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The influence of terminal chlorine on the mesomorphic properties of new thiobenzoates containing two and three benzene rings

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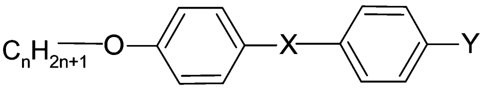
New liquid crystalline chloro-substituted thioesters containing two and three benzene rings have been synthesized. 4-Chlorophenyl 4-*n*-alkoxythiobenzoates and 4-chlorophenyl 4-*n*-alkoxybenzoyloxy-4′-thiobenzoates are referred to as *n*O.SCl and *n*O.OSCl, respectively, where *n* varies from 4 to 16 for *n*O.SCl, from 4 to 10 for *n*O.OSCl and denotes the number of carbon atoms in the alkyl chain. Their mesomorphic properties were investigated by means of polarizing optical microscopy, differential scanning calorimetry, transmittance light intensity and X-ray diffraction measurements. The *n*O.SCl homologous series possesses smectic A (SmA) and nematic (N) phases for $n=4$, 5, 6 while higher homologues have only an enantiotropic SmA phase. Those from the *n*O.OSCl homologous series have enantiotropic N and SmA phases and higher transition temperatures. The range of the N phase decreases, and of the SmA increases, with the elongation of the alkoxy chain in the *n*O.OSCl homologous series. The effect on mesomorphic behaviour of terminal alkoxy chain lengthening and replacement by chlorine on the other side of the molecule is discussed.

1. Introduction

For many years rod-like mesogens have been the object of intensive investigation. Many of the molecules of these compounds have unsymmetrical structures, as shown below:



X= -COO-; -CHN-; -COS-;
Y= H; RO; halogen; CN; NO_2.

The stronger electrophilic terminal substituents such as $Y=$halogen, CN, NO_2, are responsible for the stabilization of smectic phases which appear in such compounds. In esters ($Y=$halogen, $X=$–COO–) the smectic A (SmA) phase can be observed; however compounds with the opposite orientation of the ester bond, $X=$–OOC–, are not mesogens [1, 2]; thus the existence of smectic phases depends on the orientation of the ester group relative to the alkoxy group. A similar trend is seen in the class of azomethine compounds, substances with $Y=$halogen or CN and $X=$–CHN– having more stable smectic phases than compounds containing the –NCH– bond.

Compounds possessing the –COS– bond, 4-*Y*-phenyl 4-*n*-alkoxythiobenzoates with electron-donating terminal substituents $Y=$alkoxy [3] or alkyl [4–7], are characterized by their wide diversity of smectic phases; whereas compounds with $Y=NO_2$ possess only the SmA phase [7]. In the triphenyl system with two ester groups, i.e. 4-*Y*-phenyl 4-octyloxybenzoyloxy-4′-benzoates, with strongly electronegative terminal substituents $Y=$Cl, Br, OCF_3, NO_2, the observed range of the SmA phase was much wider than in compounds with $Y=OCH_3$, OC_8H_{17}, CH_3, C_8H_{17} [8]. The influence of the terminal substituent *Y* on the formation of the SmA phase is disparate in the case of the other conformation of the ester group relative to the phenyl rings; for example, the SmA phase occurs in 4-(4-octyloxybenzoyloxy)phenyl 4-*Y*-benzoates for strongly electrophilic *Y* substituents such as Cl, NO_2, CN, only [9]. A few classes of compound can be obtained by replacing the –COO– bonding by other groups, such as –CHN– and –COS– [7]. It was our interest to determine how chloro-substitution would influence the phase behaviour of thiobenzoates. The *n*O.SCl (**A**) and *n*O.OSCl (**B**) compounds have the structures:

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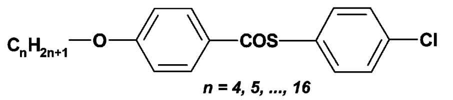
A



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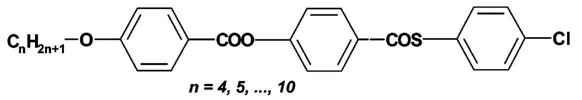
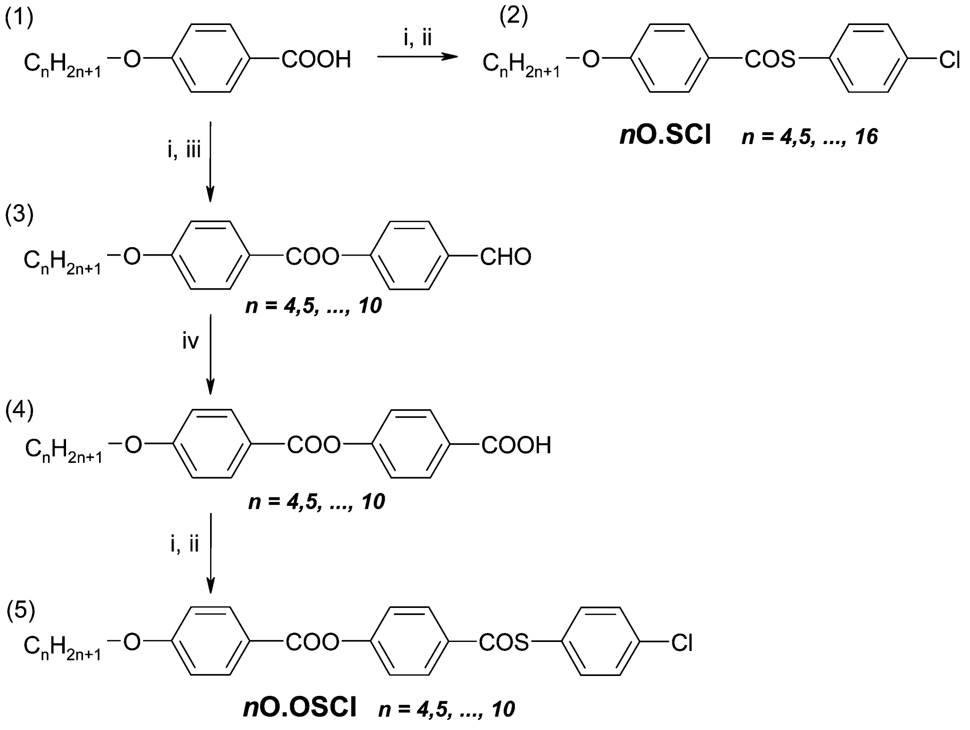


This paper reports the convenient synthesis and properties of mesogens, containing two and three phenyl rings, belonging to two new homologous series of thiobenzoates, 4-chlorophenyl 4-*n*-alkoxythiobenzoates, C_nH_{2n+1}O–Ph–COS–Ph–Cl, and 4-chlorophenyl 4 -*n*-alkoxybenzoyloxy-4′-thiobenzoates, C_nH_{2n+1}O–Ph–COO–Ph–COS–Ph–Cl, which we refer to as *n*O.SCl (series **A**) and *n*O.OSCl (series **B**), respectively (*n* varies from 4 to 16 for *n*O.SCl, from 4 to 10 for *n*O.OSCl, and denotes the number of carbon atoms in the alkyl chain), in which the chlorine is *p*-substitued in the phenyl ring. Thermal properties are discussed in terms of the electrostatic nature of the substituent.

2. Experimental

2.1. *Characterization*

The structure of the compounds was confirmed by elemental analysis, IR and ^{1}H NMR. The NMR spectra were obtained using an NMR Varian 500 spectrometer (CDl_3, TMS as internal standard); IR spectra were recorded using an FTIR Nicolet Magna 760 spectrometer and a minimum of 64 co-added scans at a resolution of 1 cm^{-1}. The mass spectrum were obtained using a TOF MS ES+ spectrometer. Transition temperatures were determined by polarizing optical microscopy (POM) with a Linkam programmable heating stage THMSE 600. Heating and cooling rates were $\pm 2\,K\,min^{-1}$. The enthalpy and entropy changes were determined by differential scanning calorimetry (DSC 822e Mettler Toledo Star System) with heating and cooling rates ± 2 K or $4\,K\,min^{-1}$. The transition temperatures were also examined using transmittance light intensity (TLI), the experimental set-up for which was described in detail in a previous paper [10]. X-ray measurements were made using a Philips X'Pert



i: $SOCl_2$, toluene; ii: HSC_6H_4Cl, $(C_2H_5)_3N$;
iii: HOC_6H_4CHO, $(C_2H_5)_3N$, toluene; iv: $KMnO_4$, acetone

Scheme. Synthesis of *n*O.SCl and *n*O.OSCl.

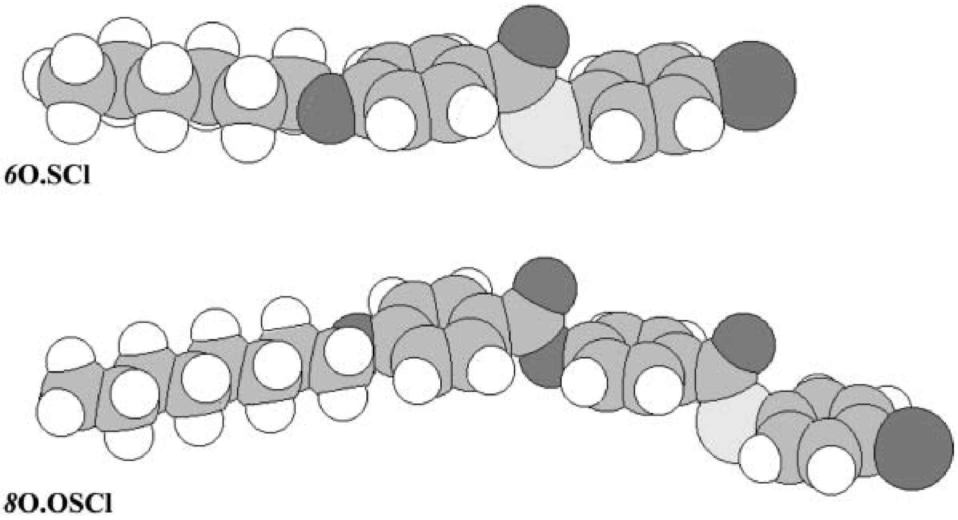


Figure 1. Molecular models of 6O.SCl and 8O.OSCl.

diffractometer and a Guinier symmetrical focusing transmission camera.

2.2. *Synthesis*

The *n*O.SCl and *n*O.OSCl compounds were synthesized according to the general route shown in the scheme. The 4-*n*-alkoxybenzoic acids $C_nH_{2n+1}OC_6H_4COOH$, *n*OB (1) were used as the starting compounds for the synthesis of the 4-*n*-chlorophenyl 4-*n*-alkoxythiobenzoates (*n*O.SCl) and 4-chlorophenyl 4-*n*-alkoxybenzoyloxy-4′-thiobenzoates (*n*O.OSCl). Alkoxybenzoyl chlorides, the intermediates for the synthesis of *n*O.SCl (2) and 4-*n*-alkoxybenzoyloxy-4′-benzaldehydes (3), were obtained by reaction of the 4-*n*-alkoxybenzoic acid and thionyl chloride in anhydrous toluene. Compounds (2) were purified by recrystallization from ethanol, giving 80–95% yields.

Table 1. Calculated molecular length *l* as a function of the number of carbon atoms in the alkoxy chain of the *n*O.SCl and *n*O.OSCl compounds.

*n*O.SCl	*l*/Å	*n*O.OSCl	*l*/Å
4O.SCl	17.0	4O.OSCl	23.6
5O.SCl	17.9	5O.OSCl	24.9
6O.SCl	19.3	6O.OSCl	26.2
7O.SCl	20.2	7O.OSCl	27.3
8O.SCl	21.6	8O.OSCl	28.6
9O.SCl	22.4	9O.OSCl	29.7
10O.SCl	23.8	10O.OSCl	31.0
11O.SCl	24.7	—	—
12O.SCl	26.2	—	—
13O.SCl	27.1	—	—
14O.SCl	38.6	—	—
15O.SCl	29.5	—	—
16O.SCl	31.0	—	—

The final liquid crystals, *n*O.OSCl (5), were obtained by potassium permanganate in acetone oxidation of the aldehydes (3) to the acids (4) which were crystallized from ethanol. To a solution of the compounds (4) in toluene, thionyl chloride was added. The final compounds *n*O.OSCl (5) were obtained by esterification of the acid chloride and 4-chlorothiophenol in toluene in the presence of triethylamine. The final compounds were isolated from the reaction mixture using gel column chromatography (2.5 × 40 cm) in $CHCl_3$. The crude products thus obtained were crystallized from ethyl acetate.

2.2.1. General procedure for the preparation of nO.SCl.

To a solution of 4-chlorothiophenol (3.615 g, 25 mmol) in toluene (60 ml) was added triethylamine (4.62 g, 45.6 mmol). To this mixture, 4-*n*-pentyloxybenzoyl chloride (5.17 g, 22.8 mmol) dissolved in 40 ml of toluene was added dropwise at room temperature, and the mixture was stirred at 45–50°C then heated under reflux for 6 h. The reaction mixture was cooled to room temperature and added to water with ice and hydrochloric acid (10 ml, 20%). The toluene layer was washed several times with water and an aqueous solution of sodium carbonate, and the organic phases were dried over anhydrous magnesium sulphate. Rotary evaporation gave the crude final product, which was purified by column chromatography on silica gel using $CHCl_3$ as eluant. The crude product was crystallized several times from ethanol until colourless crystals were obtained; 6.5 g (85%) of 5O.SCl, m.p. 78.5°C. FTIR (KBr) 1668 (s), 1275 (s), 817 (m), 1604 (s), 661 (m), 642 (m), 2900 (m). ^1H NMR ($CDCl_3$, ppm): δ 1.02 (3H, t, CH_3), 1.5 (4H, m, $-CH_2-$), 1.9 (2H, m, $-CH_2$), 4.1 (2H,

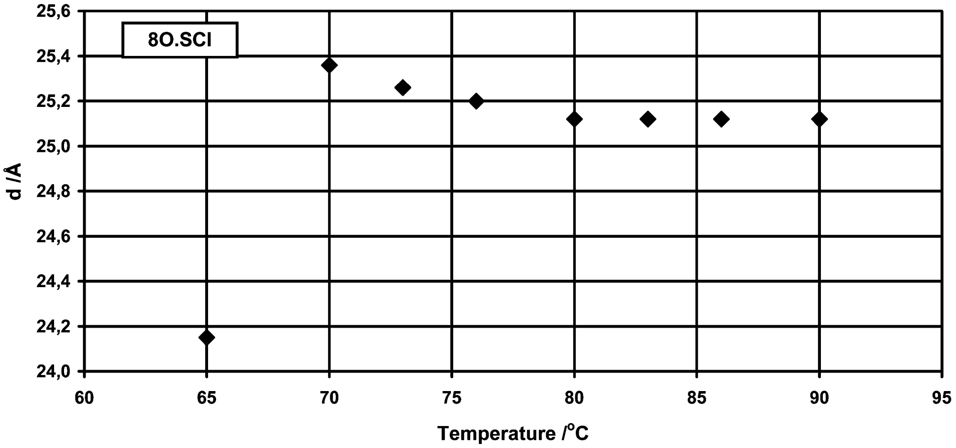


Figure 2. Temperature dependence of the layer spacing *d* for 8O.SCl.

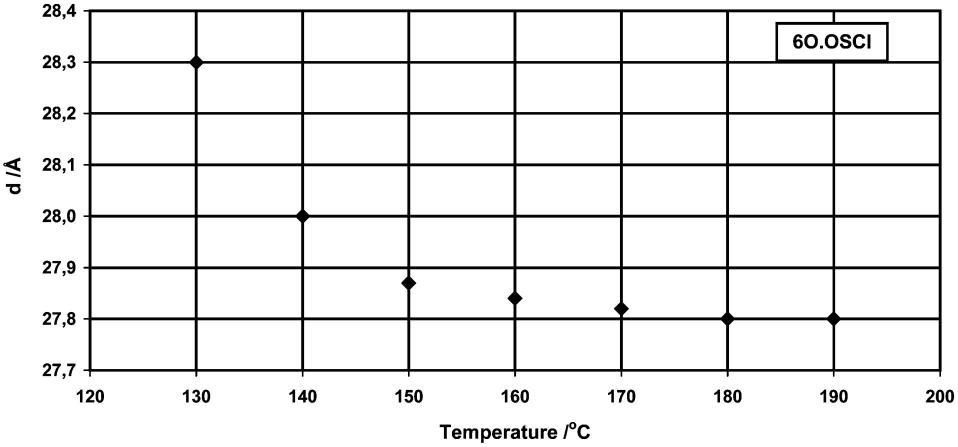


Figure 3. Temperature dependence of the layer spacing *d* for 6O.OSCl.

Table 2. Phase transition temperatures (°C), enthalpies (k cal mol^{-1}) and entropies (cal mol^{-1} K^{-1}) of transition for the *n*O.SCl series determined using DSC at 2 K min^{-1}; Cr, SmA, N and I are crystal, smectic A, nematic and isotropic phases.

	Cr–SmA			→N			→I			I–N	→SmA	→Cr
*n*O.SCl	*T*	Δ*H*	Δ*S*	*T*	Δ*H*	Δ*S*	*T*	Δ*H*	Δ*S*	*T*	*T*	*T*
4O.SCl	—	—	—	89.6[a]	—	—	90.1	5.15	14.18	90.0	71.7	53.2
5O.SCl	—	—	—	78.7	6.83	19.41	87.7	0.08	0.22	87.7	79.5	55.5
6O.SCl	66.0	2.42	7.13	87.3	0.27	0.74	92.1	0.07	0.20	92.0	87.8	48.6
7O.SCl	70.2	4.46	12.97	—	—	—	92.7	0.73	1.99	—	92.5	56.2
8O.SCl	63.2	7.43	22.09	—	—	—	96.2	0.91	2.47	—	96.2	47.7
9O.SCl	69.1	5.56	16.24	—	—	—	97.3	0.85	2.29	—	97.3	54.6
10O.SCl	66.9	5.21	15.31	—	—	—	91.3	0.91	2.49	—	91.0	53.4
11O.SCl	74.2	8.24	23.72	—	—	—	98.5	1.17	3.15	—	98.2	57.8
12O.SCl	73.1	6.33	18.28	—	—	—	96.2	0.92	2.48	—	96.1	58.3
13O.SCl	80.0	11.52	32.61	—	—	—	97.6	1.39	3.74	—	97.6	62.9
14O.SCl	79.9	7.65	21.67	—	—	—	96.2	0.98	2.65	—	96.0	60.4
15O.SCl	84.4	9.49	26.54	—	—	—	93.5	1.01	2.75	—	93.5	71.4
16O.SCl	84.9	8.77	24.50	—	—	—	92.9	0.95	2.59	—	92.8	69.2

[a] Determined by POM.

Table 3. Phase transition temperatures (°C), enthalpies (kcal mol^{-1}) and entropies (cal mol^{-1} K^{-1}) of transition for the *n*O.OSCl series determined using DSC at 2 K min^{-1}. Key as for table 2.

*n*O.-OSCl	CrII–CrI			CrI–SmA			SmA–N			N–I			I–N	N–SmA	SmA–SmX	–CrI	CrI–CrII
	T	Δ*H*	Δ*S*	*T*	Δ*H*	Δ*S*	*T*	Δ*H*	Δ*S*	*T*	Δ*H*	Δ*S*	*T*	*T*	*T*	*T*	*T*
4	86.8	0.99	2.75	138.3	6.54	15.90	161.7	0.15	0.34	265.9	0.32	0.59	265.8	151.6	—	126.8	90.7
5	—	—	—	123.6	9.25	23.30	183.8	0.23	0.50	254.5	0.30	0.56	254.4	183.3	—	112.2	85.6
6	—	—	—	116.0	8.38	21.52	197.3	0.26	0.54	245.3	0.37	0.72	245.2	192.4	—	100.4	70.9
7	—	—	—	120.0	9.96	25.32	208.4	0.40	0.82	242.8	0.30	0.57	242.8	208.5	—	98.4	—
8	—	—	—	112.3	9.95	25.80	211.9	0.43	0.89	232.6	0.37	0.74	232.4	210.8	—	86.2	80.6
9	—	—	—	111.0	6.66	17.33	213.0	0.34	0.70	226.5	0.17	0.35	226.4	214.2	—	85.3	—
10	—	—	—	102.5	6.13	16.33	212.7	0.49	1.02	220.1	0.25	0.52	220.0	214.1	81.4	75.4	—

t, –CH$_2$–O–Ar–), 7.0 (2H Ar, d, *ortho* to *R*O–Ar–), 7.5 (4H, m, ArCl), 8.05 (2H, Ar, d, *ortho* to Ar–COS–). Elemental analysis: calcd for $C_{18}H_{19}O_2SCl$, C 64.57, H 5.68, S 9.56, Cl 10.61; found, C 64.42, H 5.71, S 9.48, Cl 10.54%.

2.2.2. Preparation of compound (3).

To a solution containing 2.61 g (21.4 mmol) of 4-hydroxybenzaldehyde in 40 ml of dichloromethane, 4.32 g (42.7 mmol) of triethylamine was added; a solution of 4-*n*-hexyloxybenzoyl chloride (5.14 g, 21.4 mmol) dissolved in 40 ml of methylene chloride was then added dropwise over a period of 3 h, while the temperature of the reaction mixture was maintained at 20–24°C. The reaction mixture was neutralized by cold 2% aqueous hydrochloric acid. The organic phase was separated, washed with water, aq Na_2CO_3, water, dried (anhyd. $MgSO_4$) and the solvent removed; the final product was obtained by recrystallization from ethanol; yield 4.6 g (66%). The phase transition temperatures are: 39.1–40.4°C (Cr$_{II}$–Cr$_I$), 59.6–61.6°C (Cr$_I$–N), 63.5–64.0°C (N–I); 63.5–62.8°C (I–N), 35.3–34.4°C (N–Cr$_{II}$). FTIR (KBr): 1701.03 (ArCHO), 1734.67 (ArCOO), 1270.17 and 1071.50 cm^{-1} (*R*OAr). ^{1}H NMR (CDCl$_3$, ppm): δ 1.0 (3H, t, –CH$_3$), 1.45 (6H, m, (–CH$_2$)$_3$–), 1.9 (2H, m, –CH$_2$), 4.1 (2H, t, –CH$_2$–O–Ar–), 7.05 (2HAr, d, *ortho* to *R*O–Ar–), 7.47 (2HAr, d, *ortho* to Ar–COS–), 8.0–8.1 (4Har, q, ArCHO), 10.1 (1H, s, –CHO).

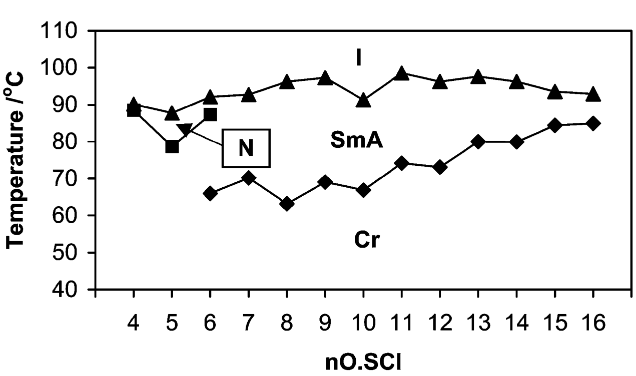


Figure 4. Dependence of the transition temperatures on the length of the alkyl chain for the *n*O.SCl homologous series obtained during heating.

2.2.3. General procedure for the preparation of nO.OSCl.

To a mixture of 0.99 g (2.8 mmol) of 4-*n*-hexyloxybenzoyloxy-4′-benzoyl chloride, 0.48 g (3.3 mmol)

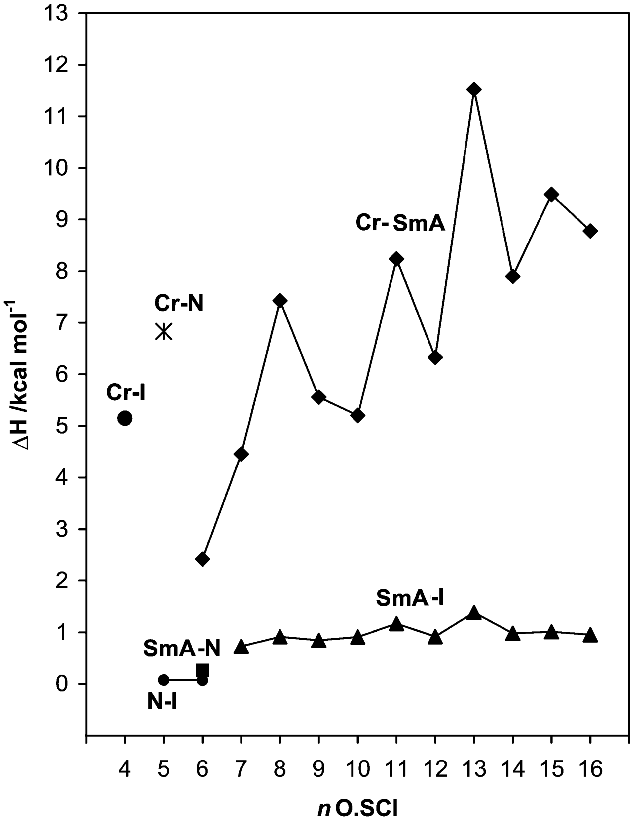


Figure 5. The enthalpy changes, Δ*H*, for the *n*O.SCl homologous series obtained during heating.

of 4-chlorothiophenol and 0.77 ml (5.5 mmol) of triethylamine, 45 ml of dry toluene were added. This final compound was obtained as described for *n*OSCl, at 70°C. The crude product was purified by recrystallization from ethyl acetate. The final product, 1.29 g (94%) of 6O.OSCl, was obtained as a white solid. ^{1}H NMR ($CDCl_3$, ppm): δ 1.0 (3H, t, $-CH_3$), 1.5 (6H, m, $-CH_2-$), 1.9 (2H, m, $-CH_2-$), 4.15 (2H, t, $-CH_2-O-Ar-$), 7.05 (2HAr, d, *ortho* to *R*O–Ar), 7.47 (m, 6HAr, 4HArCl and 2H *para* to Ar–COS), 8.2 (q, 4HAr, 2H *ortho* to Ar–COO– and 2H Ar–COS–). Elemental analysis: calcd for $C_{26}H_{25}O_4SCl$, C 66.60, H 5.34, S 6.83, Cl 7.57; found, C 66.49, H 5.26, S 6. 79, Cl 7.68%.

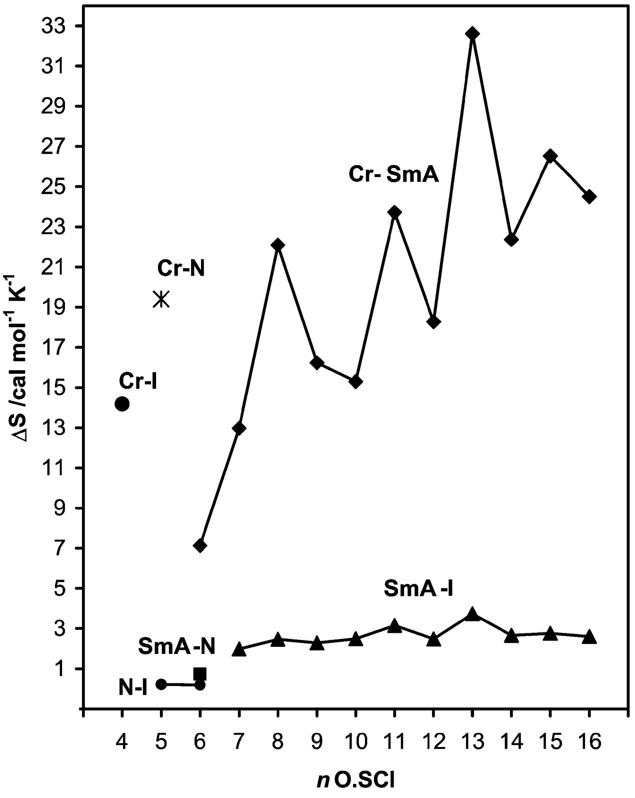


Figure 6. The entropy changes, ΔS, for the *n*O.SCl homologous series obtained during heating.

3. Results and discussion

Molecular models of the two classes of compounds **A** and **B** are shown in figure 1. Compounds from both homologous series **A** and **B** possess large dipole moments of around 5.5–5.6 and 6.0–6.4 D, respectively. For the **A** compounds the benzene rings are almost coplanar. The COS group lies in a perpendicular plane with the sulphur coplanar with the phenyl connected to the COS group. In the case of the compounds of the **B** series, two benzene rings lie in almost parallel planes and the third is tilted. It is noteworthy that the all-*trans* conformations for the alkoxy chains are characteristic for the described molecules, as they are for the

Table 4. A comparison of two-ring (*n*O.OCl and *n*O.SCl) chloro-substituted mesogens.

*n*O.OCl	*n*O.SCl	Cr→SmA	→N	→I	ΔT ($T_c - T_m$)	Ref.
4O.OCl	—	—	—	105.0	—	[15, 16]
—	4O.SCl	—	89.6	90.1	0.5	this work
5O.OCl	—	—	—	94.5	—	[15]
—	5O.SCl	—	78.7	87.7	9.0	this work
6O.OCl	—	—	—	86.0	—	[15, 16]
—	6O.SCl	66.0	87.3	92.1	26.1	this work
7O.OCl	—	—	—	79.5	—	[15, 16]
—	7O.SCl	70.2	—	92.7	22.5	this work
8O.OCl	—	76.0	—	77.0	1.0	[15, 16]
—	8O.SCl	63.2	—	96.2	33.0	this work
9O.OCl	—	—	—	—	—	—
—	9O.SCl	69.1	—	97.3	28.2	this work
10O.OCl	—	70.3	—	80.5	10.2	[15–18]
—	10O.SCl	66.9	—	91.3	24.4	this work
11O.OCl	—	—	—	—	—	—
—	11O.SCl	74.2	—	98.5	24.3	this work
12O.OCl	—	—	—	—	—	—
—	12O.SCl	73.1	—	96.2	23.1	this work
13O.OCl	—	—	—	—	—	—
—	13O.SCl	80.0	—	97.6	17.6	this work
14O.OCl	—	—	—	—	—	—
—	14O.SCl	79.9	—	96.2	16.3	this work
15O.OCl	—	—	—	—	—	—
—	15O.SCl	84.4	—	93.5	9.1	this work
16O.OCl	—	—	—	—	—	—
—	16O.SCl	84.9	—	92.9	8.0	this work

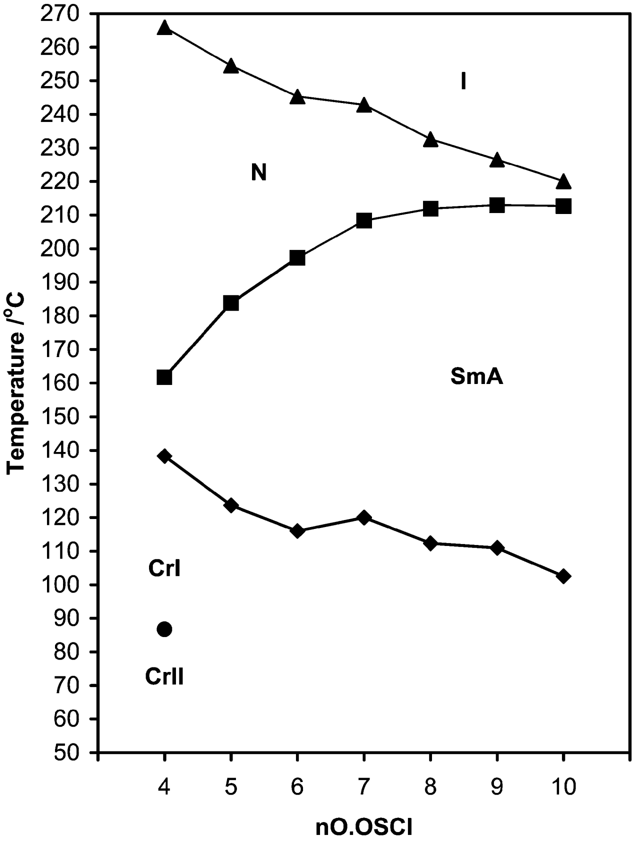


Figure 7. Dependence of the transition temperatures on the length of the alkyl chain for the *n*O.OSCl homologous series obtained during heating.

homologous series *n*OS5 [11, 12]. The calculated molecular lengths of *n*O.SCl and *n*O.OSCl are presented in table 1.

Generally, in the case of small polar terminal groups and alkoxy substituents, enantiotropic or monotropic SmA phases are observed [10, 11]. The interlayer distances from X-ray measurements for 8O.SCl and 6O.OSCl are shown in figures 2 and 3.

In the SmA phase the layer spacing *d* is approximately 1.10–1.15 times the calculated molecular length *l* for the *n*O.SCl and *n*O.OSCl series, in their fully extended conformations, including the covalent radii of the H and Cl atoms. This indicates the presence of smectic structure of the SmA_{1e} subtype. Such smectic A phases are called enhanced monolayer smectic A_1 phases [13]. The *n*O.SCl or *n*O.OSCl compounds therefore possess better conditions for dimerization in the SmA_{1e} than in the SmA_1 phase. Generally, liquid crystal molecules with long aromatic cores and –CN, $-\mathrm{NO}_2$ polar terminal groups are able directly to form the smectic A_d phase (classical SmA_d with the ratio $d/l=1.4$) and have a strong tendency to invoke the dimerization of compounds similar to them [14].

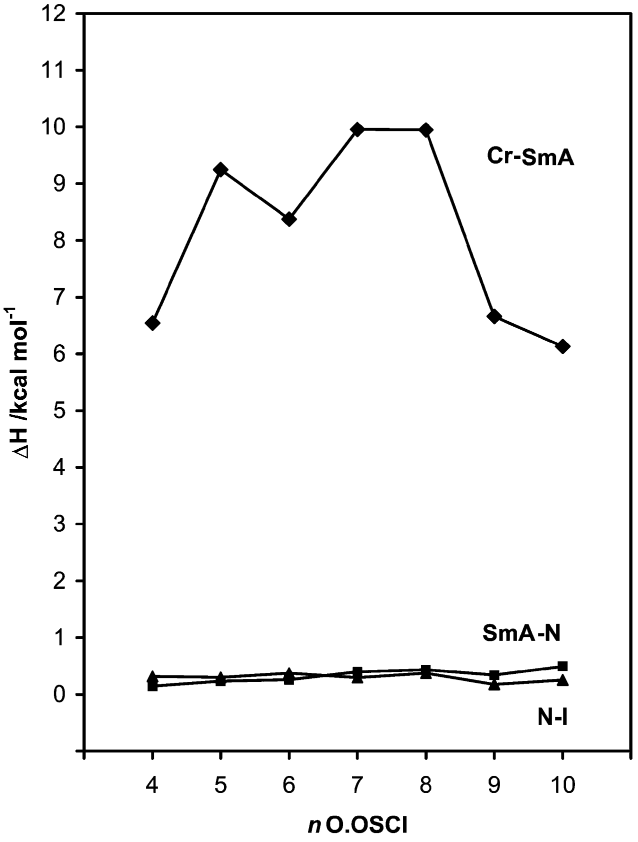


Figure 8. The enthalpy changes, Δ*H*, for the *n*O.OSCl homologus series obtained during heating.

The phase transition temperatures and associated enthalpy and entropy changes of the synthesized compounds are collected in table 2 for the *n*OS.Cl series and in table 3 for the *n*O.OSCl series.

Figure 4 shows the dependence of the N–I, SmA–I and Cr–SmA transition temperatures on the number of carbon atoms, *n*, in the terminal alkoxy chain, for the *n*O.SCl series. For compounds from homologous series A with $n=4$, 5, narrow range N phases and monotropic SmA phases were observed. With $n=6$, enantiotropic SmA and N phases are seen. Higher homologues have only enantiotropic SmA phases, whose temperature ranges reach a maximum in the compounds with $n=8$, 9, 10 and decrease on elongation of the alkoxy chain (figure 4).

The melting temperatures in this homologous series show a distinct odd–even effect in which the odd members of the series exhibit the higher values, although this alternation attenuates with increasing *n*. The melting enthalpies and entropies for the *n*O.SCl series are also shown in figures 5 and 6. They show a very pronounced, but irregular alternation with the elongation of the terminal chain. The values of Δ*H* for the Cr–SmA transition change in the range

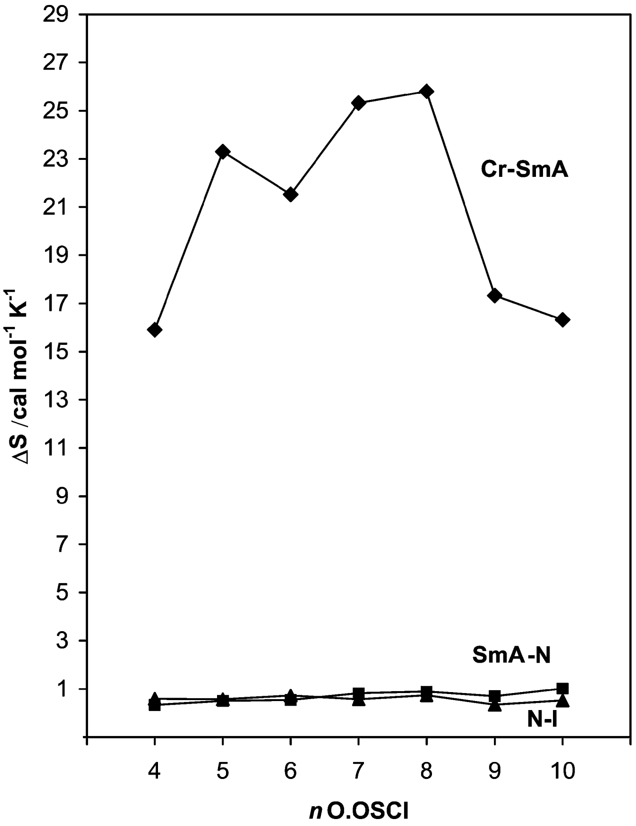


Figure 9. The entropy changes, ΔS, for the *n*O.OSCl homologous series obtained during heating.

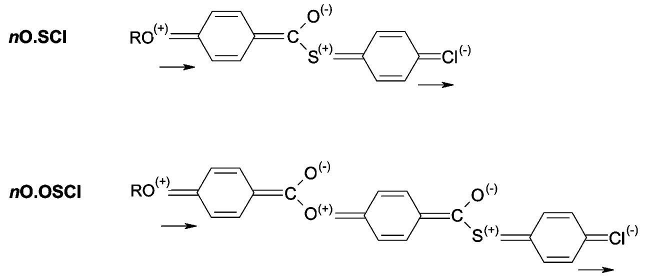
2–12 kcal mol^{-1}, but for the SmA–I transition oscillate near 1 kcal mol^{-1}. The values of ΔS for the Cr–SmA transition varied in the range 7–33 cal mol^{-1} K^{-1} and for the SmA–I around 2.5 cal mol^{-1} K^{-1}.

A comparison of the *n*O.OCl benzoates and *n*O.SCl thiobenzoates is shown in table 4. The temperature range of the SmA phase for the chloro-thioester is greater than for the chloro-benzoate ester (see 8O.OCl and 8O.SCl or 10O.OCl and 10O.SCl, table 4). Lower members of the *n*O.OCl series (n=4–7) exhibit rather high melting temperatures (T_m) and do not have liquid crystalline phases.

All the compounds from the *n*O.OSCl series (n=4–10) possess enantiotropic N and SmA phases (table 3). During heating the temperature range of the liquid crystalline phases is *c.* 115°C and 130°C for 9O.OSCl and 6O.OSCl, respectively (figure 7). For all compounds from this **B** series the temperature range is wider, *c.* 20°C on cooling, and an unidentified smectic phase (SmX) was observed at 81.4°C for 10O.OSCl during cooling.

The nematic range is over 104°C for 4O.OSCl and decreases with elongation of the terminal alkoxy chain to 6°C for 10O.OSCI. The opposite situation was observed for the SmA phase, its range changing from 23°C for 4O.OSCI to 109°C for 10O.OSCl. The Cr–SmA and N–I transition temperatures increase rapidly for larger *n*. The enthalpy and entropy changes for the Cr–SmA phase transitions increase initially with the elongation of the alkoxy chain, reaching maxima for n=7 and 8; then the ΔH and ΔS values decrease with increasing *n* (figures 8 and 9). The changes in and magnitudes of ΔH and ΔS for the SmA–N and N–I phase transitions are comparable.

The large increase of the thermodynamic parameters observed for n=4, 5, 6, 7 and then the decrease for n=9, 10, if not explained by different crystal forms, may be connected with dipole–dipole correlations between neighbouring molecules in the crystal phase (parallel for small *n* and antiparallel for n=9, 10):



In both classes of compound the thioester linkage is orientated towards the chloro-substituent. Such a molecular structure favours the occurrence of the SmA phase, stabilized by the strong electrophilic terminal substituent. The phase transition temperatures for all the compounds from the homologous *n*O.OSCl series are much higher than for the mesogens from the *n*O.SCl series. Conjugation between the electron-releasing nature of the alkoxy group and the ester carbonyl group on one side of the *n*O.OSCl molecule increases the polarity of the carbonyl oxygen. The competitive interaction between the chloro-substituent and the thioester group on the other side of the molecule, could decrease, to a small extent, the electron density at the centre of the mesogenic system. The result is a relatively even distribution of electron density in *n*O.OSCl, on one side of the molecule involving the electron-withdrawing substituent and the electron-donating substituent on the other side of the molecule. Such an electron density configuration may possibly lead to donor–acceptor complex formation. All the compounds from the *n*O.OSCl series possess high transition temperatures which may be the result of such intermolecular interactions in the solid or mesophases, but the major effect on transition temperatures must be associated with the extra ring in the *n*O.OSCl molecules.

Together with elongation of the alkoxy chain, the temperature range of the SmA phase for *n*O.SCl

Table 5. A comparison of three-ring (*n*O.OOCl and *n*O.OSCl) chloro-substituted mesogens.

*n*O.OOCl	*n*O.OSCl	CrII→CrI	CrI→SmA	→N	→I	ΔT ($T_c - T_m$)	Ref.
4O.OOCl	—	—	—	—	—	—	—
—	4O.OSCl	86.8	138.3	161.7	256.9	118.6	this work
5O.OOCl	—	—	—	—	—	—	—
—	5O.OSCl	—	123.6	183.8	254.3	130.7	this work
6O.OOCl	—	—	—	165.4	231.7	66.3	[9]
—	6O.OSCl	—	116.0	197.3	245.3	129.3	this work
7O.OOCl	—	—	—	—	—	—	—
—	7O.OSCl	—	120.0	208.4	242.8	122.8	this work
8O.OOCl	—	—	123.0	200.0	209.0	86.0	[19, 20]
—	8O.OSCl	—	112.3	211.9	232.6	120.3	this work
9O.OOCl	—	—	—	—	—	—	—
—	9O.OSCl	—	111.0	213.0	226.5	115.5	this work
10O.OOCl	—	—	—	—	—	—	—
—	10O.OSCl	—	102.5	212.7	220.1	117.6	this work

decreases, whereas for *n*O.OSCl it systematically increases with *n* ($4 \leqslant n \leqslant 10$). For 4, 5 and 6O.SCl the nematic phase is present in small ranges, whereas the phase has a wide range for all the *n*O.OSCl homologues; this range decreases rapidly for larger *n*. By contrast, the benzoate esters [1, 2] have only small SmA phase ranges. Phase range apart, the two homologous series with the thioester central group (COS) also have thermally more stable SmA phases (tables 4 and 5) as shown by the relative SmA–N and SmA–I transition temperatures.

8O.OOCl has smaller nematic and smectic ranges (*c.* 20°C) in comparison with analogues with the thioester group 8O.OSCl (table 5). The crystal–smectic transition temperature (melting point) is higher (13.5°C) and the clearing point is lower (21.7°C) for the compound containing two –COO– groups than for 8O.OSCl. 8O.OOCl does not show a smectic phase; only the nematic phase is seen [9]. The SmA phase alone was observed for *n*O.OOCl compounds with $n=14$ and 16 and no nematic phase was observed.

TLI measurements were carried out at a rate of $\pm 2\,\mathrm{K\,min^{-1}}$ for *n*O.SCl and $\pm 4\,\mathrm{K\,min^{-1}}$ for *n*O.OSCl. Using other liquid crystals we have shown the utility of the set-up constructed to use the TLI method for studies of phase polymorphism [10]. The curves obtained for 6O.SCl (figure 10) and for 6O.OSCl (figure 11) are shown as examples. Clear differences are visible on the transitions from isotropic to nematic, nematic to SmA and SmA to crystal. The Cr–SmA, SmA–N and N–I transition temperatures are consistent with results

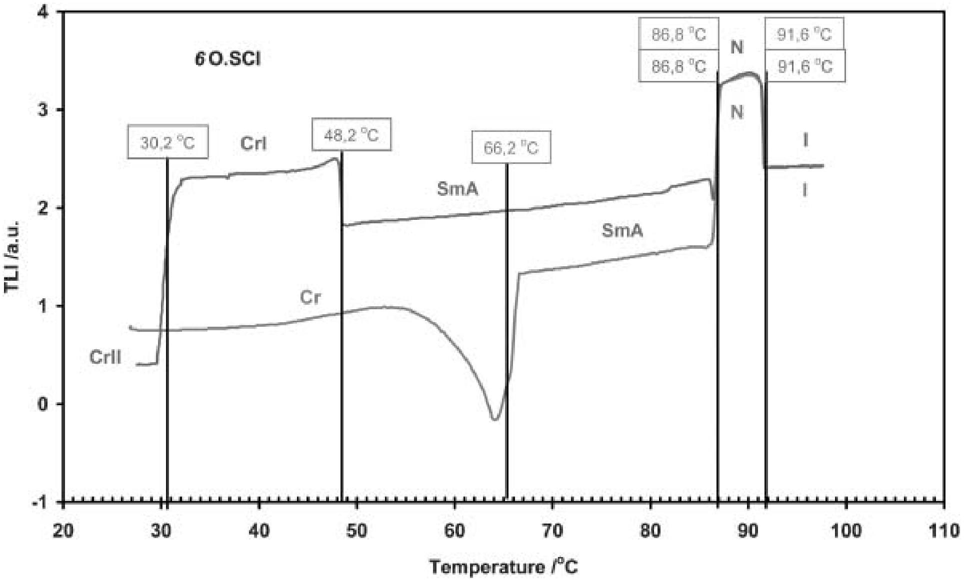


Figure 10. TLI curves for 6O.SCl for heating (lower line) and cooling (upper line) of the sample.

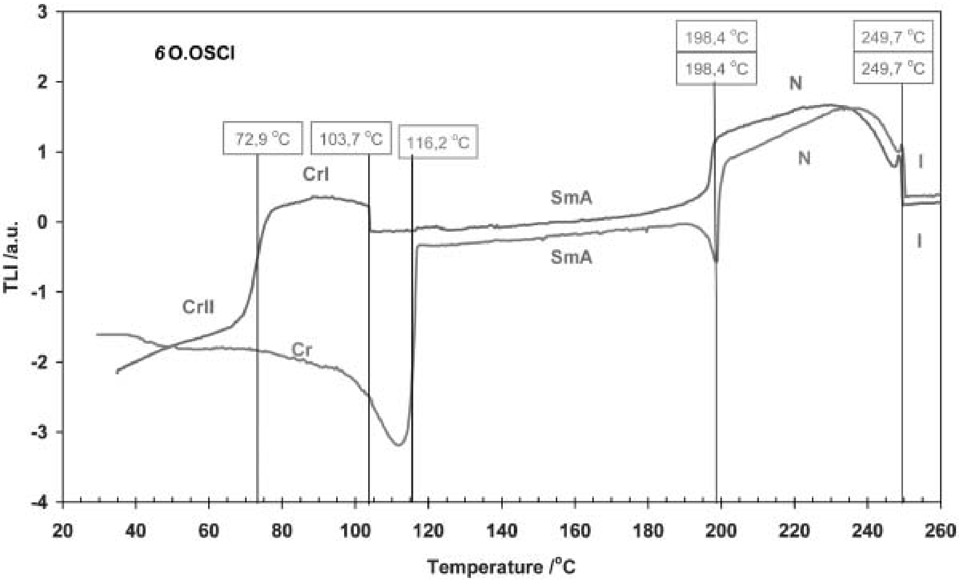


Figure 11. TLI curves for 6O.OSCl for heating (lower line) and cooling (upper line) of the sample.

obtained from other methods (DSC and POM). Figures 10 and 11 show additional phase transitions in the solid phase observed during cooling. Our results confirm the usefulness of this method in research on phase polymorphism as a complementary method to DSC.

4. Conclusions

This paper describes the synthesis of two new classes of thiobenzoate liquid crystals, the *n*O.SCl and *n*O.OSCl homologous series. These compounds have smectic A and nematic phases. The *n*O.SCl homologous series possesses much smaller ranges of mesophase than *n*O.OSCl. The presence of the terminal chloro substituent, as established many years ago for several systems, and the polar group –COS– in *n*O.SCl and *n*O.OSCl liquid crystals, increase mesophase thermal stability considerably. The lower *n*O.OSCl members exhibit only nematic phases (4O.SCl and 5O.SCl), while the higher homologues exhibit only the smectic A phase. The lower three phenyl ring systems, *n*O.OSCl, exhibit wide nematic ranges and small SmA ranges, e.g. for 4O.OSCl, the nematic and SmA ranges are 104.2 and 23.4°C, respectively.

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References

[1] J. Malthete, J. Billard, J. Canceill, J. Babard, J. Jacques. *J. Phys.*, **37**, C–1 (1976).
[2] J. Billard, J.C. Dubois, A. Zann. *J. Phys.*, **36**, C1–55 (1975).
[3] M.E. Neubert, B. Ziemnicka-Merchant, M.R. Jirousek, S.J. Laskos Jr., D. Leonhardt, R. Sharma. *Mol. Cryst. liq. Cryst.*, **154**, 209 (1988).
[4] J. Chruściel, S. Wróbel, B. Gestblom, W. Haase. In *Modern Topics in Liquid Crystals*, World scientific, Singapore (1993).
[5] M.D. Ossowska-Chruściel, J. Chruściel, S. Wojciechowska, S. Wróbel. *Mol. Cryst. liq. Cryt.*, **363**, 61 (2001).
[6] P.A.C. Gane, A.J. Leadbetter, P.A. Tacker, G.W. Gray, A.R. Tajbakhsh. *J. chem. Phys.*, **77**, 6215 (1982).
[7] D.H. Demus, H. Zaschke. *Flüssige Kristalle in Taabellen II*, Lepzig (1984).
[8] M. Duan, T. Tasaka, H. Okamoto, V.F. Petrov, S. Takenaka. *Liq. Cryst.*, **27**, 1195 (2000).
[9] M.M. Nauom, R.I. Nesim, G.R. Saad, T.Y. Labeeb. *Liq. Cryst.*, **29**, 929 (2002).
[10] M.D. Ossowska-Chruściel, S. Zalewski, A. Rudzki, A. Filiks, J. Chruściel, C.J. Carlile. *Liq. Cryst.* (submitted).
[11] M.D. Ossowska-Chruściel, Z. Karczmarzyk, J. Chruściel. *Mol. Cryst. liq. Cryst.*, **382**, 37 (2002).
[12] Z. Karczmarzyk, M.D. Ossowska-Chruściel, J. Chruściel. *Mol. Cryst. liq. Cryst.*, **382**, 37 (2001).
[13] R. Dąbrowski, K. Czupryński, J. Przedmojski, B. Ważyńska. *Liq. Cryst.*, **14**, 1359 (1993).

[14] D. Demus, J. Goodby, G.W. Gray, H-W. Spiess, V. Vill (Eds). *Handbook of Liquid Crystals*, Vol. 1, Willey-Vch (1998).

[15] J. Malthete, J. Billard, J. Canceill, J. Gabard, J. Jacques. *J. Phys. (Paris), Suppl.*, **37**, C3, 1 (1976).

[16] M.E. Neubert, K. Leung, W.A. Saupe. *Mol. Cryst. liq. Cryst.*, **135**, 283 (1986).

[17] S. Gauza, M. Brodzik. *Biul. Wojsk. Akad. Tech.*, **44**, 85 (1995).

[18] S. Gauza, M. Brodzik, R. Dąbrowski, J. Przedmojski, B. Ważyńska. *Phase Transitions*, **60**, 223 (1997).

[19] S. Takenaka, Y. Sakurai, H. Takeda, T. Ikemoto, H. Miyake, S. Kusabayashi, T. Takagi. *Mol. Cryst. liq. Cryst.*, **178**, 103 (1990).

[20] S. Takenaka, H. Takeda, Y. Sakurai, A. Tamatani, S. Kusabayashi, T. Takagi. In Proceedings of the 16th Japanese Symposium on Liquid Crystals, Hiroshima, 3L315 (1990).