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The Thermal Properties of Liquid Crystalline Materials Incorporating Cyanothiophene and Cyanofuran

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Some homologous series of cyanothiophene and cyanofuran compounds have been prepared. 4-Alkoxyphenyl 3-(5-bromo-2-thienyl)acrylate (**1**) and 4-alkoxyphenyl 3-(5-cyano-2-thienyl)acrylate (**2**), and 4-alkoxyphenyl 4-(5-bromo-2-furylcarbonyloxy)benzoate (**3**) and 4-alkoxyphenyl 4-(5-cyano-2-furylcarbonyloxy)benzoate (**4**) give rise to a nematic phase. For compound **4**, a smectic A phase which commences from the hexyloxy homolog has a bilayer (S_{A2}) arrangement of the molecules. The thermal stabilities of the mesophases are lower than those of the corresponding benzonitrile compounds. This arises from an increased molecular breadth around the terminal portion and the change of the dipole moment arising from the terminal cyano group bending with respect to the long molecular axis.

Liquid crystalline materials incorporating a cyanophenyl group as the terminal function are good nematogens for devices employing a twisted nematic mode. The molecules frequently give rise to very interesting phenomena such as an induced smectic A phase[1—3] or an enhancement of smectic A thermal stability[4,5] in some binary mixtures and reentrant phenomena.[6—8] In such cases, it is well known that a dipole moment arising from the terminal cyano group plays a very important role in determining the thermal behavior of the molecule.[8—10]

In this paper, we describe the preparation, and thermal and dielectric properties of cyanothiophene and cyanofuran compounds, **1**, **2**, **3**, and **4**, and some related compounds. In these series, the cyano group would occur at an angle with respect to the rotational axis of the entire molecule because of the thiophene and furan rings, and increase the molecular breadth.

Experimental

Method. The transition temperatures were determined by using a Nikon POH polarizing microscope fitted with a Mettler FP 52 heating stage and a control unit. The transition temperatures were also measured by using a Dainiseikosha SSC-560 differential scanning calorimeter. Indium (99.9%) was used as a calibration standard at a heating rate of 5 °C/min. The dielectric constants were measured by using an Andodenki TR-10 precision capacitance measurement system. The capacitor cell consisted of two indium coated glass electrodes separated by a 25 μm Mylar spacer. The cell temperature was controlled by means of a brass housing. The voltage applied was 0.4 V at 1 kHz. The alignment of molecules in the cell was achieved by applying a 1.0 T magnetic field. The capacitor cell was calibrated by highly purified benzene and acetonitrile.

Materials. 3-(5-Bromo-2-thienyl)acrylate was prepared by the reaction of 5-bromo-2-thiophenecarbaldehyde and malonic acid.[11] 3-(5-Bromo-2-thienyl) acryloyl chloride was reacted with 4-alkoxyphenols in dry benzene containing pyridine (5%), giving the homologous series of **1**. A similar reaction of 5-bromo-2-furancarbonyl chloride and 4-alkoxyphenyl 4-hydroxybenzoates[12] gave the homologous series of **3**.

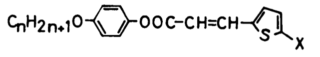
4-Nonyloxyphenyl 4-(5-Cyano-2-furylcarbonyloxy)benzoate. A mixture of 4-nonyloxyphenyl 4-(5-bromo-2-furylcarbonyloxy)benzoate (3.4 g, 6.4 mmol) and copper(I) cyanide (0.86 g, 9.6 mmol) in anhydrous *N*,*N*-dimethylformamide (20 ml) was refluxed for 3 h.[13] After cooling, the dark brown solution was poured onto cold water (100 ml) containing ethylenediamine (8.0 g, 0.13 mol). The resulting solution was extracted with ether (50 ml×4 times). The purification was carried out by column chromatography on silica gel where a solvent mixture of pet. ether and ether (95:5) was used as an elution solvent, followed by recrystallization from absolute ethanol: 0.8 g, IR: ν_{CN}=2250 cm^{-1}. The homologous series of **2** and **4** were prepared similarly. The purity was checked by elemental analysis.

Results and Discussion

The transition temperatures for thiophene compounds **1** and **2** are summarized in Table 1. In the present study, three related compounds were prepared; 4-butylcyclohexyl 3-(5-cyano-2-thienyl)acrylate (T_{mp}=70.5 and $T_{N\text{-}I}$=51.7 °C), 4-pentylcyclohexyl 3-(5-cyano-2-thienyl)acrylate (T_{mp}=85.7 and $T_{N\text{-}I}$=70.2 °C), and 4-hexylphenyl 3-(5-cyano-2-thienyl)acrylate (T_{mp}=92.4 and $T_{N\text{-}I}$=73.0 °C). For these compounds both melting points and nematic-isotropic transition temperatures are lower than those for series **2**.

The transition temperatures for the furan compounds **3** and **4** are summarized in Table 2. The nematic-isotropic transition temperatures reveal a familiar even-odd effect. The smectic properties for

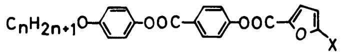
Table 1. The transition temperatures for series **1** and **2** (T/°C)


$C_nH_{2n+1}O-C_6H_4-OOC-CH=CH-C_4H_2S-X$

Compound	n	X	C		N		I
1	3	Br	.	89.9	—		
	4		.	89.5	—		
	5		.	79.2	(.	57.3)	.
	6		.	77.3	(.	66.8)	.
	7		.	76.4	.	63.7)	.
	8		.	76.4	(.	70.7)	.
2	3	CN	.	115.0	(.	105.8)	.
	4		.	115.4	(.	96.6)	.
	5		.	99.2	(.	92.2)	.
	6		.	85.9	(.	97.3)	.
	7		.	95.7	.	95.8	.
	8		.	95.4	.	99.0	.

The values in the parentheses indicate the monotropic transitions.

Table 2. The transition temperatures for series **3** and **4** (T/°C)



Compound	n	X	C	S_A	N	I
3	3	Br	.	129.1 —	. 132.6	.
	4		.	128.1 —	(. 124.1)	.
	5		.	115.5 —	. 120.6	.
	6		.	118.9 —	. 119.2	.
	7		.	121.3 —	. *1	.
	8		.	118.3 —	. 122.1	.
	9		.	122.1 —	. *1	.
	10		.	121.6 —	(. 113.4)	.
4	3	Br	.	147.2 —	. 157.3	.
	4		.	136.9 —	. 158.3	.
	5		.	142.5 —	. 153.5	.
	6		.	139.0 (. 126.4)	. 125.6	.
	7		.	137.2 (. 133.8)	. 147.4	.
	8		.	134.9 . 140.1	. 147.6	.
	9		.	134.3 . 143.1	. 144.1	.
	10		.	134.6 . 149.2	—	.

The values in the parentheses indicate the monotropic transitions. *1 Solidification proceeded.

series **4** commence from the hexyloxy homolog. In the present study, three related compounds were prepared; 4-butoxyphenyl 5-cyano-2-furancarboxylate (T_{mp}=104 °C) and 4-hexylphenyl 5-cyano-2-furancarboxylate (T_{mp}=95.5 °C), but none of them turned out to be mesogenic. 4-Hexylphenyl 4-(5-cyano-2-funylcarbonyloxy) benzoate gives rise to a nematic phase monotropically (T_{mp}=135 and T_{N-I}=129 °C). The assignment of the smectic phase for the heptyloxy homolog of series **4** was done by an examination of the isobaric diagrams shown in Fig. 1.

In the binary mixture of the heptyloxy homolog and 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate (Fig. 1a), the smectic A-nematic transition temperatures reveal a weak nonideal behavior in the range between 80 and 0 mol% of the heptyloxy homolog. However, both smectic phases are discontinuous in the range between 95 and 85 mol% of the heptyloxy homolog. A similar trend is observed in Fig. 1b. For the binary mixture of the heptyloxy homolog and 4-pentylphenyl 2-cyano-4-(4-octylbenzoyloxy)benzoate, an interesting fact is that the smectic A-nematic (isotropic) transitions show a linear correlation with additivity, whereas both smectic phases appear to be essentially immiscible. Here, it would be reasonable to assume that both nonpolar mesogens have a monolayer arrangement of the molecules in the smectic A phase. In Fig. 1c, the smectic phase of the heptyloxy homolog is also immiscible with the smectic A phase of *N*-[4-(4-octyloxybenzoyloxy)-benzylidene]-4-cyanoaniline where the molecules form a partially bilayer arrangement (S_{Ad}) in the smectic A phase.[14] For the binary phase diagram of the heptyloxy homolog and 4-pentylphenyl 4-(4-cyanobenzoyloxy)benzoate (5DB)[15] in Fig. 1d, on the other hand, both smectic phases are isomorphous, though the smectic-nematic transition temperatures show a nonideal behavior with additivity. 5DB has been known to form a bilayer arrangement (S_{A2}) of the molecules in the smectic A phase. These facts lead to the conclusion that the smectic phase of the heptyloxy homolog forms a smectic A modification with a bilayer arrangement of the molecules (S_{A2}). In Fig. 1a and 1b, the S_A-N transition temperatures show an ideal behavior in the range between 80 and 0 mol% of the heptyloxy homolog of series **4** and the apparent discontinuity in the range between 95 and 85 mol%. This indicates that the S_{A2} phase, although similar to the S_{A1} phase, is essentially different and immiscible with it and that the S_{A2} arrangement of the molecules is easily destroyed by a small amount of the nonpolar mesogens. In Fig. 1c, the rapid reduction of the S_A-N transition temperatures with increasing the composition of *N*-[4-(4-octyloxybenzoyloxy)benzylidene]-4-cyanoaniline indicates that the S_{A2} phase of the heptyloxy homolog of **4** has low affinity with the S_{Ad} phase.

From geometrical and electrical points of view, 3-(5-cyano-2-thienyl)acrylate and 5-cyano-2-furancarboxylate are very different from 3-cyanobenzoate. The geometries of cyanothiophene, cyanofuran, and benzonitrile are illustrated in Fig. 2. The cyano group in series **2** lies in the volume of a cylinder defined by rotation of the rest of the molecule about its longer molecular axis. The nematic-isotropic transition temperaturs for series **2** are lower by *ca.* 50 °C than those for the 4-alkoxyphenyl 4-cyanocinnamates,[16] whereas the cyano group does not increase the molecular breadth so much. Similarly, the nematic-isotropic transition temperatures for series **4** are lower by *ca.* 130 °C than those for the corresponding benzonitrile compounds.[15] The increased molecular breadth around the cyanofuran portion is one of the reasons for the low nematic stability. When the molecules form antiparallel correlations due to strong dipole-dipole interaction, however, the bend of the terminal cyano group would be very unfavorable for the thermal stabilities of the mesophases, especially in the thermal stabillity of the nematic phase. The situation is shown in Fig. 3.

As a result, the bend of the cyano group would increase the breadth of the antiparallel dimer formed by the dipole-dipole interaction. The increased molecular breadth is assumed to be the other reason for the low nematic stabilities of series **2** and **4**. On the other hand, the axial separation of the molecules due to the bent geometry would reduce a repulsive interaction around the core portion. This, in turn, leads to an increase in relative thermal stability of the smectic A phase. Indeed, the ratios of the smectic A-nematic/nematic-isotropic transition temperatures for the series **4** lie in the range between 0.94 and ≈1. The values are very large compared with those for three ring compounds incorporating a cyano group at the terminal position,[17] indicating that for series **4** the thermal stabilities of the smectic A phase are relatively higher than those of the nematic phase.

From an electrical point of view, the cyano groups in series **2** and **4** are rather similar to the cyano group in 4-cyanobenzoate compounds, because a conjugation of the cyano group with the π electron system of the entire molecule generates greater polarity and polarisability, a general requisite of the mesophase stability. However, the bend of the cyano group strongly affects the dielectric behavior. The dielectric constants $\varepsilon_{/\!/}$ and $\varepsilon_{\perp}$ for the octyloxy homolog of series **2** are plotted against temperature in Fig. 4.

The dielectric anisotropy ($\Delta\varepsilon$) for the octyloxy homolog is *ca.* 1.8 at 90 °C, indicating that the anisotropy of the dipole moment arising from the cyano group is quite small. The anisotropy ($\Delta\varepsilon$) for the heptyloxy homolog of series **4** is *ca.* −3.0 at 139 °C. The negative value is expected from the theoretical calculation of the group dipole moments.[18] Therefore, the cyano groups in series **2** and **4** tend to

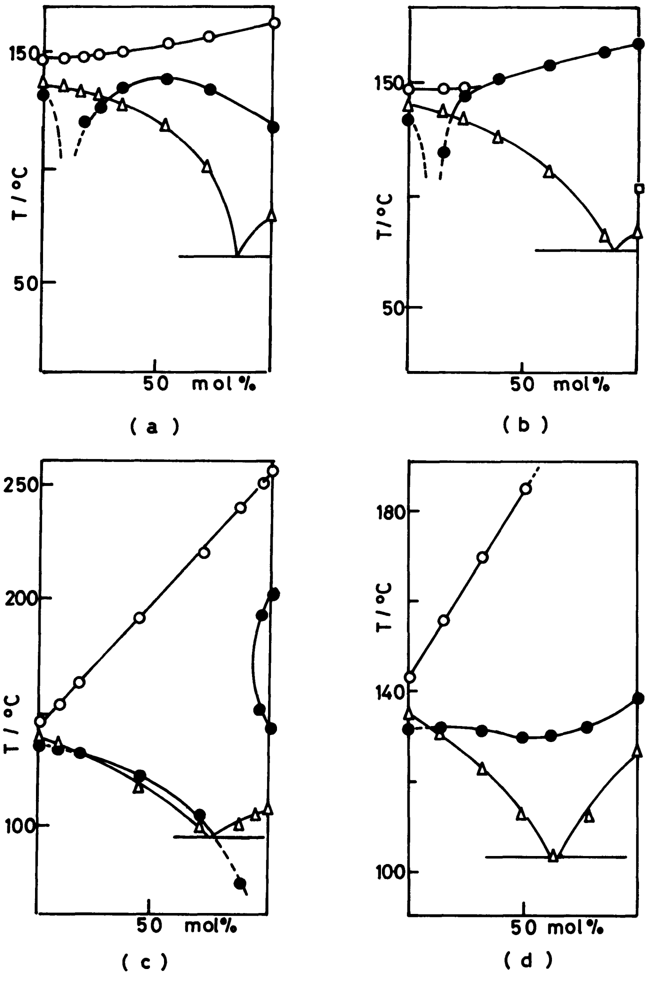


Fig. 1. The isobaric diagrams for the mixtures of (a) the heptyloxy homolog of **4** (on left) and 4-heptylphenyl 4-(4-octylbenzoyloxy)benzoate (on right), (b) the heptyloxy homolog of **4** (on left) and 4-heptylphenyl 4-(3-cyano-4-octylbenzoyloxy)benzoate (on right), (c) the heptyloxy homolog of **4** (on left) and *N*-[4-(4-octyloxybenzoyloxy)benzylidene]-4-cyanoaniline(on right), (d) the heptyloxy homolog of **4**(on left) and 4-pentylphenyl 4-(4-cyanobenzoyloxy)benzoate (on right). ○: nematic-isotropic, ●: smectic A-nematic (isotropic), and △: solid-mesophase transitions.

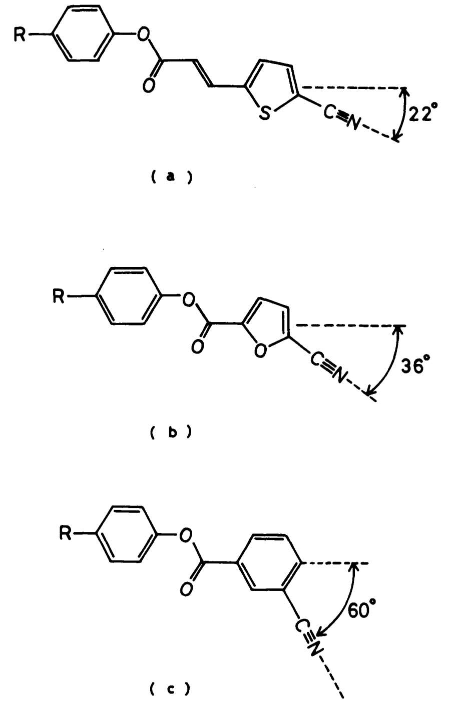


Fig. 2. The geometries of 3-(5-cyano-2-thienyl)acrylate (a), 5-cyano-2-furancarboxylate(b), and 3-cyanobenzoate(c).

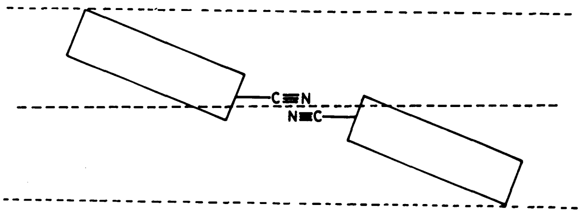


Fig. 3. A possible model for the antiparallel dimer for series **2** and **4**.

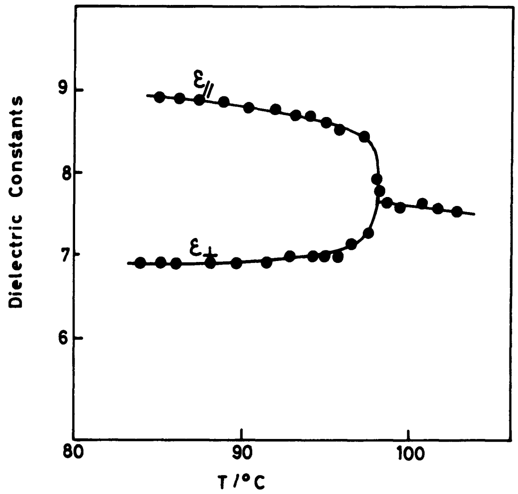


Fig. 4. Plot of the dielectric constants against temperature for the octyloxy homolog of series **2**.

increse the dipolarity perpendicular to the long molecular axis, as does the cyano group in 3-cyanobenzoate compounds.

Conclusion

The terminal cyano group has a very important role in determining the thermal and dielectric properties, and the bend of the cyano group with respect to the long molecular axis results in a decrease in the thermal stabilities of the mesophases and a reduction of the dielectric anisotropy. The formation of the bilayer smectic A phase (S_{A2}) for series **4** appears to be a rare case.

References

1) J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975).

2) C. S. Oh, *Mol. Cryst. Liq. Cryst.*, **42**, 1 (1977).

3) G. Heppke and E.-J. Ricter, *Z. Naturforsch.*, **33**, 185 (1978).

4) A. C. Griffin, R. F. Fisher, and S. J. Havens, *J. Am. Chem. Soc.*, **100**, 6329 (1978).

5) M. Domon and J. Billard, *J. Phys.*, **C3-40**, C3-413 (1979).

6) P. E. Cladis, R. K. Bogardus, and D. Aadsen, *Phys. Rev. A*, **18**, 2292 (1978).

7) W. Weissflog, G. Pelzl, and D. Demus, *Mol. Cryst. Liq. Cryst.*, **76**, 261 (1981).

8) N. H. Tinh, *Mol. Cryst. Liq. Cryst.*, **91**, 285 (1983).

9) A. M. Levelut and R. J. Tarento, *Phys. Rev. A*, **24**, 2180 (1981).

10) N. V. Madhusidana, B. S. Srikanta, and M. Subramanya, *Mol. Cryst. Liq. Cryst.*, **97**, 49 (1983).

11) G. W. Gray and B. Jones, *J. Chem. Soc.*, **1954**, 1467.

12) J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 285 (1973).

13) J. C. Dubois and A. Beguin, *Mol. Cryst. Liq. Cryst.*, **47**, 193 (1978).

14) N. H. Tinh, A. Zann, J. C. Dubois, and J. Billard, *Mol. Cryst. Liq. Cryst.*, **56**, 323 (1980).

15) F. Hardouin, A. M. Levelut, and G. Sigaud, *J. Phys.*, **42**, 71 (1981).

16) F. B. Jones and J. J. Ratto, *J. Phys.*, **C1-36**, C1-413 (1975).

17) For example, see References 7 and 8.

18) R. T. Klingbiel, D. J. Genova, T. R. Criswell, and J. P. Van Meter, *J. Am. Chem. Soc.*, **96**, 7651 (1974).