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Novel liquid crystals having a thiocyno group at the terminal position

by HIROAKI OKAMOTO, MITSUAKI HAYASHI and SHUNSUKE TAKENAKA*

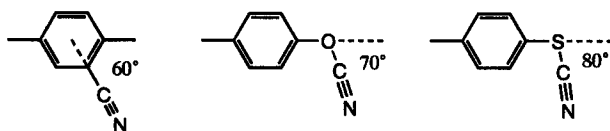
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This paper describes the preparation and thermal properties of some liquid crystalline materials having a thiocyno group at the terminal position. 4-Thiocyanophenyl 4-alkoxybenzoate derivatives are non-mesogenic. 4-Thiocyanophenyl 4-(4-alkoxybenzoyloxy)benzoate and 4-thiocyanophenyl 4-alkoxybiphenyl-4'-carboxylate derivatives show nematic and smectic A phases. The nematic-isotropic (smectic A-isotropic) transition temperatures are fairly low compared with those for the corresponding cyano compounds, and the smectic A phase commences from the early members. The thermal properties of the smectic A phase were examined by some binary phase diagrams, suggesting that the homologous members have two kinds of smectic A phase having different thermal properties, while the smectic-smectic transition was not detectable by either DSC or microscopic observations.

1. Introduction

Liquid crystals having a cyano group at the terminal position are very useful materials for display devices of the TN mode. They show very interesting polymesomorphism including a reentrant nematic and different forms of the smectic A phase, where the large dipole moment along the longitudinal direction of the molecule plays very important role. Generally, such a dipole gives rise to a large positive dielectric anisotropy [1]. On the other hand, some liquid crystals having a polar group at the lateral position, such as cyclohexane [2] and phenyl [3] compounds, have a negative dielectric anisotropy due to the lateral dipole moment. In such compounds the effect of the dipole on the thermal properties has not been clarified. In this communication thiocyno and oxycyano groups have proved interesting.



As shown above, the cyano groups in these moieties at the terminal position have bent angles of *c.* 80° and 70° for -S-CN and -O-CN to the long axis, respectively. These angles are larger than that of the lateral cyano groups (60°) so that these groups will generate a larger dipole moment along the transverse direction of the molecule, even if the substituent is located at the terminal

position. Some liquid crystalline materials having the -SCN [4, 5] and -OCN [6] groups at the terminal position have been prepared, and are known, interestingly, to have large positive dielectric anisotropies similar to those of the terminal cyano derivatives. 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 some materials having the thiocyno group at the terminal position, and the results will be discussed in terms of the molecular properties calculated by the molecular orbital.

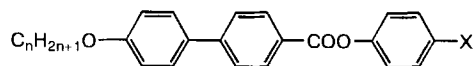
2. Preparation

The synthesis of 4-(4-alkoxybenzoyloxy)benzoic acids was reported in an earlier paper [7]. 4-Thiocyanophenol was kindly supplied by Sanshinkagaku Co. The esterification of the acids and the phenol was carried out according to the reported method [7]. The structure was confirmed by NMR and IR spectroscopy, where the stretching vibration of the thiocyno group for the 4-thiocyanophenyl 4-(4-butoxybenzoyloxy)benzoate was observed at 2160 cm⁻¹, and the two protons adjacent to the thiocyno group were observed at $\delta = 7.62$ ppm (d, *J* = 8.6 Hz, from TMS). The purity was checked by elemental analysis and DSC by using the 'DSCPURITY' program (Seiko-dennshi).

3. Analysis

Transition temperatures and latent heats were determined by using a Seiko SSC-5200 differential scanning

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Table 1. Transitional data for the 4'-substituted biphenyl-4-carboxylates (**2**).

compound	<i>n</i>	X	Cr	S _A	N	I	ΔH_{Cr-S_A}	$\Delta H_{S_A-N(I)}$	ΔH_{N-I}
2a	5	SCN	● 109	● 171	● 177	●	30.7	2.2	0.3
2b	6		● 106	● 173	● 177	●	32.7	2.0	0.3
2c	7		● 102	● 176		●	40.0	3.6	
2a'	6	CN†	● 121		● 223	●			
2b'	7		● 114.5		● 228	●			
2c'	8		● 114		● 228	●			
2d'	9		● 118	● 197	● 221	●			

Cr, S_A, N, I indicate crystal, smectic A, nematic, and isotropic phases, respectively. †From [9].

calorimeter (DSC), with indium (99.9 per cent) as the calibration standard (m.p., 156.6°C, ΔH , 28.4 J g⁻¹). The DSC thermogram was performed with 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.

4. Results

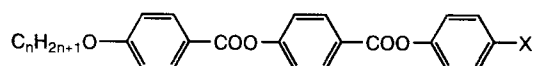
The 4-thiocyanophenyl 4-pentyloxy (**1a**, m.p. 51°C) and 4-octylbenzoates (**1b**, m.p. 36°C) were non-mesogenic. The determined nematic-isotropic (N-I) transition temperature for **1a** extrapolated from the binary phase diagram for the mixture of **1a** and 4-ethoxyphenyl 4-methoxybenzoate was 14°C; this value is lower by 82°C than that for the corresponding cyano compound (4-cyanophenyl 4-pentyloxybenzoate [8]).

The thermal properties for the 4'-substituted biphenyl-4-carboxylates (**2**) are summarized in table 1.

The clearing points for **2** are lower than those for the corresponding cyano derivatives [9]. The smectic phase for the homologues of **2** is assigned to the A modification from examination of the miscibility diagrams. Interestingly, the smectic A phase appears to commence from the early members, while it commences from the nonyloxy homologue for the corresponding cyano compounds (**2'**) [9]. These facts indicate that the terminal thiocyno group facilitates the layer arrangement of the molecules.

The transition temperatures and latent heats for 4-thiocyanophenyl 4-(4-alkoxybenzoyloxy)benzoates (**3**) are summarized in table 2.

For the homologous series of the cyano compound, **3'**, the smectic A phase having a partially bilayer (S_{A_d}) arrangement commences from the nonyloxy homologue [11]. On the other hand, the thiocyno derivatives **3** show lower clearing points than **3'**, the smectic A phase

Table 2. Transitional data for the 4-thiocyanophenyl 4-(4-alkoxybenzoyloxy)benzoates (**3**).

compound	<i>n</i>	X	Cr	S _A	N	I	ΔH_{Cr-S_A}	$\Delta H_{S_A-N(I)}$	ΔH_{N-I}
3a	1	SCN	● 149		● 204	●	41.3		0.4
3b	2		● 158		● 208	●	40.1		0.3
3c	3		● 139	● 144	● 194	●	30.5		0.4
3d	4		● 129	● 156	● 191	●	42.1	1.1	0.4
3e	5		● 120	● 162	● 184	●	29.4	1.3	0.4
3f	6		● 114	● 170	● 183	●	28.9	1.3	0.5
3g	7		● 112	● 172	● 178	●	31.3	2.5	0.2
3h	8		● 110	● 179		●	38.8	3.8	
3i	9		● 105	● 180		●	35.3	4.1	
3'a	6	CN†	● 132		● 248	●			
3'b	8	CN‡	● 116		● 229	●			
3'c	9		● 121	● 198	● 229	●			
3'd	10		● 108	● 208	● 222	●			

Cr, S_A, N, I indicate crystal, smectic A, nematic, and isotropic phases, respectively. †From [10]. Interestingly, this compound has been reported to show a smectic B phase, where the smectic B - nematic transition occurs at 100°C. ‡From [11].

commences from the propoxy homologue, indicating that the thiocyno group facilitates the layer arrangement of the molecules.

The transition temperatures are plotted against the number of carbon atoms in the alkoxy chain in figure 1.

The N-I transition temperatures show a typical even-odd effect and reduce with increasing the carbon number. Interestingly, the S_A -N(I) transition also shows an apparent even-odd effect. In order to characterize the smectic A phase, the miscibility relation of liquid crystalline phases was examined with binary phase diagrams for the mixture of 4-(4-heptylphenoxy carbonyl)-phenyl 4-cyanobenzoate and 3 d, 3 g, and 3 i, as shown in figure 2.

4-(4-Heptylphenoxy carbonyl)phenyl 4-cyanobenzoate, a reference compound, is reported to have a mesomorphic sequence of an S_{A_2} 168 S_{A_d} 172 N 233 I, where S_{A_2} and S_{A_d} indicate the smectic A phases with bilayer and partially bilayer arrangements [12]. In all diagrams the N-I transitions show a linear correlation with the molar composition of each component. On the other hand, the S_A -N(I) transition shows remarkable non-linear behaviour. In figure 2(a), one S_A -N transition shows an almost linear correlation against the molar composition of each component, and the S_A -N transition arising from the reference compound shows very non-linear behaviour and disappears at *c.* 90 mol % of the reference compound. In figure 2(b), the S_A -N transition in the range between 100 and 50 mol % of the butoxy homologue shows the non-linear behaviour, and a S_A - S_A

transition could be observed at 55 and 80 mol % of the reference compound, while such transition could not be observed in the other compositions. These facts indicate that in the diagram three kinds of S_A phases having very similar thermodynamical properties, are present. In figure 2(c), a reentrant nematic phase was observed at 88 mol % of the reference compound, giving rise to the mesomorphic sequence of S_A -N_{re}- S_A -N-I. However, the S_A - S_A transition could not be observed in the range between 40 and 60 mol % of the reference compound. In figure 2(d), neither the reentrant phenomenon or the S_A - S_A transition could be observed. From these results, the smectic region may be divided into three kinds. The first is the smectic A region arising from the reference compound (S-2), and the smectic phase has been assigned as the S_{A_d} phase. The second is the smectic A phase arising from the thiocyno compound 3 (S-1). The characteristic feature of the S_A -N(I) transition suggests that the smectic A phase has a partially bilayer nature, while this phase has no affinity with the S_{A_d} phase of the reference compound. The third region is S-3, where the smectic phase has a typical focal-conic texture, and the latent heat for the S_A -N transition is very small. As we can see from the figures, the S_A -N transition shows an almost linear correlation with the mol % of the components. Therefore, we assume that the S_A phase is assigned as the monolayer or the bilayer modification. Four diagrams have two tricritical points, where the texture of the smectic phase around the points shows a characteristic focal-conic texture with ellipses, while the smectic phases in the other region show the typical focal-conic fan texture. The ellipse texture gradually changes to the typical focal-conic texture with decreasing temperature.

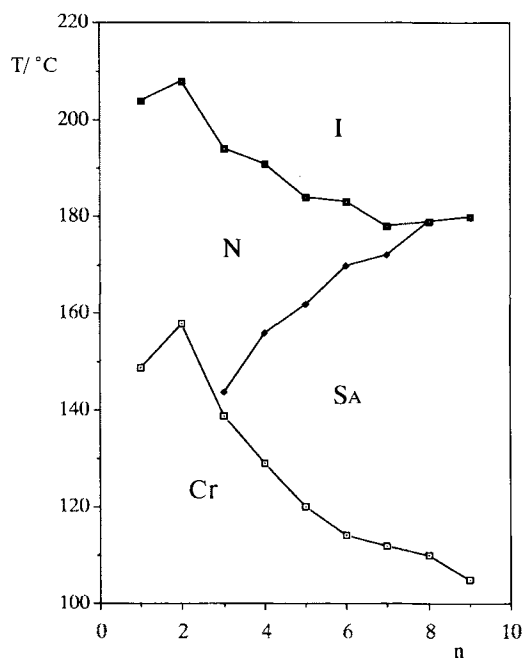


Figure 1. Plots of transition temperatures against the number of carbon atoms (*n*) of the alkoxy chain for 3.

5. Structural consideration

The most probable conformation (model *a*) calculated by the AM1 method [13] is shown in figure 3.

The rotational barrier for COO-phenyl bond is 5.36 kJ mol⁻¹, and adjacent phenyl rings for the most stable conformation has an angle of 45°, indicating that phenyl rings rotate almost freely at the liquid crystalline temperature. For the phenyl-SCN bond the rotational barrier is 0.84 kJ mol⁻¹ (model *b*), where the SCN group for the most stable conformation lies on the same plane as the phenyl ring. The energy difference between two conformers, that is, the SCN group orients to the same and opposite directions with respect to the adjacent ester group, is only 0.42 kJ mol⁻¹ which probably arises from the dipole-dipole interaction between the SCN and ester groups. These facts suggest that the SCN group rotates almost freely at the liquid crystalline temperature.

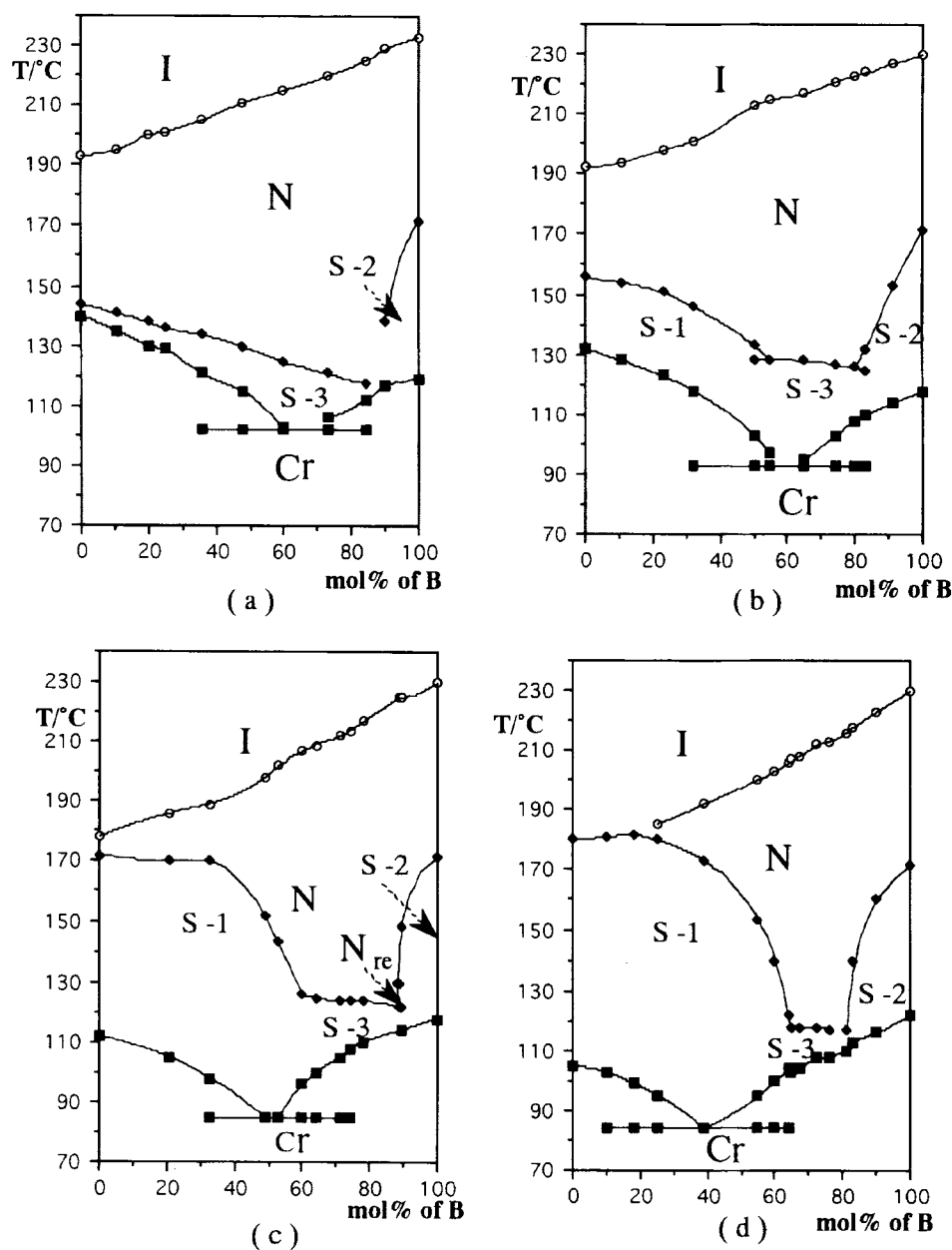


Figure 2. Phase diagrams for the mixtures of 4-heptylphenyl 4-(4-cyanophenoxycarbonyl)benzoate (**B**; on the right) and (a) the propoxy, (b) butoxy, (c) heptyloxy, and (d) nonyloxy homologues of **3** (on the left).

In such a condition, the transverse component of the dipole moment arising from the thiocyanate group may cancel, while the longitudinal component contributes to the increase in the dielectric anisotropy along the longitudinal direction.

6. Discussion

The terminal thiocyanate group shows two characteristic effects on the mesomorphic properties. First, it reduces the N-I transition temperatures. For example, the N-I transition temperatures for compound **1** are

lower by *c.* 80°C than those for the corresponding cyano compounds. This trend is also realized in the three ring compounds, **2** and **3**. Second, the thiocyanate group facilitates the layer arrangement of the molecules, giving rise to the formation of the smectic A phase. These effects should result from the geometrical and electrostatic effects of the terminal thiocyanate group.

In the present systems, there is no doubt that the homologous series have two kinds of smectic A phases, though the smectic A-smectic A transition was observed only in the binary phase diagrams shown in figure 2.

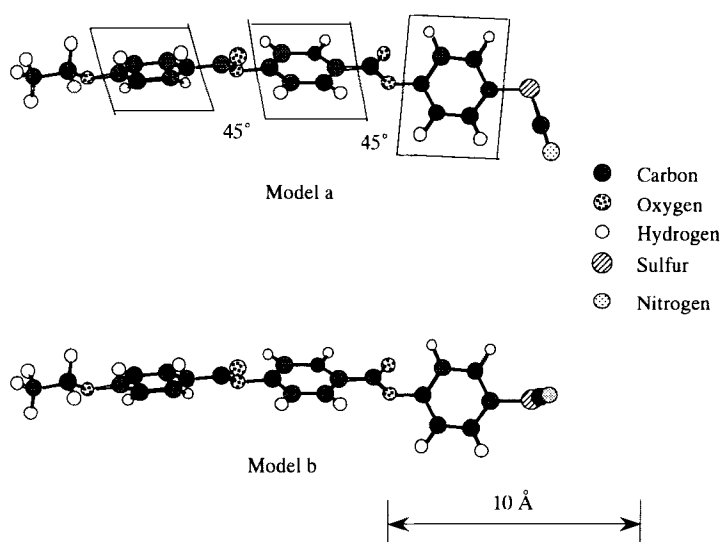


Figure 3. The molecular structures for the ethoxy homologue of **3** calculated by the AM1 method.

The figures suggest that the upper smectic A phase has a partially bilayer nature from a thermodynamical point of view. As shown in figures 2(a) and 2(b), the smectic A(S-3)–nematic(smectic A(S-1)) transition temperature shows a linear correlation with the molar concentration of each component. From this fact, we can assume that the S-3 phase has a monolayer or a bilayer nature from a thermodynamical point of view. It is well known that the terminal cyano group in benzonitrile compounds increases the dipole moment along the longitudinal direction of the molecules, and facilitates the antiparallel orientation of the molecules, giving rise to the complex smectic modifications. In the present case, the cyano group directs rather the lateral direction so that the dipole moment arising from the cyano group would not increase the longitudinal dipole very much. In addition, the cyano group would not increase the lateral dipole moment since the free rotation of the thiocyanate group would cancel the lateral dipole. In spite of the disadvantageous condition, the present homologues show a smectic A phase having a partially bilayer structure [14] similar to the benzonitrile compounds. These facts indicate that the terminal longitudinal dipole is not indispensable for the formation of the S_{Ad} phase. However, we assume that in both polar systems the dipole–dipole interaction as shown in figure 4, plays an important role

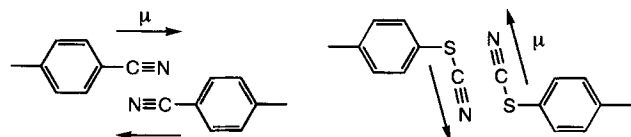


Figure 4. A possible dipole–dipole interaction at the terminal position for cyano and thiocyanate compounds.

for the complex polyomesomorphism in the N and S_A phases.

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- [14] The layer spacing for the smectic A phase is dependent on the carbon number of the alkoxy chain, and is strongly dependent on the temperature. For example, the layer spacing for the pentyloxy homologue is 1.1 (at 137°C) and 1.0 (at 127°C) times the fully extended molecular length. The details will be published elsewhere.