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Liquid Crystalline Properties of 4-Alkoxyphenyl 4-Thiocyanatophenyl Terephthalates

Hiroaki Okamoto,* Mitsuaki Hayashi, and Shunsuke Takenaka

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University,
Tokiwadai 2557, Ube, Yamaguchi 755

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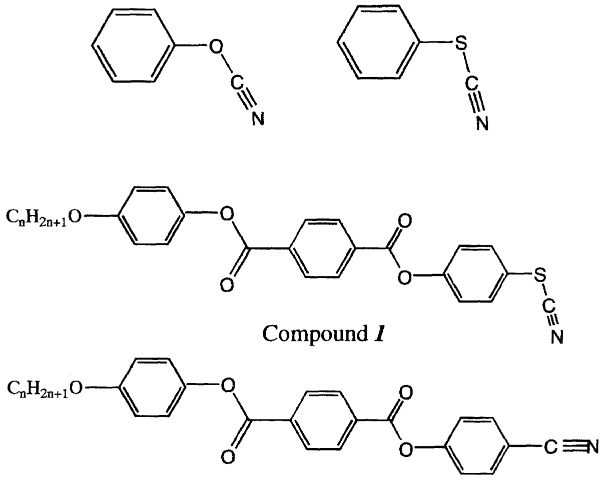
This paper describes the preparation and thermal properties of a homologous series of 4-alkoxyphenyl 4-thiocya natophenyl terephthalates. The homologous series shows nematic and smectic A phases commencing from the pentyloxy homolog. The smectic A phase is immiscible with the smectic A phase of polar liquid crystals having a terminal cyano group. Interestingly, the smectic B phase is also formed from the hexyloxy homolog, while the compound has a polar group at the terminal position.

Liquid crystals having a cyano group at the terminal position are very useful materials for display devices of a TN (twisted nematic) mode, and show very interesting polymesomorphisms including a reentrant nematic and several smectic A phases, where the large dipole moment along the longitudinal direction of the molecule plays a very important role.[1] In this connection, thiocyanato and cyanato groups are somewhat interesting (Chart 1). As shown above, the cyano groups in these moieties at the terminal position have bent angles of ca. 80° and 70° for –S–CN and –O–CN, respectively, to the long axis. Although some liquid crystalline materials having the –SCN[2—4] and –OCN[5] groups at the terminal position have been prepared, the effect of the terminal bent cyano group on the thermal and dielectric properties has not been clarified.

This paper describes the preparation and the thermal properties of a homologous series of 4-alkoxyphenyl 4-thiocyanatophenyl terephthalates and the results are discussed in terms of the molecular structure.



Compound *1*

Compound *2*

Chart 1.

Experimental

Materials. 4-Thiocyanatophenol was kindly supplied by Sanshinkagaku Co.

4-(4-Octyloxyphenoxycarbonyl)benzoic acid: Dibenzyl terephthalate (10.0 g, 29 mmol) obtained by the esterification of terephthaloyl dichloride with benzylalcohol was hydrogenolyzed with Pd–C (10%, 0.5 g) in a solvent mixture of toluene and ethanol (1 : 1, 300 ml). After uptaking hydrogen (37% of the theoretical amount), the catalyst was removed by filtration, and the residual solution was concentrated to dryness. The crude product was purified by column chromatography on silica gel. The second eluent was recrystallized from ethanol, giving 4-benzyloxycarbonylbenzoic acid as colorless needles, 2.0 g (7.8 mmol yield 27%), mp 181 °C. Thereby, 6.0 g of dibenzyl terephthalate was recovered from the first eluent. 4-Benzyloxycarbonylbenzoyl chloride prepared from 4-benzyloxycarbonylbenzoic acid (10.0 g, 39 mmol) and phosphorus pentachloride (8.4 g) in thionyl chloride (10 ml), and 4-octyloxyphenol (8.9 g 40 mmol) in a solvent mixture of dry pyridine and toluene (1 : 1, 50 ml) were heated at 80 °C for 5 h. The reaction mixture was concentrated to dryness, and the residue was extracted with ether. The product was purified by column chromatography on silica gel, followed by recrystallization from a solvent mixture of pet. ether and ether, giving benzyl 4-octyloxyphenyl terepthalate as colorless needles, 15.5 g (33.5 mmol, yield 86%), mp 84 °C. The benzyl group of benzyl 4-octyloxyphenyl terephthalate was removed by hydrogenolysis with Pd–C, and 4-(4-octyloxyphenoxycarbonyl)benzoic acid was recrystallized from ethanol. This compound experiences a phase transition of crystal. 172. nematic. 236. isotropic (*T*/°C).

4-Octyloxyphenyl 4-Thiocyanatophenyl Terephthalate (1h): A similar treatment of 4-(4-octyloxyphenoxycarbonyl) benzoyl chloride, obtained by the reaction of the acid (3.0 g, 8.1 mmol) with phosphorus pentachloride (2.1 g, 10.1 mmol) in thionyl chloride (5 ml), with 4-thiocyanatophenol (1.35 g, 8.9 mmol) in a mixed solvent of dry pyridine and toluene (1 : 1, 60 ml) gave 4-octyloxyphenyl 4-thiocyanatophenyl terephthalate (**1h**) as colorless needles, 2.85 g (yield 70%). The purity (99.7%) was checked by a differential scaning calorimetry (DSC) thermogram by using the "DSCPURITY" program (Seiko Denshi). IR: 2160 cm^{-1} (ν_{CN}). ^{13}C NMR $\delta = 164.5$, 163.8, 157.2, 151.9, 144.0, 134.5, 133.0, 131.9, 130.3, 123.7, 122.2, 121.7, 115.2, 110.3, 68.5, 31.8, 29.4, 29.3, 26.1 (2C), 22.7, and 14.1. ^{1}H NMR $\delta = 8.33$ (2H, d, $J = 8.9$ Hz), 8.30 (2H, d, $J = 8.9$ Hz), 7.63 (2H, d, $J = 8.9$ Hz), 7.37 (2H, d, $J = 8.9$ Hz), 7.14 (2H, d, $J = 9.0$ Hz), 6.94 (2H, $J = 9.0$ Hz), 3.97 (2H, t, $J = 6.6$ Hz), 1.74 (2H, quin., $J = 6.6$ Hz), 1.4—1.2 (10H, m), and 0.90 (3H, t, $J = 6.6$ Hz).

Method. IR spectroscopy was performed on a Horiba FT-200 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were taken with a Nihon-Denshi EX-270 spectrometer in chloroform-*d* solution, transition temperatures and latent heats were determined by using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp 156.6 °C, 28.4 J g^{-1}). The DSC thermogram was operated at a heating rate of 5 °C min^{-1}. Phase transitions were observed using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system FP-900.

Results and Discussion

Transition temperatures and latent for compounds **1** are summarized in Table 1.

For the comparison, transition temperatures for the corresponding cyano derivatives (**2**) are also shown in the table.[6] Compounds **1** have rather high melting points, probably due to the terephthalic acid core. Compounds **1** show a nematic (N) phase with a typical schlieren texture, and a smectic A ($\mathrm{S_A}$) phase commences from the pentyloxy homolog. The transition temperatures are plotted against the carbon number in Fig. 1.

The N–I transition temperatures show a typical even-odd effect, and decrease with increasing carbon number. The N–I transition temperatures are ca. 50 °C lower than those for the cyano derivatives (**2**). On the other hand, the $\mathrm{S_A}$ phase commences from the pentyloxy homolog (**1e**), while the cyano derivatives (**2**) are reported to commence from the octyloxy homolog (**2b**).

We can conclude that the terminal thiocyanato group reduces the liquid crystalline properties due to increased molecular breadth around the terminal position, while it facilitates the layer arrangement of the molecules.

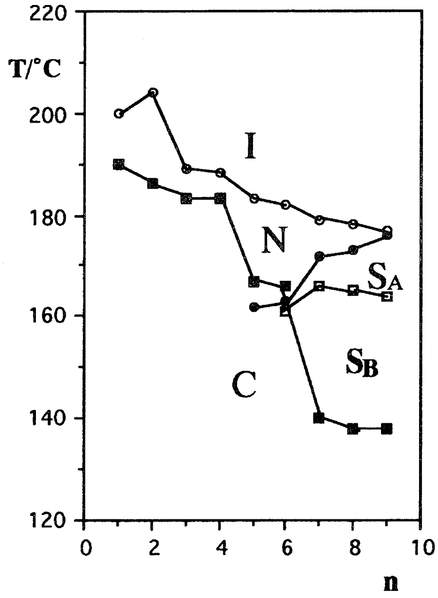


Fig. 1. Transition temperatures against carbon number (*n*) for compounds **1**. C, N, $\mathrm{S_A}$, $\mathrm{S_B}$, and I indicate crystal, nematic, smectic A and B, and isotropic phases, respectively.

The smectic properties of **1** were examined by some binary phase diagrams, as shown in Fig. 2. In Figure 2a, the $\mathrm{S_A}$ phase of the nonyloxy homolog (**1i**) is miscible with the $\mathrm{S_A}$ phase of 4-thiocyanatophenyl 4-(4-octyloxybenzoyloxy) benzoate (**2b**).[5] The $\mathrm{S_A}$ phase of 4-thiocyanatophenyl 4-(4-octyloxybenzoyloxy) benzoate has a partially bilayer arrangement ($\mathrm{S_{Ad}}$) of the molecules.[5] In Figure 2, the $\mathrm{S_{Ad}}$–N transition temperature shown a liner correlation with the molar concentration of each component, while the orientation of the ester linkages is different. The smectic–smectic A (S–$\mathrm{S_A}$) transition decreases almost linearly with decreasing molar concentration of **1i**, indicating that 4-thiocyanatophenyl 4-(4-alkoxybenzoyloxy) benzoates have poor S properties.

Table 1.

											Latent Heats (kJ mol^{-1})			
		Transition Temperature (T/°C)												
Compound	n	C		$\mathrm{S_B}$		$\mathrm{S_A}$		N		I	C-$\mathrm{S_{B,A}}$,N	$\mathrm{S_B}$–$\mathrm{S_A}$	$\mathrm{S_A}$–N(I)	N–I
1a	1	·	190	—		—		·	200	·	41.6			0.2
1b	2	·	186	—		—		·	204	·	28.7			0.4
1c	3	·	183	—		—		·	189	·	36.9			0.3
1d	4	·	183	—		—		·	188	·	38.3			0.4
1e	5	·	167	—	(	·	162)	·	183	·	34.8		0.7	0.3
1f	6	·	166	(·	161	·	163)	·	182	·	43.1	26.9	1.8	0.4
1g	7	·	166	·	166	·	172	·	179	·	a)	21.6	0.9	0.6
1h	8	·	138	·	165	·	173	·	178	·	2.0	27.2	1.1	0.6
1i	9	·	138	·	164	·	176	·	177	·	21.9	25.8	2.7	1.0
2a	7	·	151	—		—		·	236	·				
2b	8	·	148	—		·	158	·	233	·				
2c	9	·	143	—		·	202	·	226	·				

a) Latent heat was difficult to calculate because of overlapping of two peaks.

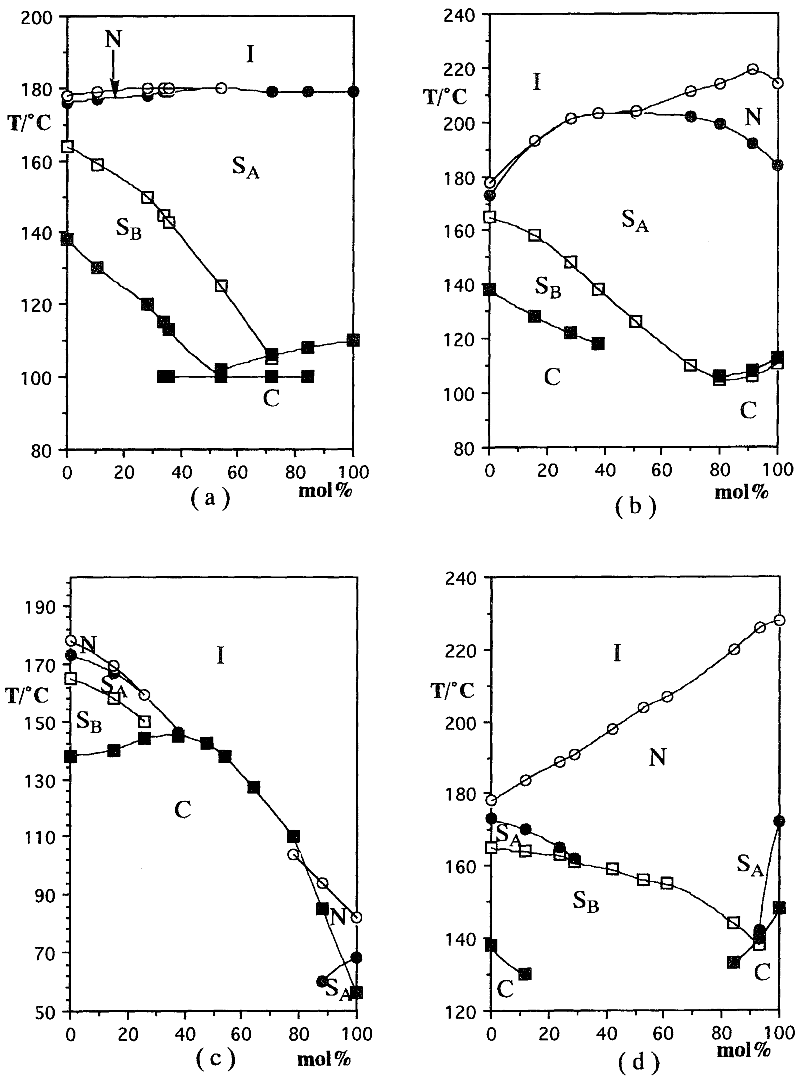


Fig. 2. Phase diagrams for the mixtures of: (a) **1i** (on left) and 4-octyloxypheyl 4-thiocyanatophenyl terephthalate (on right). (b) **1i** (on left) and 4-methoxyphenyl 4′-octyloxybiphenyl-4-carboxylate (on right). (c) **1h** (on left) and 4-octyloxy-4′-cyanobiphenyl (on right). (d) **1i** (on left) and 4-cyanophenyl 4-(4-octyloxybenzoyloxy)benzoate (on right). Footnotes refer to Fig. 1.

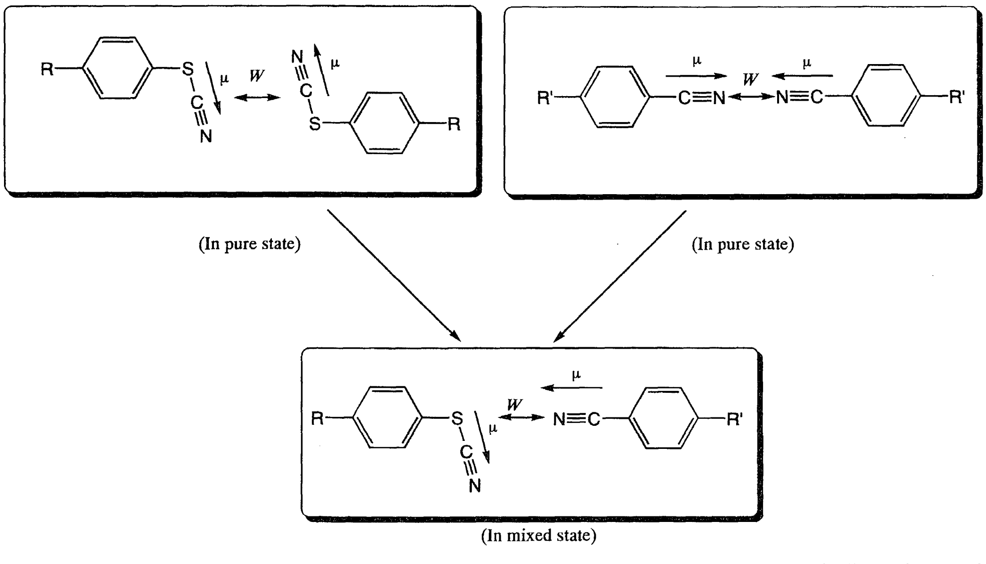
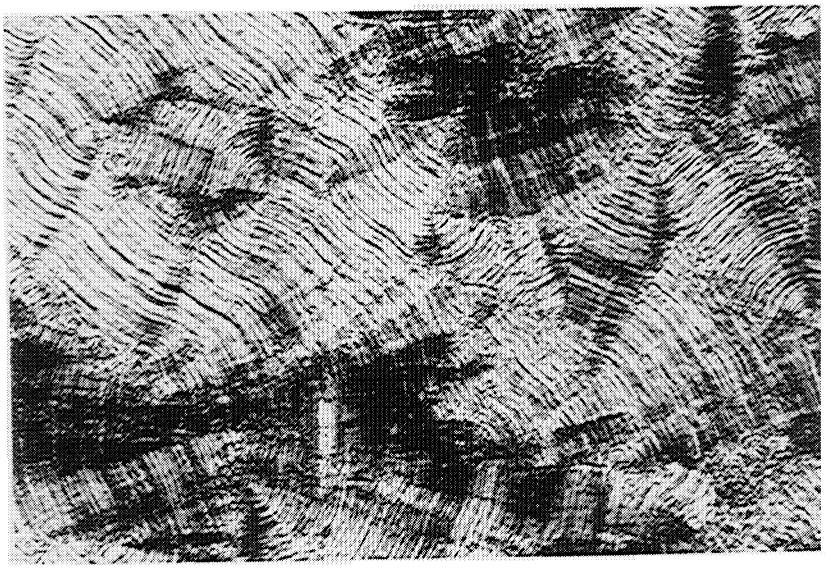


Fig. 3. Dipole correlation models for thiocyanatophenyl and cyanophenyl compounds. *W* and μ indicate interaction energy and dipole mement, respectively.

(a)



(b)

Fig. 4. Micrographs for **1h** (×100). (a) smectic A phase (at 170 °C), (b) smectic B phase (at 150 °C).

Figure 2b shows the binary phase diagram for a mixture of the nonyloxy homolog (**1i**) and 4-methoxyphenyl 4′-octyloxybiphenyl-4-carboxylate.[7] The S_{Ad} phase of the nonyloxy homolog is miscible with the S_A phase of less polar liquid crystals, and a slight enhancement of the S_A–N (I) transition is recognized. In addition, the S phase of the reference compound is miscible with the S phase of **1i**, though the S–S_A transition shows a slight downward concavity. Figure 2c shows the binary phase diagram for a mixture of the octyloxy homolog (**1h**) and 4-octyloxy-4′-cyanobiphenyl, where the smectic A phase has been assigned to the S_{Ad} modification.[8] In the mixture, the solid phase of **1h** is insoluble in the isotropic solution of the reference compound so that the diagram shows an abnormal feature. The N–I transition shows a linear correlation with the molar concentration of each component, while a part of the N phase is hidden by the solid phase. On the other hand, both S_{Ad}–N transitions show nonlinear behavior, and are discontinuous. The S–S_{Ad} transition also steeply decreases with increasing concentration of the reference compound. Figure 2d shows the binary phase diagram for a mixture of the octyloxy homolog (**1h**) and 4-cyanophenyl 4-(4-nonyloxyphenoxycarbonyl)-benzoate. The S_{Ad} phase of the octyloxy homolog has no affinity with the S_{Ad} phase of the reference compound, even though both compounds have the same structure except for the terminal groups. These results indicate that the terminal polar group plays very important roles in the miscibility relation between the S_{Ad} phases. According to the present results, the S_{Ad} phase of **1** is hard to mix with the S_{Ad} phase of various benzonitrile compounds.

The dipole correlation of these compounds is shown in Fig. 3. There in no doubt that polar interactions arising from the cyanophenyl group play very important roles in displaying the S_{Ad} phase in the pure state. Similar interactions must be present in the thiocyanatophenyl system. By mixing these two components, a lapse of these interactions and production of new interactions between the cyanatophenyl and thiocyanatophenyl groups will happen simultaneously. We assume that polar interactions of the dipoles directed in different directions in the mixed systems are unfavorable for the miscibility between the S_{Ad} phases.

Interestingly, the hexyloxy and above members show another smectic phase having a broken fan texture, as shown in Fig. 4. The broken fan texture is frequently observed in the smectic B phase below the S_A phase for nonpolar liquid crystals.[1] The homeotropic textures of the smectic phases of the octyloxy homolog obtained by treatment with trimethylcetyl ammonium bromide are optically uniaxial. As we can see from the table, the latent heats for the smectic–smectic A transitions are fairly large, and the transition temperatures are almost independent of the carbon chain length.

As shown in Fig. 2b, the smectic phase of the nonyloxy homolog (**1i**) is quite miscible with the S_B phase of 4-methoxyphenyl 4′-octyloxybiphenyl-4-carboxylate,[7] while in the diagram the S–S_A transition shows a slight nonlinear correlation against the molar concentration of each component. From these results, the smectic phase of **1** is assigned to the B modification. As far as we know, formation of such a hard smectic phase is very rate in polar liquid crystals having a cyano or a nitro group at the terminal position.[9,10] As we can see from Fig. 2d, interestingly, 4-cyanophenyl 4-(4-octyloxybenzoyloxy)benzoate also has the S_B–S_A transition at ca. 130 °C, and the S_B phase might be observed if the recrystallization is not very fast. Further studies are now underway.

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