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Sulphur containing mesogens. The mesophasic behaviour of di(4-alkyloxybenzoates) of 4,4'-dimercaptobiphenyl

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Sulphur containing mesogens
The mesophasic behaviour of di(4-alkyloxybenzoates)
of 4,4'-dimercaptobiphenyl

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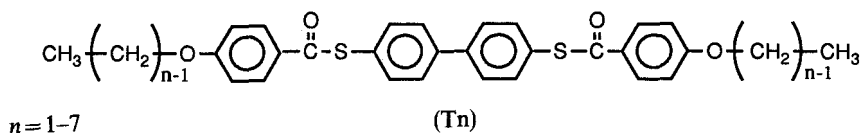
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A homologous series of di(4-alkyloxybenzoates) of 4,4'-dimercaptobiphenyl: $\text{CH}_3(\text{CH}_2)_{n-1}\text{O}-\text{C}_6\text{H}_4-\text{COS}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{SOC}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_{n-1}\text{CH}_3$, $n=1-7$, has been synthesized and the thermotropic liquid-crystalline behaviour investigated. All compounds exhibit enantiotropic mesomorphism over a remarkable temperature range. While the mesophase thermal stability is moderately higher than that found for the corresponding oxygenated analogues, the smectic stability is definitely lower. In fact, all the compounds are nematic but smectic mesomorphism (S_C) is observed for $n=7$. Compounds with $n=6$ or 7 exhibit enantiotropic highly ordered smectic (or disordered crystal) phases, probably S_G in type.

1. Introduction

Steric and electronic features both influence the mesogenic behaviour of a molecule and the evaluation of the relative importance of these two factors is one of the key points in the experimental and theoretical study of liquid crystals. The comparative analysis of the mesomorphic behaviour of strictly homologous compounds is a simple means of casting light upon the role played by specific structural parameters. Comparison of the phase behaviour of two compounds which differ by the nature of atoms having a specific stereochemical function is but one of many possible cases.

This paper reports the synthesis of some di(4-alkyloxybenzoates) of 4,4'-dimercaptobiphenyl:



their basic liquid-crystalline properties are discussed and compared to literature data for the oxygen-containing analogues. This research is complementary to our study of liquid-crystalline sulphur-containing main chain polymers [1].

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2. Experimental

The compounds were synthesized from 4,4'-dimercaptobiphenyl (DMB) and 4-alkyloxybenzoyl chlorides under interfacial conditions. Thioesters T1, T4 and T6 were also synthesized in pyridine solution.

2.1. Interfacial synthesis (exemplary procedure)

The syntheses were performed at room temperature with mechanical stirring. The apparatus was charged with DMB (2.0 mmol), sodium hydroxide (4.5 mmol), benzyltriethylammonium chloride (BTEAC) (0.22 mmol) and 30 ml of water under a nitrogen atmosphere. To this solution, the 4-alkyloxybenzoyl chloride (4.2 mmol) dissolved in 30 ml of CH_2Cl_2 was added and the mixture stirred for 1 h. The white precipitate was then filtered off. The organic phase was washed with dilute hydrochloric acid (2×50 ml, 10 per cent) and with distilled water (3×100 ml), dried and the solvent removed on a rotary evaporator. The solid residue was added to the precipitate and recrystallized from CHCl_3 /ethanol. For T1, precipitation during reaction was virtually complete and the compound was crystallized directly from toluene. Yields and characteristic data are reported in table 1.

2.2. Synthesis in solution (exemplary procedure)

The syntheses were performed using boiling pyridine. The apparatus was charged with DMB (2.0 mmol) and 45 ml of pyridine under a nitrogen atmosphere. To this solution, the 4-alkyloxybenzoyl chloride (4.2 mmol) dissolved in 5 ml of pyridine was added with stirring. The mixture was boiled for 20 min. It was then cooled to 60°C and 50 ml of ethanol was added. The precipitated product was recovered and recrystallized from CHCl_3 /ethanol (T4 and T6) or from toluene (T1). Yields are reported in table 1. All products were further purified by silica gel chromatography using chloroform as eluant and successive recrystallization from chloroform/ethanol solution.

4,4'-dimercaptobiphenyl (DMB) was synthesized according to Marvel and Caesar [2]. 4-Alkyloxybenzoyl chlorides were prepared by standard procedures from the acids (Aldrich Co.) They were distilled in vacuum immediately before use. Only 4-hexyloxybenzoyl chloride was purchased (Aldrich Co.) and utilized with no previous treatment. Pyridine was previously dried by distillation over molecular sieves. IR spectra were recorded on a Bruker IFS 48 FT-IR spectrometer. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer (chemical shifts are in ppm downfield from TMS).

The phase behaviour was examined by means of DSC, X-ray diffraction and polarizing microscopy. The DSC analysis was performed with a DSC-7 Perkin-Elmer apparatus under a dry nitrogen atmosphere and a scanning rate of $10^\circ\text{C min}^{-1}$. The X-ray diffraction patterns were recorded by the photographic method (flat-film camera) with Cu-K_α radiation. Samples were kept under a nitrogen atmosphere inside sealed glass capillaries. The temperature was controlled to within $\pm 2^\circ\text{C}$ by use of a microfurnace. Microscopic observation of phase transitions and liquid-crystalline textures were performed with a Leitz polarizing microscope equipped with a Linkam microfurnace. Samples were examined under a nitrogen atmosphere.

3. Results and discussion

The chemical structure of the thioesters T_n ($n = 1-7$) was confirmed by their FT-IR and ^1H NMR spectra (see table 1).

All the compounds are mesomorphic with large mesophase ranges. Thermal data concerning phase transitions are reported in table 2. Although the isotropization of

Table 1. Yields and characteristic data of the thioesters.

Compound	Yield % (a)	ν/cm^{-1} (b)	σ/ppm (c)
T1	83(I), 87(S)	1664	3.88 (s, 6 H) 7.12, 8.00 (2d, 8 H arom.) 7.65, 7.85 (2d, 8 H arom.)
T2	84(I)	1666	1.48 (t, 6 H) 4.15 (q, 4 H) 6.98, 8.02 (2d, 8 H arom.) 7.60, 7.70 (2d, 8 H arom.)
T3	68(I)	1659	1.08 (t, 6 H) 1.78, 1.95 (m, 4 H) 4.03 (t, 4 H) 6.98, 8.02 (2d, 8 H arom.) 7.60, 7.70 (2d, 8 H arom.)
T4	87(I), 84(S)	1662	1.00 (t, 6 H) 1.40, 1.62 (m, 4 H) 1.72, 1.90 (m, 4 H) 4.06 (t, 4 H) 6.97, 8.03 (2d, 8 H arom.) 7.60, 7.70 (2d, 8 H arom.)
T5	70(I)	1659	0.95 (t, 6 H) 1.35, 1.55 (m, 8 H) 1.75, 1.92 (m, 4 H) 4.04 (t, 4 H) 6.96, 8.02 (2d, 8 H arom.) 7.60, 7.70 (2d, 8 H arom.)
T6	83(I), >95(S)	1659	0.93 (t, 6 H) 1.30, 1.55 (m, 12 H) 1.72, 1.90 (m, 4 H) 4.06 (t, 4 H) 6.95, 8.03 (2d, 8 H arom.) 7.60, 7.70 (2d, 8 H arom.)
T7	70(I)	1659	0.82-1.00 (m, 6 H) 1.22, 1.58 (m, 16 H) 1.72, 1.90 (m, 4 H) 4.04 (t, 4 H) 6.95, 8.01 (2d, 8 H arom.) 7.60, 7.70 (2d, 8 H arom.)

(a) Yield after purification, I=interfacial synthesis, S=solution synthesis. (b) Carbonyl stretching band. (c) In CDCl_3 for T2-T7, in (dimethylsulphoxide)- d_6 for T1, downfield from TMS. s=Singlet, d=doublet, t=triplet, q=quartet, m=multiplet.

compounds T1–T4 is detectable both by DSC and microscopic methods, the temperatures reported in table 2 are only indicative and, for compounds T1 and T2, it is very likely that they are significantly lower than the thermodynamic equilibrium values, due to chemical decomposition.

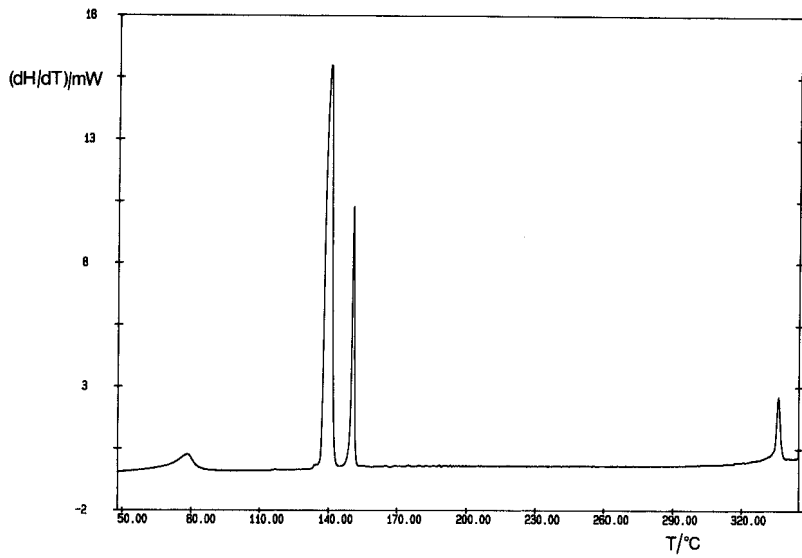
The enantiotropic mesomorphism of compounds T1–T5 is simple. The mobile schlieren texture usually observed and the absence of sharp Bragg lines in the X-ray diffraction pattern of the liquid crystal phase indicate purely nematic properties. The X-ray diffraction pattern of samples of T5, which undergo spontaneous orientation in the glass capillary, indicate the cybotactic structure of the nematic phase. T5 shows a monotropic transition from the nematic to a smectic phase. The regular mosaic texture observed and the value of the enthalpy (8.86 kJ mol^{-1}) suggest a possible analogy with the behaviour of T6 and T7. Similar behaviour has been observed for T4. However, the relatively high enthalpy and the polycrystalline appearance of the phase suggest that it is crystalline. In any case, the immediate occurrence of a further transition to the stable crystal phase, prevented us from collecting X-ray diffraction data to confirm or disprove this hypothesis.

The phase behaviour of T6 and T7 is slightly more complicated and we shall discuss it in detail. Figures 1 (a) and (b) show the DSC heating curves for samples which have undergone no previous thermal treatment. They show that the phase transition involving the most relevant enthalpic change (we shall call it melting for an easy reference) leads to a very viscous phase. A phase transformation with a considerable endothermic effect is detectable for T6 prior to melting but the significant difference with respect to T7 concerns the mesophase. Only the nematic phase is exhibited by T6,

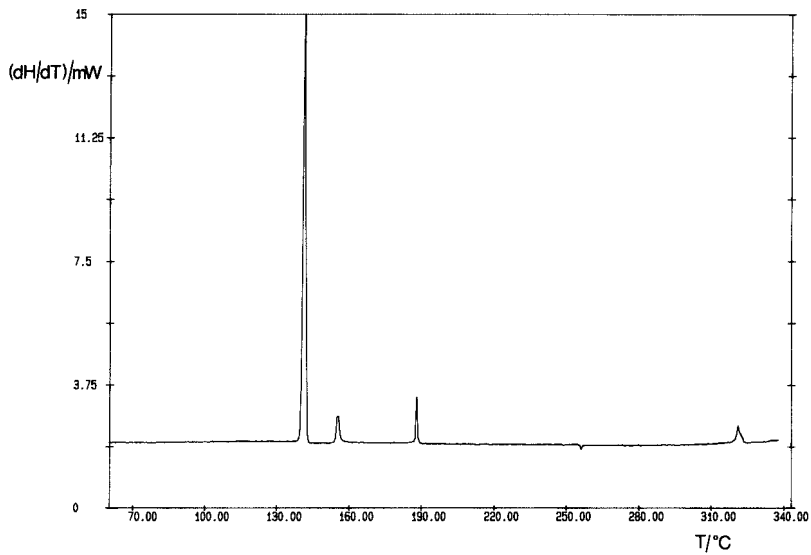
Table 2. Phase transition temperatures and enthalpies for esters T1–T7 and mixtures of T6 and T7 (a).

Tn (b)	C–LC		LC–LC		S _C –N		N–I	
	T/°C	ΔH/kJ mol ⁻¹	T/°C	ΔH/kJ mol ⁻¹	T/°C	ΔH/kJ mol ⁻¹	T/°C	ΔH/kJ mol ⁻¹
T1	228.5	50.6					390 (c)	
T2	195.5	38.3 (d)					390 (c)	
T3	185.6	46.2					380 (c)	
T4	169.7	42.1 (e)					370 (c)	
T5	153.1	49.8 (f)					346.8	4.04
T6 (g)	139.3	36.2	150.7	8.52	—		338.0	2.88
0.8	130.1	34.4	149.1	4.73	154.6	2.46	330.7	2.93
0.6	128.6	37.8	150.6	4.55	166.5	2.55	326.0	3.11
0.4	130.4	40.5	151.4	4.37	172.7	2.65	322.1	2.91
0.2	133.8	40.2	150.7	4.14	177.0	2.60	319.8	2.94
T7 (h)	141.2	47.0	155.3	4.01	188.1	3.08	321.2	3.16

(a) Temperatures ($\sigma(T)/T=0.002$ for four figure values) refer to the maximum of the transition DSC endotherm; $0.05 > \sigma(\Delta H)/\Delta H > 0.01$; data included between T6 and T7 are for binary mixtures with decreasing weight fraction of T6 (0.8 = 78.4 per cent; 0.6 = 60.0 per cent; 0.4 = 40.1 per cent; 0.2 = 21.7 per cent). (b) C–LC = C–N for T1–T5, C–S_G for T6, T7 and their mixtures; LC–LC = S_G–N for T6, S_G–S_C for T7 and binary mixtures. (c) Temperatures are indicative, isotropization with decomposition. (d) Solid phase transition observed (97.6°C, 4.3 kJ mol⁻¹ first heating run, 89.1°C, 4.6 kJ mol⁻¹ second heating run). (e) Crystallization occurs through two phase transitions of almost equal enthalpic change not entirely resolved around 140°C. (f) Monotropic N–S_G (mosaic texture) transition at 137.3°C, $\Delta H = 8.45 \text{ kJ mol}^{-1}$. (g) Endothermic phase transition (78.1°C, 4.72 kJ mol⁻¹) for solution-crystallized samples. Solid phase transitions (on cooling) at 121°C, 103°C, 90°C. (h) Multiple, not completely resolved solid phase transitions (on cooling) between 92°C and 87°C.



(a)



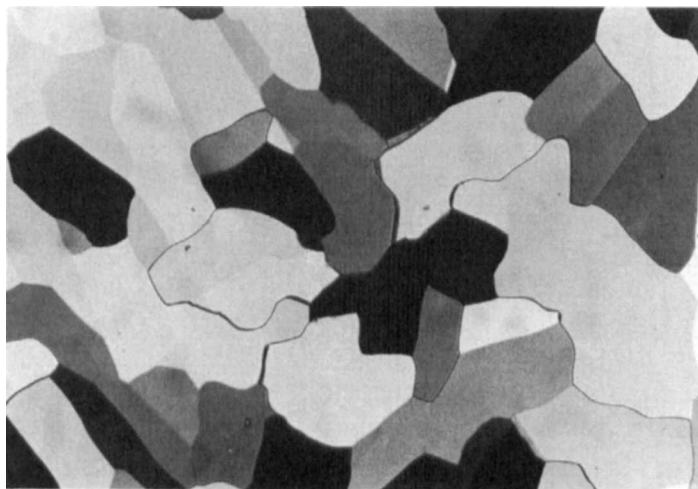
(b)

Figure 1. DSC thermogram of (a) T6 and (b) T7. Heating run, sample crystallized from solution. Scanning rate $10^\circ C \text{ min}^{-1}$.

Table 3. X-ray diffraction data for the S_G phase of T6 and T7 (a).

T6 (145°C), $d/\text{Å}$		T7 (148°C), $d/\text{Å}$	
24.2	(vs)	26.9	(vs)
12.1(6)	(mw)	13.4	(mw)
5.68	(w)	5.70	(w)
5.13	(m)	5.11	(m)
4.59	(vs)	4.59	(vs)
4.02	(m)	4.05	(m)

(a) Lattice distances are measured with $\sigma(d)/d=0.02$. Diffraction intensities are only indicative (visual estimation).

Figure 2. T6, 140°C, mosaic texture of S_G phase. Crossed polarizers.

while smectic C and nematic phases are found for T7. The viscous phase that forms from T6 or T7 on melting is characterized by an X-ray diffraction pattern (see table 3) indicating three dimensional order. The patterns for T6 and T7 are quite similar except for the lattice distance corresponding to the strong low angle reflection attributable to a smectic periodicity. For both compounds this lattice distance (24.2 and 26.9 Å for T6 and T7 respectively) is definitely shorter than the full molecular length.

As to the optical textures, the mosaic is the most significant texture observed (see figure 2). On the basis of this morphology and the X-ray diffraction evidence, the phase might be recognized as a G type smectic. This phase has also been classified as a disordered crystal phase [3]. However, notwithstanding the presence of three dimensional order, the enthalpy change at the transition to the true smectic (S_C) is a small fraction (7.4 per cent) of the total enthalpy change from the crystal phase (C-N) and quite comparable to that found for the S_C -N transition enthalpy.

The phase, stable at higher temperatures, is a cybotactic nematic for both compounds. The X-ray diffraction pattern shows a diffuse halo (at $\sim 0.1077 \text{ Å}^{-1} \sin \vartheta/\lambda$, 160°C for T6; and at $0.1065 \text{ Å}^{-1} \sin \vartheta/\lambda$, 200°C for T7) and a low

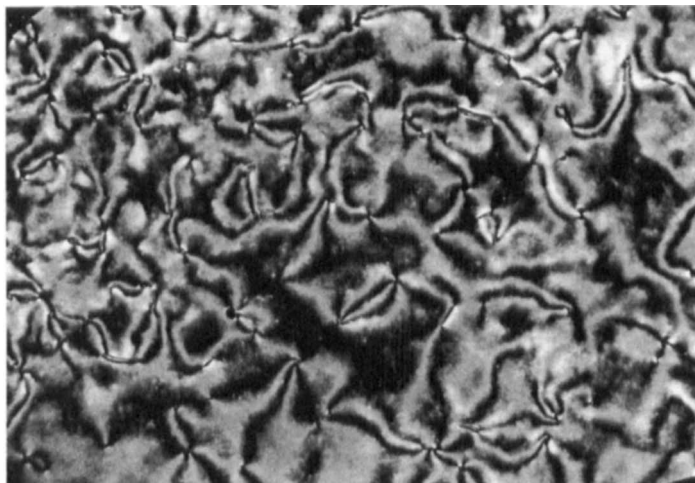


Figure 3. T7, 310°C, schlieren texture of the nematic phase. Crossed polarizers.

angle, slightly sharper diffraction that splits into a four spot pattern for oriented samples at $0.0208 \text{ \AA}^{-1} \sin \vartheta/\lambda$ ($\sim 24.01 \text{ \AA}$) for T6 at 160°C; at $0.0180 \text{ \AA}^{-1} \sin \vartheta/\lambda$ ($\sim 27.7 \text{ \AA}$) for T7 at 200°C. Schlieren (see figure 3) and marbled textures are commonly observed for both compounds.

The liquid-crystalline phase exhibited by T7 between 155.3 and 188.1°C is of a smectic C type. A diffuse halo at $0.1083 \text{ \AA}^{-1} \sin \vartheta/\lambda$ and a sharp Bragg line at $27.2 \text{ \AA}^{-1} \sin \vartheta/\lambda$ characterize the X-ray diffraction pattern of this compound at 160°C. Samples which undergo spontaneous orientation inside the glass capillary show a four spot splitting of the low angle Bragg line. This feature, which indicates the tilted nature of the smectic structure, and the schlieren texture normally observed for this phase are in support of a C type smectic.

A further check on the homology of the mesophases exhibited by T6 and T7 at higher temperature was obtained by examining the phase behaviour of binary mixtures. The results are summarized in table 2 and indicate that not only are the phases mentioned homologous but also that T6 and T7 are mutually soluble in any phase. Figure 4 shows the DSC heating curve for a composition with T6/T7 = 1.5 weight ratio. Isotropization is represented by a single, although a little broadened, endothermic peak centred at a temperature higher than for T7 and lower than for T6. This is what we should expect for the monophasic quasi-ideal mixture of two compatible mesogens. Consistently, because of the very small difference between the isotropization enthalpies of the pure components, no really significant dependence on composition is observable for the isotropization enthalpy of the mixtures. The smectic C phase is still enantiotropically stable and the same holds for a T7 content as low as 20 per cent (see table 2). S_C -N transition temperatures extrapolate to ~ 145 - 147°C for pure T6. The moderate supercooling of the nematic phase prior to the transition to the S_G phase ($\sim 5^\circ\text{C}$, equivalent to that observed for the N- S_C transition of T7) may be the reason why the monotropic S_C phase was not observed for T6.

Finally, it may be useful to emphasize that the enthalpy change measured for T6 at the S_G -N transition (8.52 kJ mol^{-1}) is quite comparable to the value of 8.86 kJ mol^{-1} measured for the monotropic smectic-nematic transition exhibited by T5. This feature,

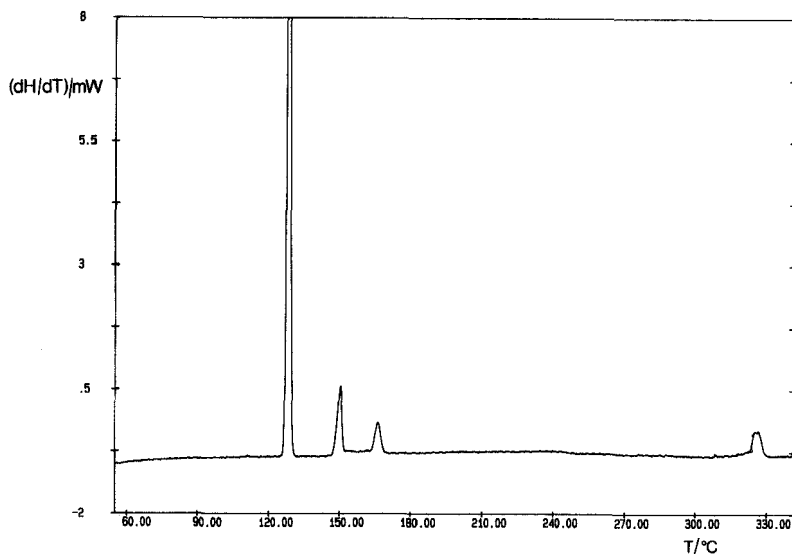


Figure 4. DSC thermogram of a T6/T7 (60 per cent T6) mixture. Heating run. Scanning rate $10^{\circ}\text{C min}^{-1}$. Sample previously brought to the nematic phase and crystallized from the melt.

together with the observed textural analogies strongly suggest the homology of the ordered smectic (or disordered crystal) phases of T5, T6 and T7.

The phase behaviour of T6 and T7 on cooling is not entirely reversible. The S_C phase of T7 does not transform directly to S_G . Two almost coalescent exothermic effects at $\sim 152^{\circ}\text{C}$ in the DSC cooling curve indicate the formation of a further monotropic smectic phase which has not been identified. Both for T6 and T7 the solid phase, stable at room temperature, is produced on cooling only after a sequence of intermediate solid phase transitions starting from the S_G phase. Nonetheless, the successive phase behaviour on heating is reproducible.

In conclusion, the mesomorphic behaviour of compounds T1–T7 follows the usual trend of a decreasing mesophase stability with increasing length of the flexible terminal chains. Not unusual is also the dependence on the same parameter of the smectic stability.

The liquid-crystalline properties of the oxygenated analogues of T1, T4, T6 and T7 have been known for a long time from the work of Dewar and Schroeder [4]. They were found to be polymesomorphic (with the exception of the analogue of T1), all of them showing a nematic phase. They systematically have slightly higher melting temperatures (for T6 and T7 the difference increases if the transition to the S_G phase is taken as the melting point) and slightly lower isotropization temperatures. As a consequence, the thermal stability interval of the mesophase is significantly larger for the sulphur containing analogue. The higher mesophase stability observed for the thio-analogues is qualitatively consistent with literature data for other low molecular weight phenyl thiobenzoates [5–7] (some literature data on phenyl benzoates are also reported in [8]). Quantitatively, however, the differences appear relatively smaller in our case as compared to mesogens containing a single phenyl thiobenzoate group (for example the nematic–isotropic transition temperature of benzenecarbothioic acid, 4-(pentyloxy)-S-(4-pentyl-phenyl)ester was measured to be 27.4°C higher than for the corresponding

oxygenated compound whereas only 8°C separate the isotropization temperatures found for T6 and for the oxygenated analogue [6]. This is not surprising if the remarkable difference in the axial ratio between the two classes of molecules is taken into account. The increased influence of the steric factor should reduce the relative effect of diversities in the electronic properties. A very significant difference between compounds T_n and their oxygenated analogues concerns the stability of the smectic phase. This is much higher for the oxygenated compounds with enantiotropic persistence observed even for the homologue of T4 up to 184°C (up to 211°C for T7) [4].

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