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Effect of introducing thioether linkages on the molecular organization of chiral twin liquid crystals

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Novel symmetric and non-symmetric chiral twin compounds possessing one or two thioether groups in a central spacer were prepared, and the effect of substituting oxygen for sulphur on the liquid crystalline properties investigated. Chiral twin compounds possessing an alkylsulphanyl spacer showed an antiferroelectric phase exclusively. However, replacing the alkyloxy chain of the analogous monomer by the alkylsulphanyl chain has no significant effect on the phase transition behaviour, i.e. both of the monomers showed the ferro- and ferri-electric phases as well as the antiferroelectric phase. Thus, different effects of introducing the thioether linkage were for the first time observed between twin and monomeric systems. The introduction of oxygen or sulphur atoms into the central alkyl spacer of the chiral twin was also investigated, and these modifications were found to stabilize the SmA phase. Furthermore, the twin compound possessing a thiaalkyl spacer showed two different molecular assemblies in the smectic A phase.

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1. Introduction

The introduction of sulphur atoms into alkyl chain moieties is an interesting structural modification of liquid crystal molecules, which is known to have a significant effect on the molecular dynamics. The molecular flexibility of alkyl (R–CH$_2$–), alkyloxy (R–O–) and alkylsulphanyl (R–S–) chains attached to the aromatic mesogenic core has been investigated and has been found to increase in the following order: $R\text{–O–} < R\text{–S–} < R\text{–CH}_2\text{–}$ [1]. The flexible conformational mobility produced by oxyethylene moieties has been well known in liquid crystal systems [2]; a similar effect was also observed in compounds having a thiaalkyl chain [3]. The effect of the substitution of the alkoxy terminal chain for an alkylsulphanyl chain has also been investigated in detail and the frustrated phase was found to be removed by the introduction of the alkylsulphanyl chain [4]. Sulphur is more polarisable than oxygen so that an alkylsulphanyl chain is a useful component in terms of producing high birefringent liquid crystal materials [5]. A liquid crystal possessing sulphur is also interesting if it shows the intriguing ferrielectric or SmC$^*_\alpha$ phase, because the resonant X-ray technique can be applied to such compounds and the numbers of layers constituting the superlattices evaluated [6]. In this study, novel chiral twin liquid crystals having an alkylsulphanyl or thiaalkyl chain were prepared and the liquid crystalline properties investigated and compared with those of the corresponding alkoxy or oxaalkyl compound (figure 1).

2. Experimental

The final chiral compounds studied were obtained by esterification between (*S*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate [7] and the respective acid intermediates by the dicyclohexylcarbodiimide/4-dimethylaminopyridine (DCC/DMAP) method [8]. The detailed preparation procedures for **Ia** [9], **IIa** [10], **IIIa** [11] and **IVa** [12] have been reported previously; the corresponding thioether compounds **Ib**, **IIb**, **IIIb** and **IVb** were prepared using similar methods from 4-mercaptobenzoic acid as starting material, the alkylation being performed under a nitrogen atmosphere. The acid intermediate for **Va** was prepared from 1,2-bis(2-chloroethoxy)ethane as a starting dihalide compound, using similar preparative procedures as for the acid part of **IIa** [10]. The acid part of **Vb** was prepared by Mitsunobu coupling [13] between ethyl 4-hydroxybenzoate and 3,6-dithia-1,8-octanediol, followed by hydrolysis of the resulting ester.

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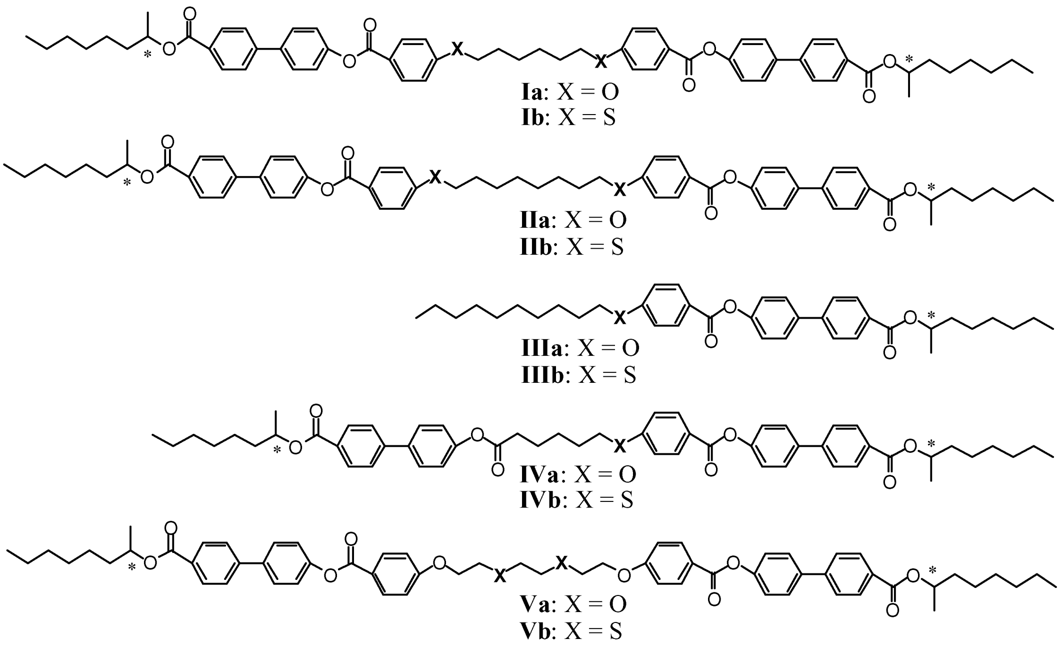

Figure 1. Molecular structures of the compounds studied.

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The structures of the final compounds were elucidated by elemental analysis, ^{1}H NMR, IR, and mass spectrometry. The phase assignments and corresponding transition temperatures were determined by thermal optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD), as reported earlier [10].

2.1. *(S,S)-α,ω-Bis{4-[(4′-(1-methylheptyloxycarbonyl)-4-biphenylyl)oxycarbonyl]phenylthio}hexane (**Ib**)*

(*S*)-1-Methylheptyl 4-hydroxybiphenyl-4′-carboxylate (1.30 g, 4.0 mmol), α,ω-bis(4-carboxyphenylthio)hexane (0.78 g, 2.0 mmol), and DMAP (0.05 g, 0.4 mmol) were added to dry dichloromethane (10 ml). DCC (1.23 g, 6.0 mmol) was then added and the resulting mixture stirred at room temperature for 3 days. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography over silica gel (70–230 mesh, Sigma-Aldrich Co.) using a mixture of dichloromethane/hexane (5/1) as eluant, and the resulting product was recrystallized from ethyl acetate (82 ml), to give a colourless solid; yield 0.76 g (38%). Elemental analysis: found C 73.7, H 7.0, S 6.1; calcd for $C_{62}H_{70}O_8S_2$ C 74.0, H 7.0, S 6.4%. NMR δH (300 MHz, $CDCl_3$, TMS): 8.13 (m, 4H, Ar-**H**), 8.10 (m, 4H, Ar-**H**), 7.66 (m, 8H, Ar-**H**), 7.38–7.26 (m, 8H, Ar-**H**), 5.18 (m, 2H, –C***H**(CH_3)–), 3.04 (t, 4H, –**C**$\mathbf{H_2}$S–, $^3J=7.3$ Hz), 1.76–1.29 (m, 34H, aliphatic-**H**), 0.88 (two overlapping triplets, 6H, –CH_2–$\mathbf{CH_3}$). ν/cm^{-1} (KBr): 2928, 2859 (C–H str.), 1745, 1723 (C=O str.), 1595 (C–C str.). *m*/*z*: 1006 (M^+).

2.2. *(S,S)-α,ω-Bis{4-[(4′-(1-methylheptyloxycarbonyl)-4-biphenylyl)oxycarbonyl]phenylthio}octane (**IIb**)*

This homologue was prepared from (*S*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate (1.44 g, 4.4 mmol) and α,ω-bis(4-carboxyphenylthio)octane (0.84 g, 2.0 mmol), using the procedure described for **Ib**. The crude product was purified by column chromatography over silica gel using a mixture of dichloromethane/hexane (1/1) as the eluant, and the resulting product was recrystallized from ethyl acetate (60 ml), to give the product as a colourless solid; yield 0.44 g (21%). Elemental analysis: found C 74.1, H 7.1, S 6.2; calcd for $C_{64}H_{74}O_8S_2$ C 74.3, H 7.2, S 6.2%. NMR δH (300 MHz, $CDCl_3$, TMS): 8.13 (m, 4H, Ar-**H**), 8.10 (m, 4H, Ar-**H**), 7.66 (m, 8H, Ar-**H**), 7.37–7.29 (m, 8H, Ar-**H**), 5.18 (m, 2H, –C***H**(CH_3)–), 3.03 (t, 4H, –**C**$\mathbf{H_2}$S–, $^3J=7.3$ Hz), 1.74–1.29 (m, 38H, aliphatic-**H**), 0.88 (two overlapping triplets, 6H, –CH_2–$\mathbf{CH_3}$). ν/cm^{-1} (KBr): 2926, 2855 (C–H str.), 1741, 1728, 1715 (C=O str.), 1593 (C–C str.). *m*/*z*: 1034 (M^+).

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2.3. *(S)-1-Methylheptyl 4′-(4″-n-decylthiobenzoyloxy)biphenyl-4-carboxylate (**IIIb**)*

This compound was prepared from (*S*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate (1.30 g, 4.0 mmol) and 4-*n*-decylthiobenzoic acid (1.23 g, 4.0 mmol), using the procedure described for **Ib**. The crude product was purified by column chromatography over silica gel using a mixture of dichloromethane/hexane (1/1) as the eluant, and the resulting product was recrystallized from ethanol (30 ml), to give a colourless solid; yield 1.34 g (56%). Elemental analysis: found C 75.5, H 8.3, S 5.1; calcd for $C_{38}H_{50}O_4S$ C 75.7, H 8.3, S 5.3%. NMR δH (300 MHz, $CDCl_3$, TMS): 8.12 (m, 4H, Ar-**H**), 7.67 (m, 4H, Ar-**H**), 7.37–7.30 (m, 4H, Ar-**H**), 5.19 (m, 1H, –C***H**(CH_3)–), 3.02 (t, 2H, –**CH**$_2$S–, $^3J=7.4$ Hz), 1.73–1.27 (m, 29H, aliphatic-**H**), 0.88 (two overlapping triplets, 6H, –**CH**$_3$). ν/cm^{-1} (KBr): 2923, 2851 (C–H str.), 1728 (C=O str.), 1597 (C–C str.). *m*/*z*: 602 (M^+).

2.4. *4′-[(S)-1-methylheptyloxycarbonyl]-4-biphenylyl 4″″-[5-[{4″-[(S)-1-methylheptyloxycarbonyl]-4‴-biphenylyl}oxycarbonyl]pentylthio]benzoate (**IVb**)*

This compound was prepared from (*S*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate (1.30 g, 4.0 mmol) and 4-(5-carboxypentylthio)benzoic acid (0.53 g, 2.0 mmol), using the procedure described for **Ib**. The crude product was purified by column chromatography over silica gel using a dichloromethane/hexane (5/2) mixture as the eluant, and recrystallized from a mixture of ethanol (50 ml) and ethylacetate (15 ml), giving a colourless solid; yield 0.92 g (53%). Elemental analysis: found C 74.5, H 7.3, S 3.4; calcd for $C_{55}H_{64}O_8S$ C 74.7, H 7.2, S 3.6%. NMR δH (300 MHz, $CDCl_3$, TMS): 8.11 (m, 6H, Ar-**H**), 7.69–7.61 (m, 8H, Ar-**H**), 7.39–7.17 (m, 6H, Ar-**H**), 5.18 (m, 2H, –C***H**(CH_3)–), 3.07 (t, 2H, –CH$_2$–**CH**$_2$S–, $^3J=7.1$ Hz), 2.63 (t, 2H, Ar–OCO–**CH**$_2$–CH$_2$–, $^3J=7.3$ Hz), 1.87–1.29 (m, 32H, aliphatic-**H**), 0.88 (two overlapping triplets, 6H, –CH$_2$–**CH**$_3$). ν/cm^{-1} (KBr): 2930, 2857 (C–H str.), 1752, 1728, 1709 (C=O str.), 1593 (C–C str.). *m*/*z*: 884 (M^+).

2.5. *(S,S-)-Triethylene glycol bis{4-[(4′-(1-methylheptyloxycarbonyl)-4-biphenylyl)oxycarbonyl]phenyl} ether (**Va**)*

This compound was prepared from (*S*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate (1.30 g, 4.0 mmol) and triethyleneglycol bis(4-carboxyphenyl) ether (0.78 g, 2.0 mmol), using the procedure described for **Ib**. The crude product was purified by column chromatography over silica gel using dichloromethane/hexane mixtures (50/2 ~ 50/0) as the eluant, and recrystallized from 40 ml of an ethanol/ethylacetate (1/1) mixture, giving a colourless solid; yield 1.38 g, (67%). Elemental analysis: found C 73.9, H 7.1; calcd for $C_{62}H_{70}O_{12}$ C 74.0, H 7.0%. NMR δH (500 MHz, $CDCl_3$, TMS); 8.16 (m, 4H, Ar-**H**), 8.11 (m, 4H, Ar-**H**), 7.65 (m, 8H, Ar-**H**), 7.30 (m, 4H, Ar-**H**), 7.02 (m, 4H, Ar-**H**), 5.18 (m, 2H, –C***H**(CH_3)–), 4.23 (t, 4H, –**CH**$_2$O–, $^3J=4.8$ Hz), 3.92 (t, 4H, –**CH**$_2$O–, $^3J=4.8$ Hz), 3.79 (s, 4H, –O–**CH**$_2$–**CH**$_2$–O–), 1.75–1.30 (m, 26H, aliphatic-**H**), 0.88 (two overlapping triplets, 6H, –**CH**$_3$). ν/cm^{-1} (KBr); 2957, 2930, 2861 (C–H str.), 1740, 1730, 1720 (C=O str.), 1605 (C–C str.), 857 (1,4-disub. C–H o.o.p.d). *m*/*z*: 1006 (M^+).

2.6. *(S,S-)-1,8-Bis-{4-[(4′-(1-methylheptyloxycarbonyl)-4-biphenylyl)oxycarbonyl]phenoxy}-3,6-dithiaoctane (**Vb**)*

This compound was prepared from (*S*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate (0.70 g, 2.1 mmol) and 1,8-bis(4-carboxyphenoxy)-3,6-dithiaoctane (0.41 g, 1.0 mmol), using the procedure described for **Ib**. The crude product was purified by column chromatography over silica gel using a dichloromethane/hexane mixture (4/1) as the eluant, and recrystallized from 35 ml of an ethanol/ethyl acetate (2/5) mixture, giving a colourless solid; yield 0.65 g, (64%). Elemental analysis: found C 71.5, H 6.7, S 6.6; calcd for $C_{62}H_{70}O_{10}S_2$ C 71.7, H 6.7, S 6.2%. NMR δH (300 MHz, $CDCl_3$, TMS): 8.19 (m, 4H, Ar-**H**), 8.11 (m, 4H, Ar-**H**), 7.65 (m, 8H, Ar-**H**), 7.30 (m, 4H, Ar-**H**), 7.00 (m, 4H, Ar-**H**), 5.18 (m, 2H, –C***H**(CH_3)–), 4.27 (t, 4H, –O–**CH**$_2$–CH$_2$–S–, $^3J=6.5$ Hz), 3.01 (t, 4H, –O–CH$_2$–**CH**$_2$–S–, $^3J=6.5$ Hz), 2.95 (s, 4H, –S–**CH**$_2$–**CH**$_2$–S–), 1.75–1.30 (m, 26H, aliphatic-**H**), 0.88 (two overlapping triplets, 6H, –**CH**$_3$). ν/cm^{-1} (KBr); 2924, 2859 (C–H str.), 1738, 1707 (C=O str.), 1609 (C–C str.), 853 (1,4-disub. C–H o.o.p.d). *m*/*z*: 1038 (M^+).

3. Results

3.1. *Phase transition behaviour*

Phase transition temperatures, phase sequences and transition enthalpies for the new compounds prepared in this study are summarized in the table. In order to clarify the effect of replacing the ether linkage by thioether, transition temperatures are compared between compounds **Ia** and **Ib**, and also between **IIa** and **IIb** in figure 2. **Ia** showed ferroelectric and ferrielectric phases as well as the antiferroelectric phase, however, the corresponding thioether compound **Ib** showed the antiferroelectric phase exclusively. The antiferroelectric phase was identified by the application of an electric field to the sample placed in a commercially available evaluation cell (E.H.C. Co. Ltd., Japan), and a clear threshold behaviour was observed

Table. Phase transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) (in square brackets) for the chiral compounds studied.

Compound	Cr		Anti-ferro		Ferri		Ferro		SmA$'$		SmA		I
Ib	●	153.8 [59.59]	●		—		—		—		—	168.0 [17.20]	●
IIb	●	153.9 [85.02]	●		—		—		—		—	(143.0)[a] [16.77]	●
IIIb	●	95.7 [40.79]	●	(83.0)[a] [-][b]	●	(85.3)[a] [-][b]	●	(91.7)[a] [-][b]	—		●	107.7 [6.14]	●
IVb	●	110.8 [41.61]	●		—		—		—		—	140.5 [12.75]	●
Va	●	135.6 [52.9]	●		—		—		—		●	141.6 [4.3]	●
Vb	●	143.5 [53.76]	●		—		—		●	123.8 [1.97]	●	134.5 [3.78]	●

[a] ( )Indicates monotropic phase transition.
[b] Enthalpy is too small to be measured.

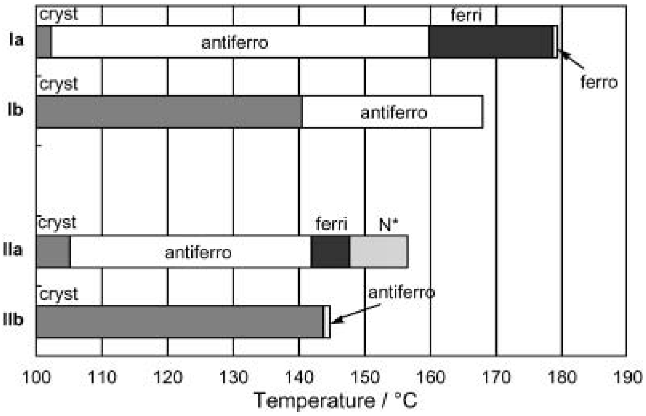

Figure 2. Comparison of the phase transition behaviour between alkoxy twins (**Ia** and **IIa**) and alkylsulphanyl twins (**Ib** and **IIb**).

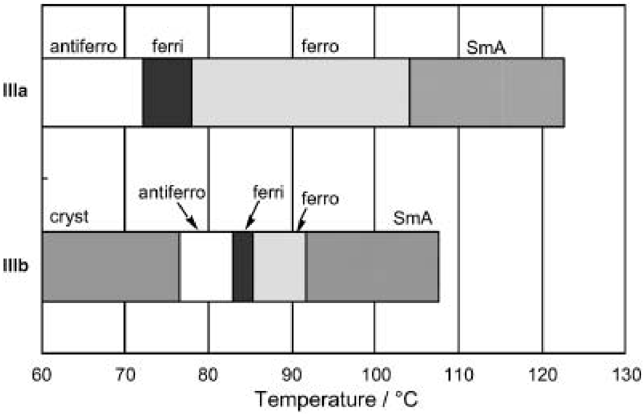

Figure 3. Comparison of the phase transition behaviour between monomeric compounds possessing an alkoxy (**IIIa**) and alkylsulphanyl (**IIIb**) chain.

at the electrically induced antiferro–ferro transition. Compound **Ib** showed a more stable antiferroelectric phase than **Ia**, i.e. the upper limit temperature of the antiferroelectric phase of **Ib** (168.0°C) is higher than that of **Ia** (159.7°C).

In the case of the monomeric system, a totally different effect was observed. The same phase sequence, i.e. I–SmA–ferro–ferri–antiferro, was this time obtained for the alkyloxy (**IIIa**) and alkylsulphanyl (**IIIb**) monomers as shown in figure 3. Thus, the different effects of introducing sulphur atoms were for the first time observed between the monomeric and twin systems. This difference may be attributed to the different flexibility between the peripheral alkyl chain of the monomer and the central alkyl spacer of the twins. The central spacer of the twin possesses two mesogenic parts at both sides, whereas only one mesogen is attached to the peripheral chain of the monomer. Therefore, the alkyl chain of the monomer is considered to move more freely, reducing the effect produced by the thioether linkage.

One may suspect that the number of thioether groups in each molecule is related to the different effects observed between the monomeric and twin compounds, because the twins **Ib** and **IIb** possess two thioether groups whereas the monomer **IIIb** has only one. In order to check this possibility, a non-symmetric chiral twin compound **IVa**, which possesses only one ether linkage in the spacer, was examined. Phase transition behaviour of **IVa** and the thioether analogue **IVb**, where the ether linkage of **IVa** is replaced by the thioether group, is compared in figure 4. Compound **IVb** showed the antiferroelectric phase exclusively as did **Ib** and **IIb**, even though **IVb** possesses just one thioether group. This result indicates that the molecular configuration, whether a twin or monomer, plays a

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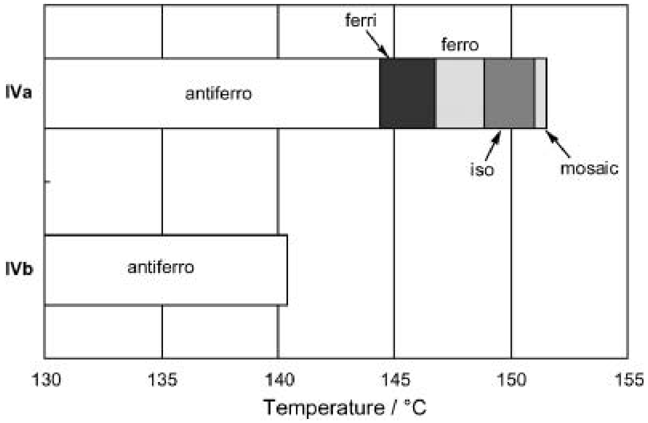

Figure 4. Comparison of the phase transition behaviour between twin compounds possessing one ether group (**IVa**) and one thioether group (**IVb**).

more important role than the number of the thioether linkages in the stabilization of the antiferroelectric phase.

Finally, the introduction of oxygen or sulphur atoms into the central spacer was studied. The octylene spacer of **IIa** was replaced by 3,6-dioxaoctylene to produce **Va**, and similarly **Vb** was produced by introducing a 3,6-dithiaoctylene central spacer. A totally different phase sequence appeared after these modifications. The parent twin **IIa** showed N*, ferri- and antiferro-electric phases, however, **Va** and **Vb** showed only the smectic A phase (figure 5). The SmA phase of **Va** showed characteristic homeotropic and fan-shaped textures. However, **Vb** showed an unusual textural change as shown in figure 6. At 132°C in the SmA phase, a common fan-shaped texture was observed, figure 6 (*a*), however, with a decrease in temperature, many stripes appeared along the layer normal, figure 6 (*b*); below the SmA–SmA′ transition, the smoothness usually observed for the SmA fan-texture was completely destroyed, producing the characteristic texture shown in figure 6 (*c*). One possible explanation for this textural change is the appearance of the modulation of the smectic layered structure, which is known to be

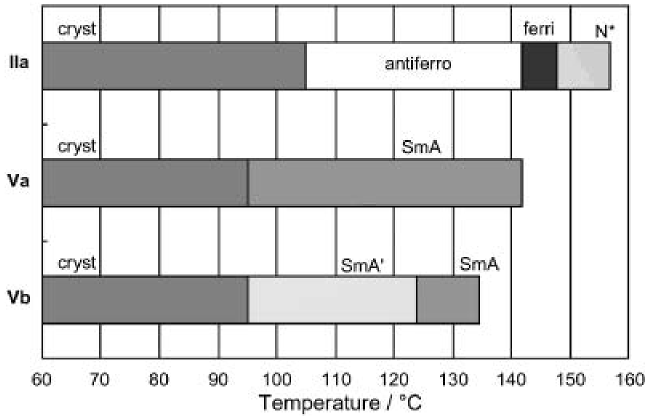

Figure 5. Comparison of the phase transition behaviour between twin compounds possessing an alkyl spacer (**IIa**), an oxaalkyl spacer (**Va**), and a thiaalkyl spacer (**Vb**).

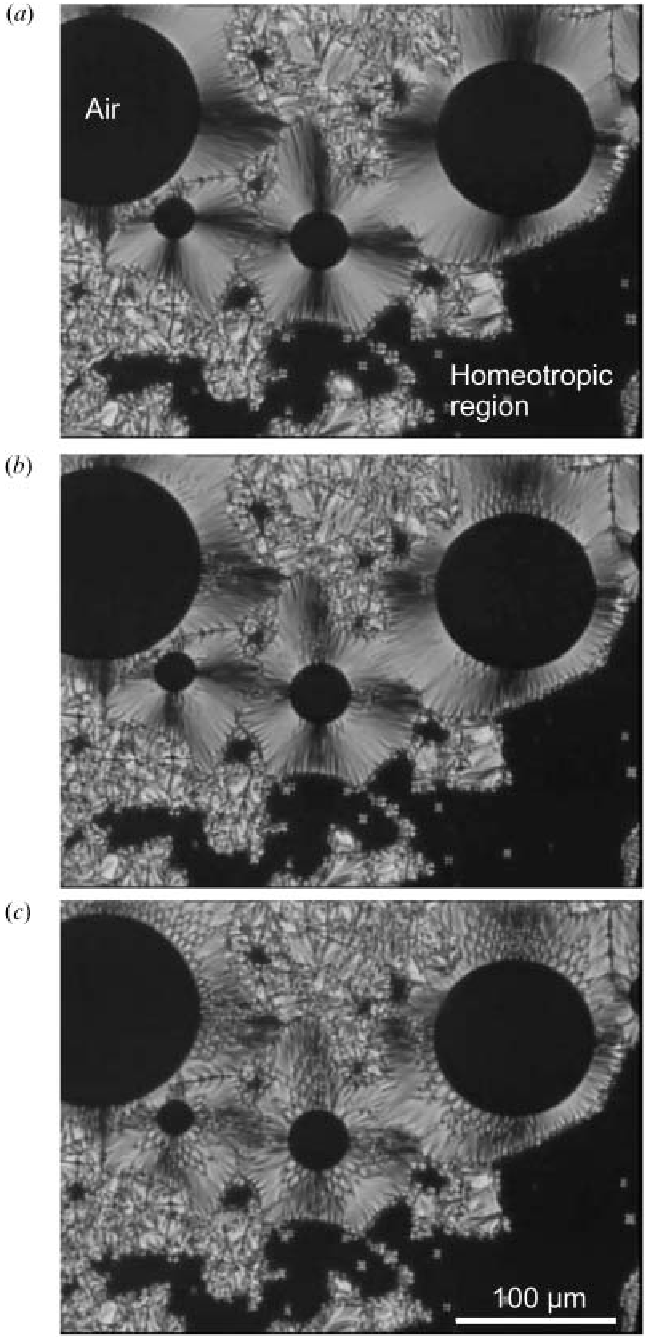

Figure 6. Optical textures of **Vb** observed in (*a*) the SmA phase (132°C), (*b*) the SmA phase (126°C), and (*c*) the SmA′ phase (122°C).

produced by the shrinkage of the layer thickness. It should be noted that a completely dark homeotropic texture was observed both in the SmA and SmA′ phases and that no textural change was observed with decreasing temperature.

3.2. *Differential diffraction*

Figure 7 shows the DSC thermograms for compounds **Ia** and the thioether analogue **Ib**. **Ia** exhibited a broad diffuse DSC peak in the isotropic phase as reported earlier [9], however **Ib** did not show such an unusual peak. Similarly, **IIb** did not show a broad DSC peak in the isotropic liquid phase. A DSC profile for **Va** is shown in figure 8, where a sharp peak was obtained corresponding to the I–SmA transition. However, **Vb** possessing a thiaalkyl spacer, showed an anomalous DSC profile (figure 8). A clear but rather broad DSC peak was obtained at the SmA–SmA′ transition, indicating that the SmA and SmA′ are thermodynamically different phases. The broad shape of the peak suggests that the transition between the phases occurs rather gradually.

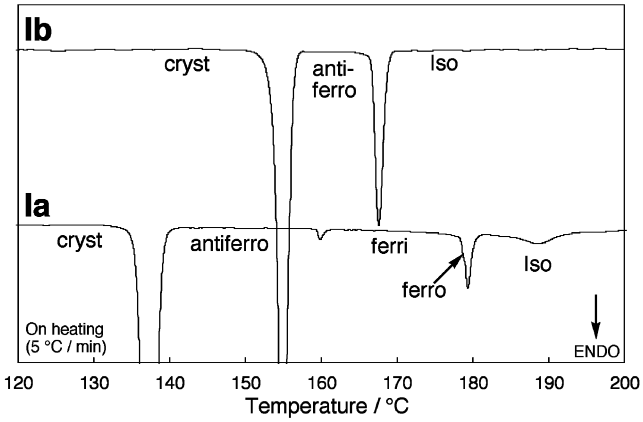

Figure 7. DSC thermograms of **Ia** and **Ib**.

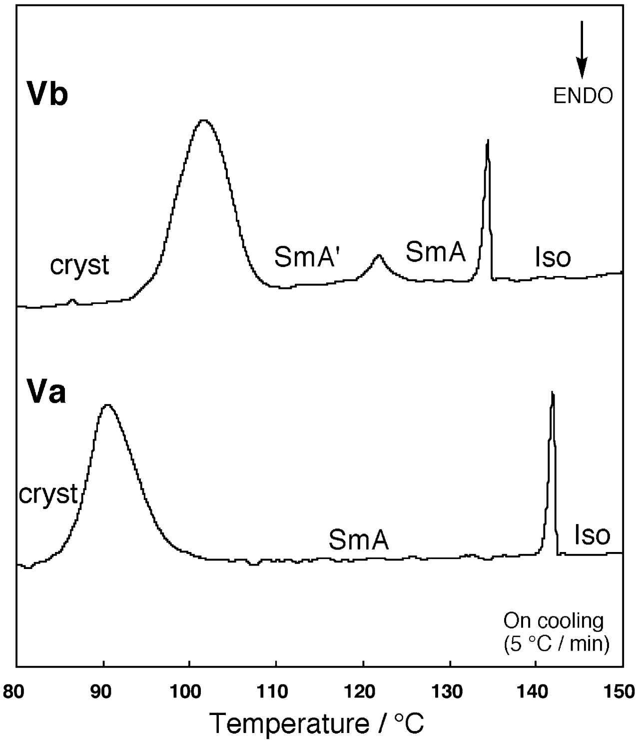

Figure 8. DSC thermograms of **Va** and **Vb**.

3.3. *X-ray diffraction*

Figure 9 shows wide angle XRD scattering patterns obtained in the smectic phases. Compounds **Ia** and **Ib** showed first and second order sharp peaks in the small angle region corresponding to smectic layer spacing. Similar profiles were obtained for **IIa** and **IIb**. The appearance of the second order peak indicates the formation of a relatively well defined smectic layer structure, which can promote the anticlinic molecular ordering of the antiferroelectric phase. Compounds **Ia** and **Ib** showed a broad scattering in the wide angle region, indicating that the antiferroelectric phase is a sub-phase of the smectic C phase. A scattering profile in the SmA phase of **Va** showed only one sharp peak corresponding to smectic layer spacing. The second order reflection was not observed this time, indicating that the layer periodicity of the SmA phase of **Va** is not well defined. The XRD pattern of the SmA phase of **Vb** is similar to that of **Va**, however in the SmA′ phase, a peak corresponding to the layer spacing shifted to larger 2θ values, i.e. the layer spacing decreased. In addition, the peak intensity increased and a very weak second order peak appeared in the SmA′ phase, indicating that a stronger smectic ordering was formed in the SmA′ phase. This phase showed just a broad scattering in the wide angle region which is consistent with the phase assignment that this is not a higher-ordered smectic phase but is in the family of SmA phases.

Figure 10 shows interlayer spacings obtained for the compounds **IIa**, **IIb**, **Va** and **Vb**, as a function of temperature. The interlayer spacing was calculated from the peak in the small angle region of the XRD profile. Compound **IIa** showed a spacing of 43 Å just below the clearing point. The smectic layer spacing of **IIb** was found to be around 40–42 Å. Shorter spacing values than the molecular length is attributable to molecular tilt in the smectic phases of **IIa** and **IIb** The layer spacing in the SmA phase of **Va** showed a gradual decrease with a decrease in temperature, from 42 Å at 141.7°C to 39 Å at 104.6°C, where no discontinuous

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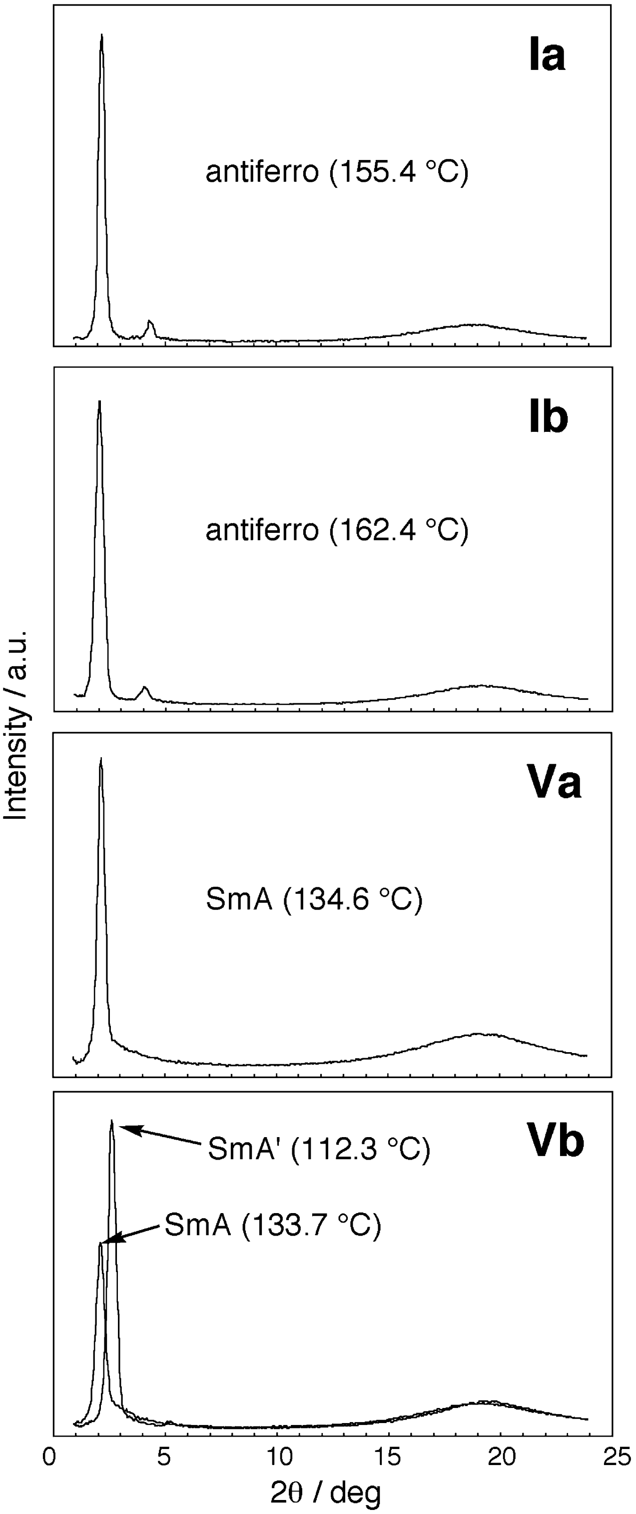

Figure 9. X-ray scattering patterns of **Ia**, **Ib**, **Va** and **Vb**.

change was observed over the whole temperature range of the SmA phase. However, the spacing of **Vb** changed significantly around the SmA–SmA′ transition.

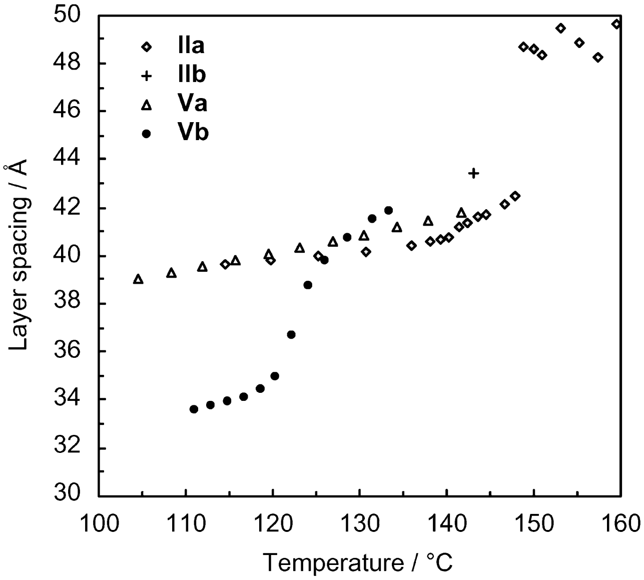

Figure 10. Layer spacing for **IIa**, **IIb**, **Va** and **Vb**, as a function of temperature.

4. Discussion

The introduction of thioether groups as links between the flexible spacer and the mesogenic rigid cores was found to stabilize the antiferroelectric phase, thus the chiral twins **Ib**, **IIb** and **IVb** showed a direct isotropic liquid–antiferroelectric phase transition. A stable antiferroelectric phase has previously been observed for bent-shaped twin compounds [14], however only a few straight-shaped twin compounds showing a stable antiferroelectric phase have been reported [9, 10, 12, 15, 16]. The bond angle of the thioether linkage is known to be smaller than that of the ether linkage, which could lead locally to a more bent configuration, however **Ib** and **IIb** are twins with an even spacer containing two C–S–C bond angles, so that the overall molecular structure is not bent but slightly S-shaped with a molecular width broader than that of the corresponding ether compounds. Few examples have been reported of the effect of introducing the thioether linkages into the twin molecular architecture [17], furthermore, to our knowledge, no systematic investigation has so far been performed on this effect. The results obtained in this work suggest that introducing thioether groups could be a useful molecular design approach, stabilizing the antiferroelectric ordering of twin molecules. The introduction of the thioether group itself has also been studied in the monomeric system. For example, replacing ether by thioether for some phenyl propiolates has been reported to reduce the stability of blue, twist grain boundary (TGB) and antiferroelectric phases [4]. No marked effect on the stabilization of the antiferroelectric phase,

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by introducing thioether, has been observed in the monomeric system.

The introduction the oxygen or sulphur atoms into the central spacer showed a significant effect on the phase type; the resulting twins **Va** and **Vb** showed the SmA phase exclusively. Since the SmA phase was also observed for the corresponding monomers possessing a short alkyl chain, the appearance of the SmA phase in **Va** and **Vb** may be attributed to the flexible conformational mobility produced by the modified spacer [2, 3]. This is because, if the correlation in motion and direction between two mesogen segments of each **Va** or **Vb** molecule is reduced due to the flexible central chain, the monomeric character is considered to be pronounced. The nature of the smectic orderings produced by compounds **I** (and also **II**) would be different from that produced by compounds **V** because of the strong difference in polarity and also in flexibility of the spacer. The smectic layer spacing (39–42 Å) of **Va** is shorter than the estimated maximum molecular length of 61 Å (by MM2 calculation) with all-*trans*-configuration, which is attributed to the higher conformational mobility of the central oxaalkyl spacer [2] making the overall molecular length shorter. Similarly, the smectic layer spacing in the SmA phase of **Vb** was found to be shorter than the molecular length, indicating that the thiaalkyl spacer also possesses a higher conformational flexibility [3]. Furthermore, **Vb** showed a marked decrease in the smectic layer thickness with decreasing temperature, which is consistent with the textural observation (figure 6) indicating possible layer shrinkage. This result suggests that the thiaalkyl spacer of **Vb** is sufficiently flexible to produce many possible conformations. The conformational variety could be the origin for the SmA–SmA′ phase transition. The DSC peak associated with this transition is rather broad which is consistent with the hypothesis that this is a kind of conformational transition between different molecular states. The strong polarity and flexibility of the central spacer of **Va** and **Vb** could even lead to U-shaped conformations due to the folding of the central spacer. In the SmA′ phase, the U-shaped conformation could be one of the major stable states, as the smectic layer spacing of the SmA′ phase is *c.* 33–35 Å, which is almost half of the molecular length.

5. Conclusions

The introduction of the thioether linkage instead of the ether group into the twin molecular configuration was found to stabilize the antiferroelectric phase, whereas that into the monomeric structure showed no significant effect on the phase transition behaviour. This is the first example showing a clearly different effect of introducing a thioether linkage between monomeric and twin systems. Introducing an oxaalkyl or thiaalkyl central chain into the chiral twin compound stabilized the SmA phase. The strong polarity and high mobility of the central spacer allows the thiaalkyl twin to produce a conformational transition in the SmA phase.

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