and disulphides have been used to prepare SAMs [8]. A literature survey reveals that while disulphide-bridged discotic dimers have been synthesized and used to prepare SAMs [9], calamitic dimesogenic compounds having a disulphide-bridge in the linking unit have not yet been explored. In the case of simple alkoxycyanobiphenyl dimers with a polymethylene spacer, the all-*trans* conformation is favoured. There is a large difference in energy between the *cis* and *trans* conformations. The *cis* conformation energy is lower as it requires steric hindrance between two hydrogens in the methylene units. On the other hand, in the case of sulphur-bridged alkoxycyanobiphenyl no hydrogen atom is attached to the sulphur group and thus there will be no steric hindrance. The statistical average of *trans* conformation will be lower in these materials. The geometry and torsional potential of the disulphide

---

*Corresponding author. Email: skumar@rri.res.in

*Liquid Crystals*
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601061280

group would influence the molecular shape and hence the transition temperatures [7].

We have recently reported the synthesis and characterization of mesogenic thiol-functionalized alkoxycyanobiphenyls [10] and their self-assembled monolayers on gold [11]. In order to study the effect of sulphur atoms in the linking unit on mesomorphism and SAMs, we have prepared the first examples of disulphide-bridged mesogenic alkoxycyanobiphenyl dimers. Their synthesis, characterization and mesomorphic behaviour are now reported.

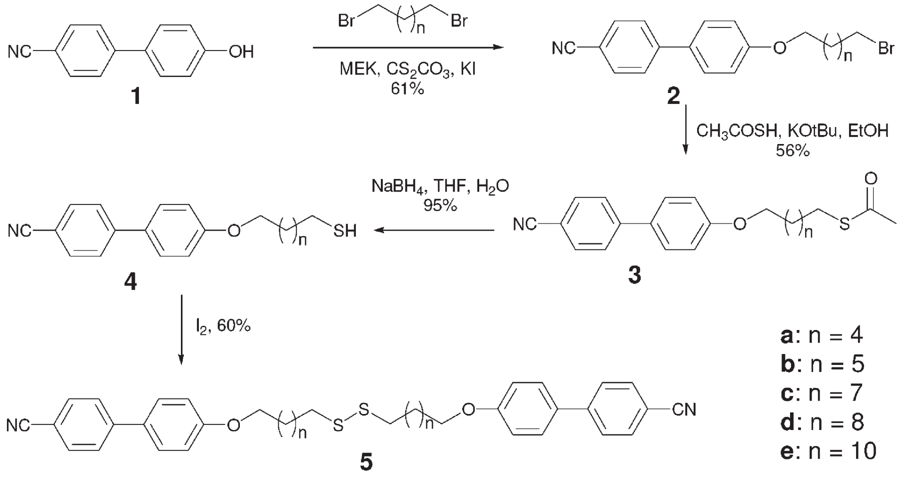
## 2. Experimental

### 2.1. *Chemical synthesis*

The synthesis of disulphide-bridged alkoxycyanobiphenyls **5** is outlined in scheme 1. Commercially available 4′-hydroxy-4-biphenylcarbonitrile **1** was alkylated under classical conditions with an excess of the appropriate $\alpha,\omega$-dibromoalkane to obtain the $\omega$-brominated product **2** [12]. The bromo-terminated alkoxycyanobiphenyls **2** were converted to thioacetates **3** by reacting with thioacetic acid. Hydrolysis of the thioacetates furnished the desired thiol-terminated alkoxycyanobiphenyls **4** which on oxidation with iodine afforded the desired dimers **5**. Since the synthetic details for the preparation of **4** and **5** for different chain lengths are essentially identical, only the procedures for the preparation of **4a** and **5a** are described. The structures of all the compounds were elucidated from their $^1$H NMR, $^{13}$C NMR, IR, and UV spectra and elemental analysis. Spectral data and elemental analysis of all the compounds were in good agreement with their structures, indicating the high purity of all the materials.

**2.1.1. 4′- [(6-Sulphanylhexyl)oxy][1,1′-biphenyl]-4-carbonitrile (4a).** Compound **3a** (100 mg) was dissolved in THF (5 ml) and the solution was degassed by bubbling $N_2$ for 5–10 min. A solution of $NaBH_4$ (45 mg) in 5 ml distilled water was added. The resulting mixture was kept at room temperature with stirring for 24 h under nitrogen. It was then poured into distilled water and the mixture extracted with dichloromethane (3 × 25 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The residue was purified by silica gel column chromatography (eluant: hexane/$CH_2Cl_2$, 1/1) to afford **4a** (84 mg, 95%). $^1$H NMR: (400 MHz, $CDCl_3$): $\delta$ 7.7 (d, $J$=8.2 Hz, 2H), 7.6 (d, $J$=8.2 Hz, 2H), 7.5 (d, $J$=8.6 Hz, 2H), 6.9 (d, $J$=8.6 Hz), 4.0 (t, $J$=6.4 Hz, 2H), 2.7 (q, $J$=7.4 Hz, 2H), 1.3–1.9 (m, 9H). $^{13}$C NMR: (100 MHz, $CDCl_3$): 159.8, 145.3, 132.5, 131.4, 128.4, 127, 119, 115, 110, 68, 33.9, 29.7, 29.1, 28, 25.5, 24.5.

**2.1.2. 4′-{[6-({6-[(4′-Cyano[1,1′-biphenyl]-4yl)oxy]hexyl}-disulphanyl)hexyl]oxy}[1,1′-biphenyl]-4-carbonitrile (5a).** Compound **4a** (100 mg, 0.32 mmol) was dissolved in dichloromethane (5 ml) and an excess of iodine (50 mg) added. The resulting mixture was stirred overnight at room temperature. It was then poured into a 5% solution of sodium thiosulphate and the mixture extracted with dichloromethane (3 × 25 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulphate and evaporated to dryness. The residue was then passed through a small silica column using 1/1 dichlomethane/petroleum ether as eluant to afford **5a** (60 mg, 60%). $^1$H NMR: (400 MHz, $CDCl_3$): $\delta$ 7.7 (d, $J$=8.2 Hz, 4H), 7.6 (d, $J$=8.2 Hz, 4H), 7.5 (d, $J$=8.6 Hz, 4H), 6.9 (d,



Scheme 1. Synthetic routes to disulphide-bridged alkoxycyanobiphenyl dimers.

Table 1. Phase transition temperatures (peak temperature in DSC, °C) and associated enthalpy changes (kJ mol$^{-1}$, in parentheses) of terminally thioacetate, thiol-functionalized alkoxycyanobiphenyl and their dimers. Cr=crystalline phase; N=nematic phase; Sm A=smectic A phase; I=isotropic phase.

| Compound | Heating scan | Cooling scan |
|---|---|---|
| **3b** | Cr 84 (43) I | I 65 (43) Cr |
| **3c** | Cr 74 (13) Cr 79 (46) I | I 62 (42) Cr |
| **4b** | Cr 60.1 (34) N 71.2 (0.5) I | I 70.4 (0.5) N 46.2 (33) Cr |
| **4c** | Cr 67.8 (39) I | I 65.5 (0.7) N 49.4 (35) Cr |
| **5a** | Cr 130.4 (55) I | I 124.2 (3) N 91.2 (44) Cr |
| **5b** | Cr 97.2 (49) N 109 (0.5) I | I 108.2 (1.7) N 75 (48) Cr |
| **5c** | Cr 96.3 (52) N 106.9 (2.5) I | I 105.8 (2.5) N 56.7 (46) Cr |
| **5d** | Cr 75.2 (2) Cr 95.8 (70) Sm A 100.2 (0.04) N 108.6 (4) I | I 107.5 (4) N 99.7 (0.04) Sm A 74.7 (55) Cr |
| **5e** | Cr 75.5 (3) 82.4 (6) Cr 96.9 (48) Sm A 100.5 (3) I | I 99.6 (6) Sm A 70.5 (44) Cr |

$J$=8.6 Hz, 4H), 4.0 (t, $J$=6.4 Hz, 4H), 2.7 (t, $J$=7.2 Hz, 4H), 1.5–1.9 (m, 16H). $^{13}$C NMR: (100 MHz, $CDCl_3$, all the derivatives **5a–e** show similar spectra): $\delta$ 159.8, 145, 132.6, 131.4, 128.4, 127.1, 119.0, 115.2, 110.2, 68, 39, 30.8, 29.1, 28.2, 25.7. Elemental analysis: calcd for $C_{38}H_{40}N_2O_2S_2$, C 73.53, H 6.48, N 4.51, S 10.35; found C 73.13, H 6.48, N 4.88, S 10.85%. IR: (KBr, all the derivatives **5a–e** show similar spectra) $\nu_{max}$ 2854.5, 2923.9, 2219.9, 1602.7, 1521.7, 1602.7, 1492, 1463.9, 1377, 1249.8, 1180.4, 1033.8, 831.3 cm$^{-1}$. UV-vis: ($CHCl_3$, all the derivatives **5a–e** show similar spectra): $\lambda_{max}$ 295.2 nm.

### 2.2. *Measurements*

Structural characterization of the compounds was carried out through a combination of infrared spectroscopy (Shimadzu FTIR-8400 spectrophotometer), $^1$H NMR as well as $^{13}$C NMR (Bruker AMX 400 spectrometer) and elemental analysis (Carlo-Erba 1106 analyser). IR spectra were obtained in Nujol mull for intermediate compounds and in KBr discs for the target compounds. $^1$H NMR spectra were recorded using deuteriated chloroform ($CDCl_3$) as solvent. Tetramethylsilane (TMS) was used as an internal standard.

The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (DSC, Perkin-Elmer, Model Pyris 1D) which was operated at a scanning rate 5°C min$^{-1}$ both on heating and cooling. The apparatus was calibrated using indium (156.6°C) as a standard. Textural observations of the mesophase were carried out using polarizing optical microscopy (Olympus BX51) provided with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90).

X-ray diffraction (XRD) was carried out on powder samples using Cu-K$_\alpha$ ($\lambda$=1.54 Å) radiation from a Rigaku ultrax 18 rotating anode generator (4 kW) monochromated with a graphite crystal. The samples were held in sealed Lindemann capillary tubes (0.7 mm diameter) and the diffraction patterns were collected on a two-dimensional Marresearch image plate. A magnetic field of about 5 kG was used to align the samples.

## 3. Results and discussion

The phase transition temperatures of all the new compounds investigated together with the transition enthalpy values determined by DSC are given in table 1. The lower homologues **5a–c** of the dimer series displayed a distinct nematic phase while smectogenic properties appeared for the higher members (**5d**, **e**).

The first member of the series **5a**, prepared by dimerization of the terminal thiol **4a** having six methylene units, showed only a monotropic nematic phase. The crystalline compound **5a** on heating melts at 130°C to the isotropic phase. However, on cooling, the nematic phase appears at 124°C, crystallizing at 91°C. The DSC traces obtained on the heating and cooling runs are shown in figure 1. Under the microscope a

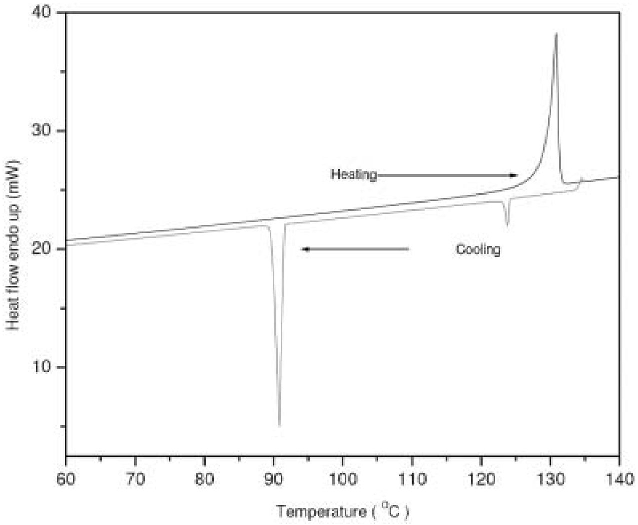


Figure 1. DSC thermogram of a sample of compound **5a** on heating and cooling; rate 5°C min$^{-1}$.

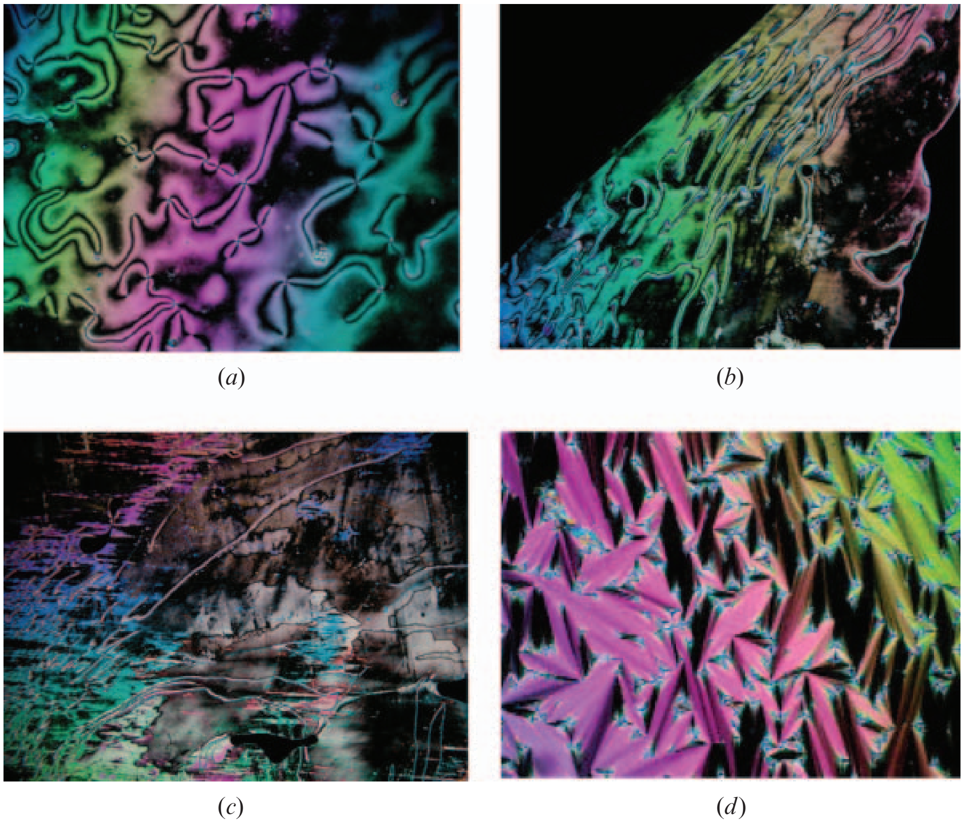


Figure 2. (*a*) Optical photomicrograph of compound **5a** at 105°C on cooling from isotropic liquid; (*b*) texture observed on cooling the isotropic liquid of compound **5b** at 100°C; (*c*) photomicrograph of the texture of the nematic phase of dimmer **5d** at 105°C; (*d*) focal-conic fan textures of SmA phase obtained on slow cooling the isotropic liquid of **5d** at 85°C (crossed polarizers, magnification ×200 for all the photomicrographs).

typical schlieren texture of the nematic phase is displayed, as shown in figure 2 (*a*).

Homologues **5b** and **5c** exhibit an enantiotropic nematic phase. Upon heating, they melt at about 97°C and 96°C to the nematic phase which clears at about 109°C and 107°C, respectively. On cooling, the nematic phase appears with only about one degree of supercooling in both compounds. The compounds crystallize at 75°C and 57°C, respectively, on further cooling. DSC traces and a photomicrograph of the nematic texture of compound **5b** are shown in figures 3 and 2 (*b*), respectively. Compound **5c** is particularly interesting. Although its DSC trace shows only a single isotropic–nematic transition at 105.8°C, POM reveals two other second order transitions. On cooling, the appearance of a SmA phase at 83°C and a reentrant nematic phase at 68°C can be clearly seen under the POM.

Compound **5d** shows both nematic and smectic mesophases; see figures 2 (*c*) and 2 (*d*) respectively. In DSC it shows first a crystal to crystal transition at about 75°C, then melts at 96°C to the Sm A phase which transforms to the nematic at about 100°C and finally clears at 109°C. On cooling, the isotropic to nematic phase transition appears at about 108°C and the N–SmA transition at 100°C. On continued cooling, the

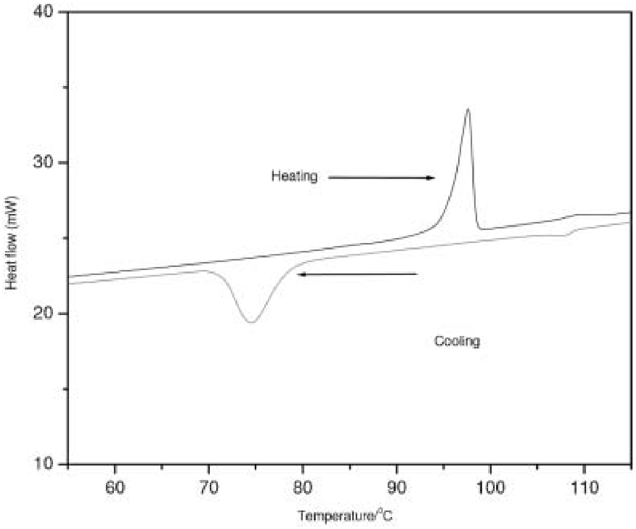


Figure 3. DSC traces for compound **5b** on heating and cooling; rate 5°C $\mathrm{min}^{-1}$.

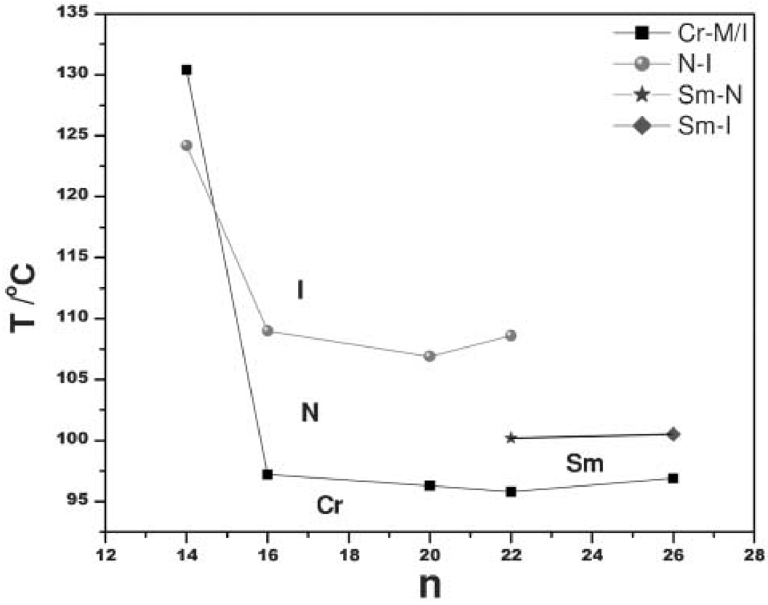


Figure 4. The dependence of the transition temperature on the number of atoms (m) in the spacer. For simplicity S atoms have been counted as carbon atoms. Cr=crystalline phase; M=mesophase; N=nematic phase; I=isotropic phase; Sm=smectic phase.

compound crystallizes at 75°C. In the 2nd heating run no crystal to crystal transition peak is discernable. Compound **5e** melts to the SmA phase at 97°C which clears at about 101°C. Before melting it also displays two crystal to crystal transitions at about 76°C and 82°C. On cooling the isotropic phase, the SmA phase appears at 99°C, crystallizing at 70°C.

The dependence of the transition temperatures on the number of atoms in the spacer for the thiol dimers is shown in figure 4. It is apparent that both melting points and the nematic–isotropic (N–I) temperatures exhibit a smooth falling tendency with increasing number of atoms in the spacer. The large change in $T_{\mathrm{N-I}}$ for the compounds with spacers of 14 and 16 atoms could be due to their different crystal packing densities. Deuterium NMR studies have shown that the order parameter for the methylene groups along the chain varies markedly and particularly, the order parameter of the methylene group at 7th and 8th position in 4-*n*-octyl-4′-cyanobiphenyl differ significantly [13].

In comparison with the well known alkoxycyanobiphenyl dimers, which show only N phases, the present series show both N and SmA phases. The $T_{\mathrm{N-I}}$ for the alkoxycyanobiphenyl series with odd and even number of methylene units alternate quite dramatically for short spacers, but for long spacers this alternation has essentially vanished and $T_{\mathrm{N-I}}$ simply decreases by a small amount with increasing number of methylene units [14]. Because of the presence of a disulphide (–S–S–) bridge, the present series of dimers always posses an even number of atoms in the spacer, though they are derived from odd- and even-numbered precursors. All these dimers adopt a more or less coparallel structure and therefore, as expected, do not display any odd–even effect. The energy-minimized structure of compound **5a** is shown in figure 5. Interestingly, the N–I transitional entropy is significantly smaller for the present series

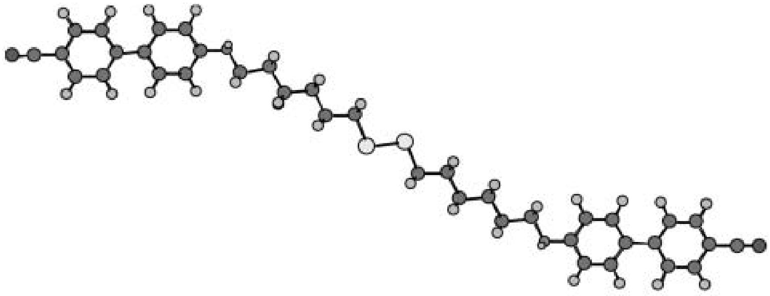


Figure 5. The MM2 energy-minimized structure of compound **5a**.

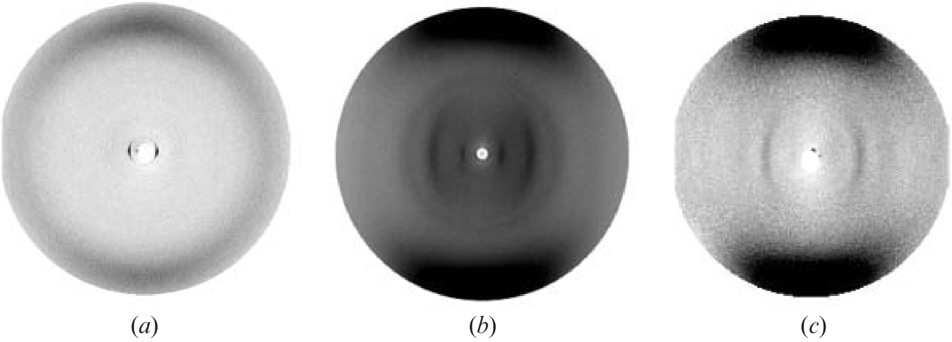

(*a*) (*b*) (*c*)

Figure 6. (*a–c*) X-ray diffraction patterns obtained for compound **5e**, **5b** and **5a** at 96, 100 and 110°C, respectively.

which suggests that the order in the nematic phase is small. This is also clear from X-ray diffraction experiments. Additionally the transition temperatures are much lower in the new compounds and the significant reduction in $T_{\mathrm{N-I}}$ from $m=14$ to $m=16$ is not shown by the alkoxycyanobiphenyl series.

Although the majority of symmetrical alkoxycyanobiphenyl dimers contain alkyl spacers, a few examples having different spacers such as diethylene oxide and disiloxane have been reported [6]. The nematic–isotropic transitions of these compounds are at much higher temperatures compared with the present dimers. This could be because of the increasing flexibility of the spacer due to the presence of a large number of carbon atoms. A similar effect has been observed in the case of oligoethylene oxide spacer [15].

## 4. X-ray diffraction studies

Diffraction patterns of the N and SmA phases of all the compounds show a diffuse peak in the wide angle region, in a direction normal to that of the magnetic field. It has a spacing of about 0.45 nm and corresponds to the average lateral separation of the molecules in these fluid phases. In the SmA phase of the dimer with the longest spacer (**5e**) a single sharp peak is observed in the small angle region of the diffraction pattern along the field direction, figure 6 (*a*). It has a spacing of 3.84 nm at 96°C, which matches very well with the spacing expected from an intercalated structure, see figure 7. This peak shifts to 3.60 nm at 100°C in the SmA phase of **5d**, consistent with the decrease in the length of the spacer. A broad peak at 3.52 nm is observed at 105°C in the N phase of **5d**, indicating the presence of SmA-like short range order in this phase. Such nematic phases with short range translational order are well known near the N–SmA transition and is related to the small enthalpy changes involved in this phase change.

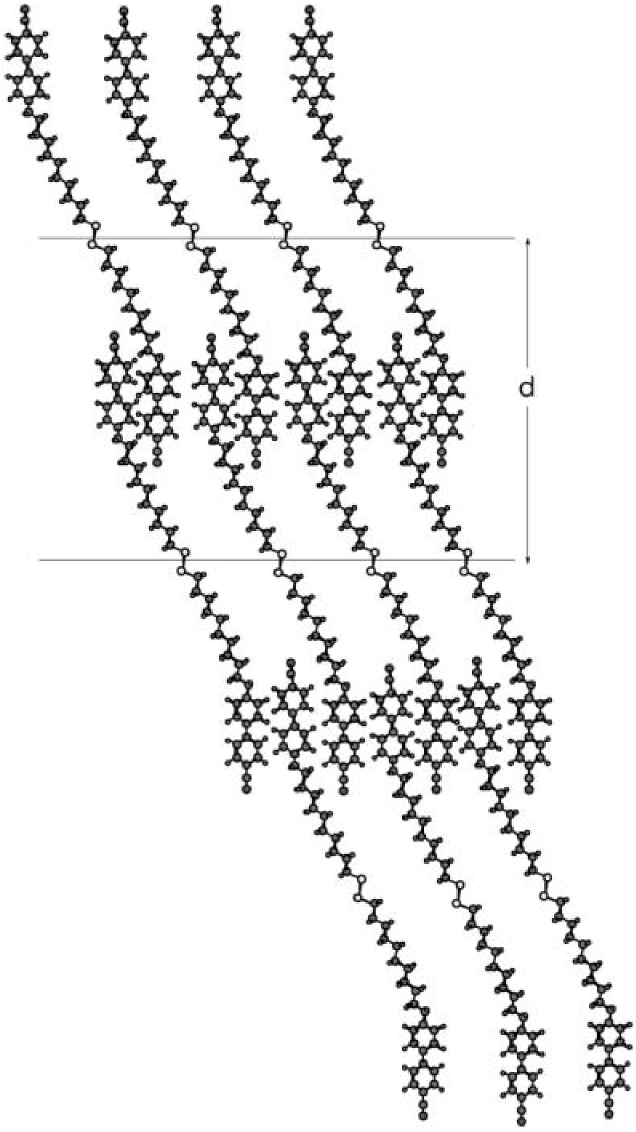


Figure 7. Sketch of the intercalated SmA phase exhibited by **5d**.

In compounds **5c** and **5b** a broad peak is observed in the N phase, at 3.35 and 2.95 nm, respectively, which indicates the presence of short range SmA-like order. Interestingly, these compounds give an additional broad peak in the small angle region of the diffraction pattern along the field direction, with spacings of 1.34 and 1.20 nm, respectively figure 6 (*b*). These spacings are approximately comparable to the length of the rigid aromatic core of the molecule. In the case of **5a** the peak corresponding to short range SmA-like order is absent and only a broad peak at 1.15 nm is observed, figure 6 (*c*). This is consistent with the observation that the SmA phase is stabilized with increasing spacer length. As the *d*-spacing in these dimers is significantly larger than the half length of the molecule, a U-shaped conformation was ruled out. The formation of intercalated smectic phases by several symmetric and non-symmetric dimers has been well documented in the literature [3, 16].

## 5. Conclusion

We have reported the first examples of alkoxycyanobiphenyl dimers having a disulphide bridge. X-ray diffraction experiments indicate an intercalated structure for the SmA phase of the higher members of the homologous series. The N phase, of all except the compound with the shortest spacer, shows the presence of short range SmA-like order. We have proposed a possible structural model for the mesophase on the basis of X-ray data. All these disulphide-bridged dimers form stable monolayers on a gold surface. The full characterization of these self-assembled monolayers is in progress and will be presented later.

## Acknowledgement

We are grateful to Professor N. V. Madhusudana for helpful discussions. The authors wish to thank Ms K. N. Vasudha for technical support and the NMR Research Center, Indian Institute of Science, Bangalore for recording the NMR spectra.

## References

[1] D. Vorlander. *Z. Phys. Chem.*, **126**, 449 (1927).

[2] A.C. Griffin, T.R. Britt. *J. Am. chem. Soc.*, **103**, 4957 (1981).

[3] C.T. Imrie, G.R. Luckhurst. In *Handbook of Liquid Crystal*, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds). Vol. 2B, p. 801, Wiley-VCH, (1998); 7lY. Maeda, H. Furuya and A. Abe. *Liq. Cryst.*, **21**, 365 (1996); D. Bauman, E. Wolarz and E. Bialecka-florjanczyk. *Liq. Cryst.*, **26**, 45 (1999); L. Melpezzi, S. Bruckner, E. Galbiati and G.R. Luckhurst. *Mol. Cryst. Liq. Cryst.*, **195**, 179 (1991); P.J. Barnes, A.G. Douglass, S.K. Heeks and G.R. Luckhurst. *Liq. Cryst.*, **13**, 603 (1993); D. Ionescu, G.R. Luckhurst and D.S. de Silva. *Liq. Cryst.*, **23**, 833 (1997); R.N. Shimizu, N. Asakawa, I. Ando, A. Abe and H. Furuya. *Magn. Reson. Chem.* **36**, S195 (1998); A. Abe and Su Yong Nam. *Macromolecules*, **28**, 90 (1995); D.J. Photinos, Edward T. Samulski and H. Toriuml. *J. chem. Soc. Faraday Trans.*, **88**, 1875 (1992); J.W. Emsley, G.R. Luckhurst and G.N. Shilstone. *Mol. Phys.*, **53**, 1023 (1984); H. Furuya, T. Dries, K. Fuhrmann, A. Abe, M. Ballauff and E.W. Fischer. *Macromolecules*, **23**, 4122 (1990); C.T. Imrie. In *Stucture and Bonding*, D.M.P Mingos (Ed.), Vol. 95, p. 149, Springer Verlag, Berlin, Heideberg (1999); J.W. Emsley, G.R. Luckhurst, G.N. Shilstone and I. Sage. *Mol. Cryst. liq. Cryst. Lett.*, **102**, 223 (1984).

[4] Jin Jung-IL. *Mol. Cryst. liq. Cryst.*, **267**, 249 (1995).

[5] B.-W. Jo, T.-K. Lim, J.-I. Jin. *Mol. Cryst. liq. Cryst.*, **157**, 57 (1988).

[6] D. Creed, J.R.D. Gross, S.L. Sullivan. *Mol. Cryst. liq. Cryst.*, **149**, 185 (1987).

[7] A.P.J. Emerson, G.R. Luckhurst. *Liq. Cryst.*, **10**, 861 (1991).

[8] X. Li, J. Huskens, D.N. Reinhoudt. *J. mater. Chem.*, **14**, 2954 (2004); J. Christopher Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo and G.M. Whitesides. *Chem. Rev.*, **105**, 1103 (2005).

[9] H. Schonherr, F.J.B. Kremer, S. Kumar, J.A. Rego, H. Wolf, H. Ringsdorf, M. Jaschke, H. Butt, E. Bamberg. *J. Am. chem. Soc.*, **118**, 13051 (1996).

[10] S. Kumar, S.K. Pal. *Liq. Cryst.*, **32**, 659 (2005).

[11] V. Ganesh, S.K. Pal, S. Kumar, V. Lakshminarayanan. *J. colloid interface Sci.*, **296**, 195 (2006).

[12] G.S. Attard, R.W. Date, C.T. Imrie, G.R. Luckhurst, S.J. Roskilly, J.M. Seddon, L. Taylor. *Liq. Cryst.*, **16**, 529 (1994).

[13] J.W. Emsley, G.R. Luckhurst, C.P. Stockley. *Proc. r. Soc. Lond. A*, **381**, 117 (1982).

[14] G.R. Luckhurst. *Liq. Cryst.*, **32**, 1335 (2005).

[15] I. Sledzinska, E. Bialecka-Florjanczyk, A. Orzesko. *Eur. poly. J.*, **32**, 1345 (1996).

[16] For example see, C.T. Imrie, P.A. Henderson. *Curr. Opin. colloid interface Sci.*, **7**, 298 (2002); A.E. Blatch, I.D. Fletcher and G.R. Luckhurst. *J. mater. Chem.*, **7**, 9 (1997); J. Watanabe, H. Komura and T. Niiori. *Liq. Cryst.*, **13**, 455 (1993).