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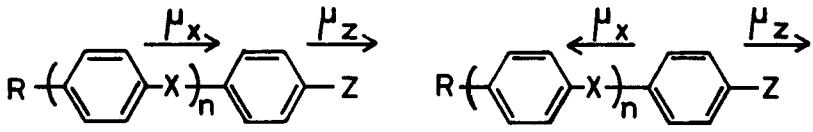
The thermal properties for a homologous series of 4-(4-alkoxyphenoxycarbonyl)phenyl 5-cyano-2-furancarboxylates have been examined. The smectic A phase commences from the hexyloxy homolog, and the octyloxy, nonyloxy and decyloxy homologs show two kinds of smectic A phases and experience the S_A–S_A transition. The lower phase which shows a typical fan shaped texture is assigned to a smectic A with a bilayer arrangement of the molecules (S_{A2}). The higher phase which shows a typical fan shaped texture on the cooling stage and a broken fan one on the heating stage, is assigned to a smectic A with a partially bilayer arrangement of the molecules (S_{Ad}). The S_A–S_A transitions could be easily detected by both differential scanning calorimeter and optical microscopic method.

INTRODUCTION

A smectic A phase has been classified into four modifications according to their molecular arrangements, i.e., monolayer (S_{A1}), bilayer (S_{A2}), antiphase ($S_{\tilde{A}}$), and partially bilayer (S_{Ad}) arrangements.[1] The S_{A1} phase is frequently formed by nonpolar mesogens. Mesomorphic compounds incorporating a polar substituent such as a cyano or a nitro group as the terminal function have been known to associate with a more or less overlap of the molecules in mesophases. In the associated pairs, a dipole-dipole interaction has been known to play an important role in determining the molecular ar-

rangement. The polar molecule is represented by:

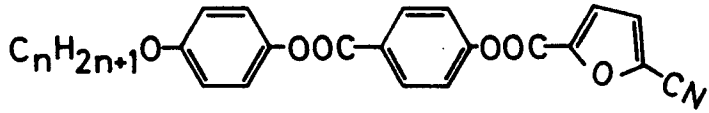


[*A*] [*B*]

R = alkyl, alkoxy, Z = cyano or nitro, X = linking group

The molecules belonging to class [A] frequently exhibit reentrant phenomena,[2,3] in which the smectic A phase has the S_{Ad} arrangement of the molecules. On the other hand, the molecules belonging to class [B] in the smectic A phase tend to form three kinds of molecular arrangements, i.e., S_{Ad}, $S_{\tilde{A}}$, and S_{A2} phases, and undergo S_A–S_A transitions.[4–8] In both cases, the S_{A1} phase is sometimes formed at low temperature.

In this paper, we describe the thermal properties of a homologous series of 4-(4-alkoxyphenoxycarbonyl)phenyl 5-cyano-2-furancarboxylates.



The homologous series have a general constitution of class [B]. Characteristics of this series are that the terminal cyano group occurs at an angle with respect to the rotational axis of the entire molecules, while the cyano group can conjugate with the other conjugating system of the molecule. Therefore, the bend of the cyano group would increase the molecular breadth, and decrease the anisotropies of the polarity and polarisability of the entire molecule.

EXPERIMENTALS

Materials: Preparation of 4-(4-alkoxyphenoxycarbonyl)phenyl 5-cyano-2-furancarboxylates has been described in a previous paper.[9]

Method: Transition temperatures were determined by using a Nikon Model POH polarising microscope fitted with a Mettler FP 52 heating stage and a FP 5 control unit, and a Daini-Seikosha SSC–560 differential scanning calorimeter (DSC). Experimental conditions are described in footnotes in Table I and Figure 1.

RESULTS

As mentioned in a previous paper, the homologous series show mesomorphic properties.[9] In this paper, we mainly describe the thermal properties of the smectic phases.

The smectic phase commences from the hexyloxy homolog, where the smectic A phase for the hexyloxy and heptyloxy homologs has been reported to have a bilayer arrangement of the molecules (S_{A2}). The DSC recordings for the heptyloxy to decyloxy homologs are shown in Figure 1.

In these figures, the thermograms being taken from the second heating illustrate only the mesophase-mesophase and mesophase-isotropic transitions.

For the heptyloxy homolog (line 1 in Figure 1), the endotherms at 133.3 and 147.3°C are assigned to the smectic A-nematic and nematic-isotropic transitions, respectively. The smectic A-nematic transition having large latent heat (4.0 kJ/mol) is assumed to have a first order nature. These transitions are also confirmed by an optical microscopic method. For the octyloxy homolog (line 2 in Figure 1), the DSC recording shows only two endotherms at 140.2 and 147.4°C, which correspond to the smectic A-smectic A and nematic-isotropic transitions, respectively. However, the homolog showed an apparent smectic A-nematic transition at 140.5°C on the microscopic observation, in addition to the smectic A-smectic A and nematic-isotropic transitions at 140.2 and 147.4°C, respectively. Here, the upper and lower smectic A phases are abbreviated as S_1 and S_2 phases, respectively. The latent heats decrease by the order of nematic-isotropic > S_2–S_1 > S_1-nematic transitions. The micrographs for the octyloxy homolog are shown in Figure 2.

The S_2 phase always exhibits a typical fan shaped texture (texture **1** in Figure 2) on both heating and cooling stages. On the other hand, The S_1 phase has two kinds of textures (textures **2** and **4** in Figure 2). Texture **2** is observed only on the heating stage. Texture **4** which is quite similar to texture **1** is observed only on the cooling stage. These facts indicate that the texture of the S_1 phase is strongly dependent on the molecular arrangement of the past phase. The S_2–S_1 and S_1–S_2 transitions always accompany with very sharp and dramatic change in texture. Therefore, we could easily observe the S_2–S_1 transition, while the textures of both phases were quite similar.

For the nonloxy homolog (line 3 in Figure 1), the DSC recording shows three transitions at 141.5, 143.8, and 145.1°C, in which these endotherms were assigned to the S_2–S_1, S_1-nematic, and nematic-

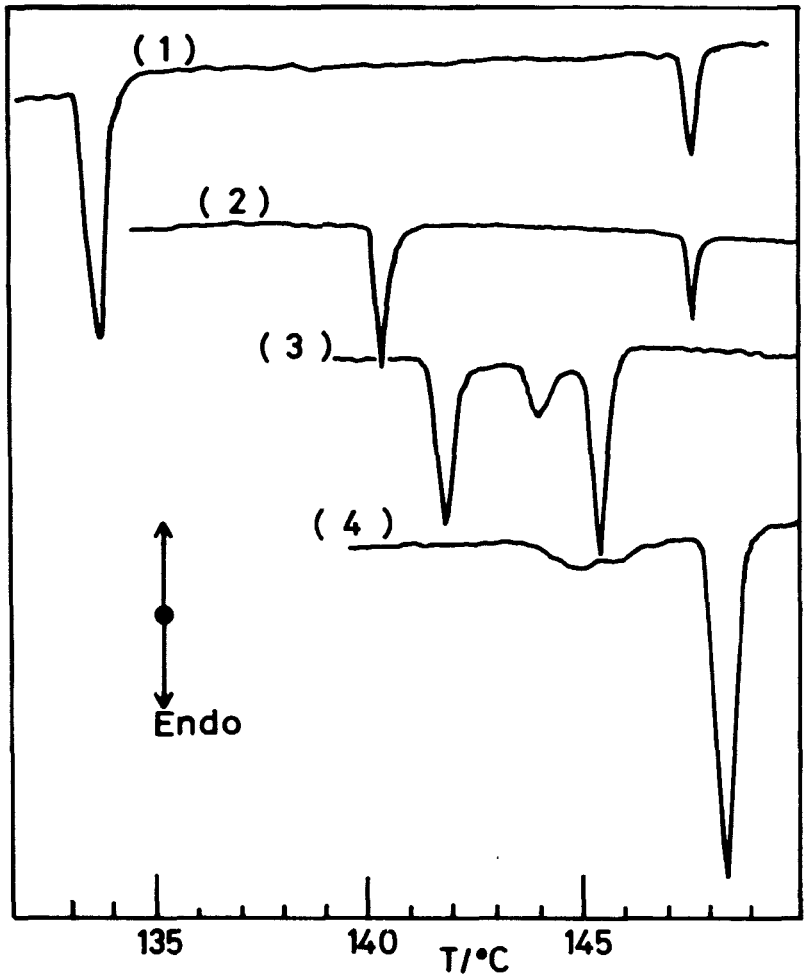


FIGURE 1 DSC thermograms: (1) the heptyloxy, (2) octyloxy, (3) nonyloxy, and (4) decyloxy homologs. DSC thermograms were recorded at a heating rate of 1°C/min, where the temperature was calibrated by indium (m.p. 156.6°C). The sample weight was 10–15 mg. All data were taken from the second heating.

isotropic transitions, respectively. The latent heats decrease by the order of nematic-isotropic > S_2–S_1 > S_1-nematic transitions. We can assume that the S_1-nematic transition has a second order nature.

All of the transitions were also observed by microscopy, where the textures of the S_2 and S_1 phases were quite similar to those in Figure 2.

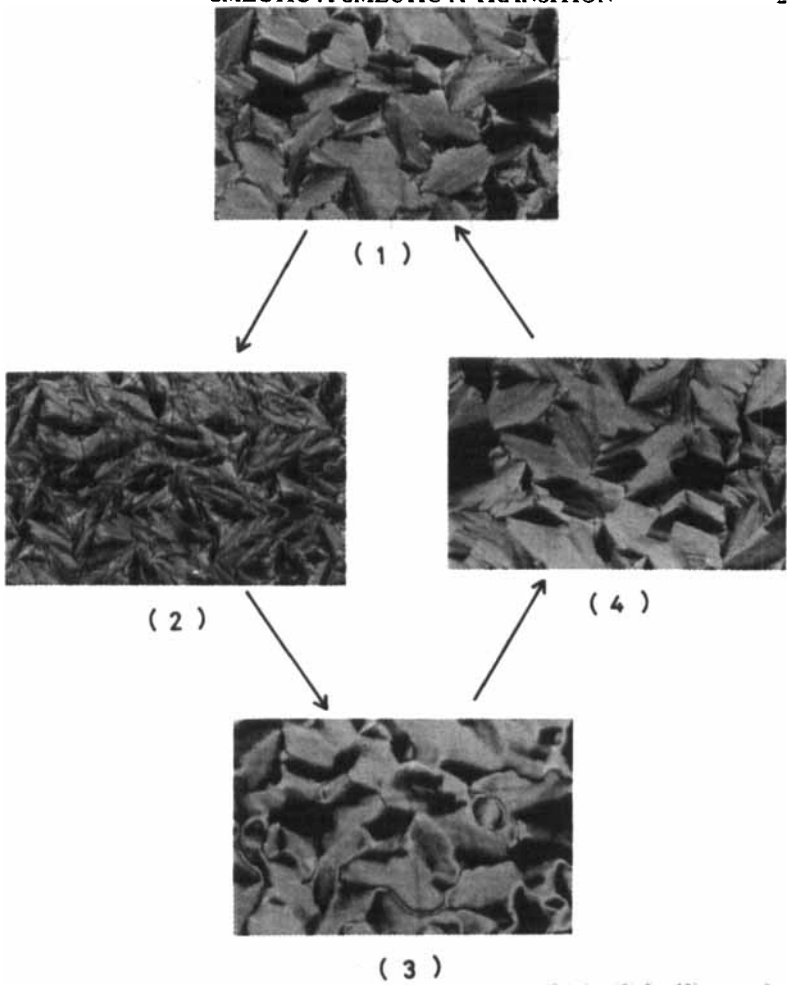


FIGURE 2 Micrographs (100X) for the octyloxy homolog: (1) S_2, (2) S_1, (3) nematic, and (4) S_1 phases. All pictures were taken from the same angle.

For the decyloxy homolog (line 4 in Figure 1), the DSC recording shows two endotherms at ca. 146 and 147.8°C, in which the latter is assigned to the smectic-isotropic transition. A noteworthy fact is that the endotherm around 146°C is very broad. The broad transition may indicate that another transitions occur in this region. Although the decyloxy homolog does not form nematic phase, the textures of the S_1 phase are quite similar to textures **1** and **3** in Figure 2.

The DSC data are summarized in Table I.

TABLE I

A: Transition temperatures (T/°C).

Carbon Number	C	S_2	S_1	N	I
3	. 147.2	—	—	. 157.3	.
4	. 136.9	—	—	. 158.3	.
5	. 142.5	—	—	. 153.5	.
6	. 139.0	(. 126.4)	—	. 152.6	.
7	. 137.2	(. 133.3)	—	. 147.3	.
8	. 134.9	. 140.2	. 140.5*1	. 147.4	.
9	. 134.3	. 141.5	. 143.8	. 145.1	.
10	. 134.6	. *2	. 147.8	—	.

The values in the parentheses indicate the monotropic transitions. *1: The value was microscopic data. *2: broad peak in the range between 144 and 147°C.

The DSC was swept at a heating rate of 1°C/min, and the transition temperatures were taken from the onset of the peaks and the data were calibrated by indium, where the melting point was 156.6°C.

The latent heats for the transitions (kJ/mol).

Carbon number	ΔH_{mp}	$\Delta H_{S_2-N}(S_2-S_1)$	$\Delta H_{S_1-N}(S_1-I)$	ΔH_{N-I}
3	41.3	—	—	0.9
4	37.5	—	—	0.8
5	46.4	—	—	1.0
6	46.8	3.2*1	—	1.2
7	39.6	4.0	—	1.2
8	41.7	3.3	*2	1.2
9	43.3	1.9	1.5	1.7
10	36.6	1.5	4.8	—

*1: The value was taken from the cooling stage. *2: The transition was hidden by the large endotherm for the S_2–S_1 transition. The experimental conditions are shown in the footnote in Table 1A.

In Figure 3, the transition temperatures are plotted against the carbon number in the alkoxy chain.

In order to characterize the smectic phases, we examined some binary phase diagrams. The results are summarized in Figures 4–6.

In a previous paper, we reported that the smectic A phase (S_2 phase in this paper) for the heptyloxy homolog was assigned to a bilayer smectic A (S_{A2}).[9] Indeed, the S_2 phase for the octyloxy hom-

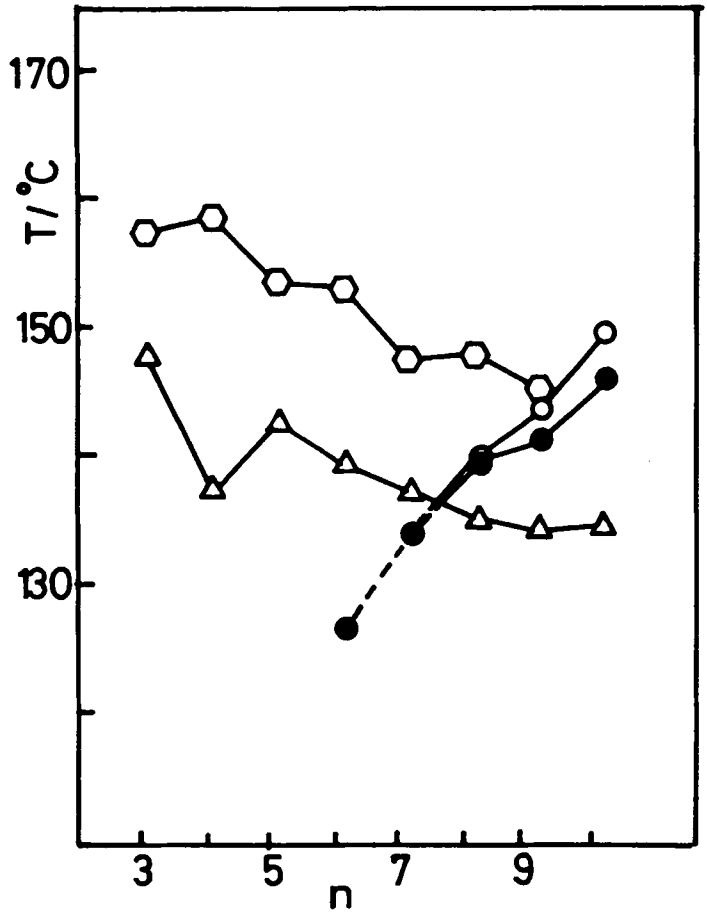


FIGURE 3 Plots of transition temperatures against carbon number in the alkoxy chain. △; crystal-mesophase, ●; S_2-nematic (S_1), ○; S_1-nematic (isotropic), and ⬡; nematic-isotropic transitions.

olog is isomorphous with the S_{A2} phase for 4-(4-pentylphenoxycarbonyl)phenyl 4-cyanobenzoate,[10] in which the S_{A2}-nematic or S_1 transition temperatures show somewhat non-linear behaviour with additivity (Figure 4a). In the figure, the S_1 phase for the octyloxy homolog disappears in the middle region of the diagram. In Figure 4b, the S_1 and S_2 phases for the nonyloxy homolog are isomorphous with the partially bilayer (S_{Ad}) and the bilayer (S_{A2}) phases of 4-(4-octylphenoxycarbonyl)phenyl 4-nitrobenzoate.[6] In the diagram, the smectic C ribbon disappears in the region of ca. 30 mol% of the octyloxy

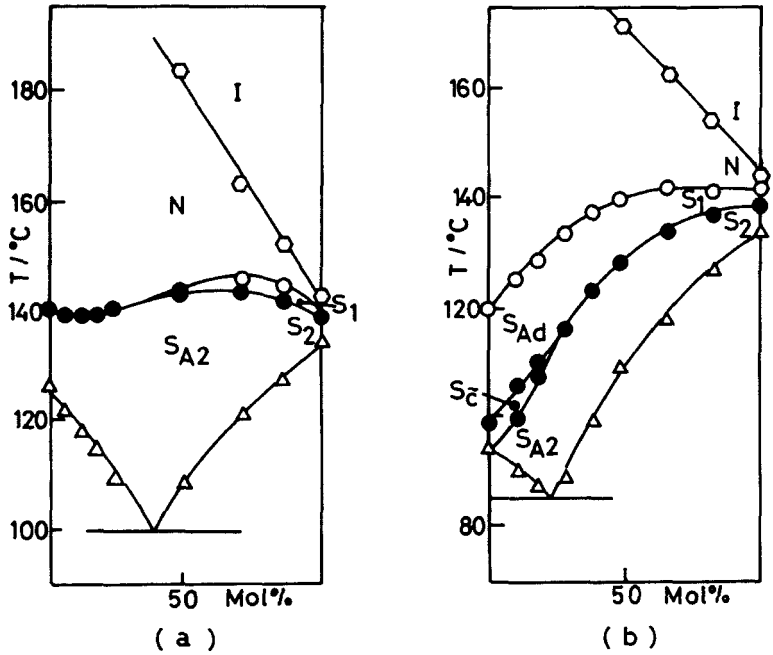


FIGURE 4 Isobaric diagrams: (a) 4-(4-pentylphenoxycarbonyl)phenyl 4-cyanobenzoate (on left) and the octyloxy homolog (on right). (b) 4-(4-octylphenoxycarbonyl)phenyl 4-nitrobenzoate (on left) and the nonyloxy homolog (on right).

homolog, giving a triple point. Thereby, the latent heats for the S_{Ad}-nematic transitions were very small, so that the transitions could be detected only by a texture change in microscopy.

In order to test an affinity between the S_{A2} and S_{A1} phases, we examined a miscibility diagram for a mixture of the heptyloxy homolog and 4-(4-pentylphenoxycarbonyl)phenyl 4-octylbenzoate,[11] in which the smectic A phase of the latter should be a monolayer type (S_{A1}). In Figure 5a, the S_{A1} and S_{A2} phases show apparent discontinuity in the range between 95 and 80 mol% of the heptyloxy homolog. This fact indicates that the bilayer arrangement of the molecules is very easily destroyed by an addition of small amount of the nonpolar mesogen. The isobaric diagram for a mixture of 4-(4-nonyloxyphenoxycarbonyl)phenyl 4-(4-nitrobenzoyl)benzoate[8] and the nonloxy homolog is shown in Figure 5b.

4-(4-Nonyloxyphenoxycarbonyl)phenyl 4-(4-nitrobenzoyl)benzoate has been reported to experience a phase transition of the C–S_{A2}–S–S_{Ad}–I type. Apparently, the S_{A1} phases for both com-

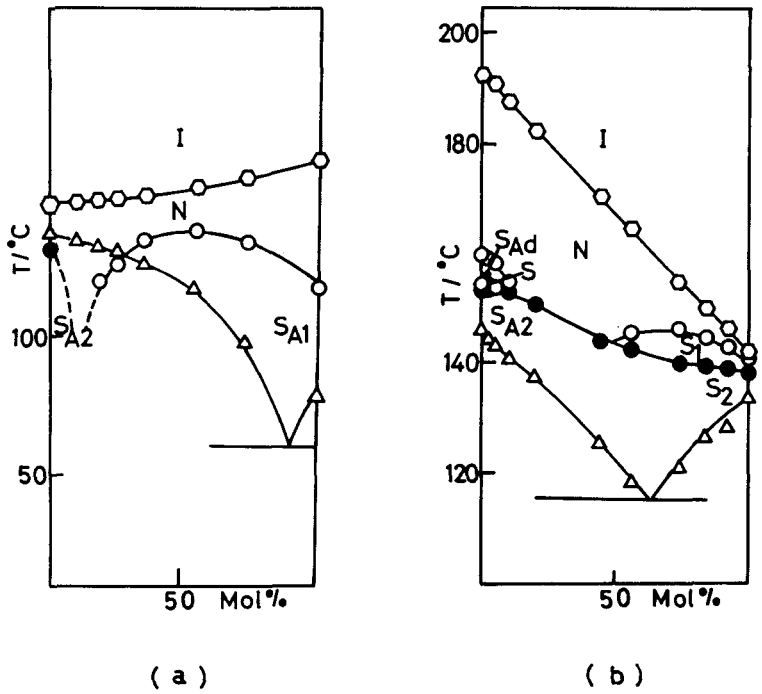


FIGURE 5 Isobaric diagrams: (a) the heptyloxy homolog (on left) and 4-(4-pentylphenoxycarbonyl)phenyl 4-octylbenzoate (on right). (b) 4-(4-nonyloxyphenoxycarbonyl)phenyl 4-(4nitrobenzoyl)benzoate (on left) and the nonloxy homolog (on right).

pounds are isomorphous, and the S_{A2}–N (S, S_{Ad}) transition temperatures show an ideal solution behaviour with additivity. However, the S_{Ad}-nematic transition temperatures show a concave trend in the region between 10 and 50 mol% of the nonyloxy homolog and are hidden by the S_{A2} phase. In the diagram, the S_{A2}-nematic transitions could be detectable only by microscopy because of low latent heat.

A miscibility relation between the S_{Ad} phase of the present series and the reentrant compounds is shown in Figure 6. In Figure 6a, the S_{Ad} phase of the octyloxy homolog is miscible with the S_{Ad} phase of 7-[4-(4-heptyloxybenzoyloxy)benzoyl]-3-cyanocoumarin.[12] However, the S_{Ad}-nematic transition temperatures show a large deviation from the linearity, and give a maximum at ca. 10 mol% of the nonyloxy homolog and a minimum at 80 mol%. In this figure, the S_{Ad}-nematic transitions could be detectable only by microscopy. Thereby, the thermal stabilities of the S_{A2} and reentrant nematic phases rapidly decrease with increasing each components. Figure 6b indicates an

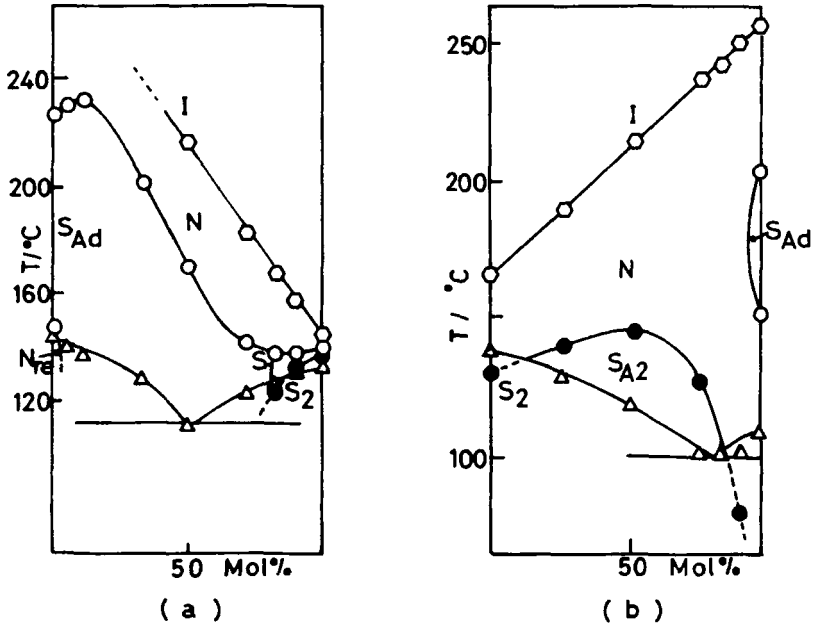
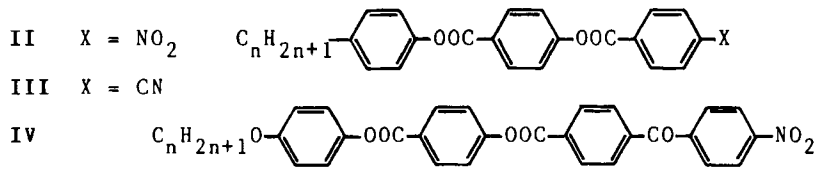


FIGURE 6 Isobaric diagrams: (a) 7-[4-(heptyloxybenzoyloxy)benzoyl]-3-cyanocoumarin (on left) and the octyloxy homolog (on right) (b) the heptyloxy homolog (on left) and 4-(4-octyloxybenzoyloxy)benzylidene-4'-cyanoaniline (on right).

isobaric diagram for a mixture of the heptyloxy homolog and 4-(4-octyloxybenzoyloxy)benzylidene-4'-cyanoaniline.[13] The S_{A2} phase of the heptyloxy homolog is immiscible with the smectic A (S_{Ad}) phase of the cyanoaniline compound. The isobaric diagrams for the mixtures of the octyloxy-, nonyloxy- and decyloxy homologs, and 4-(4-octyloxybenzoyloxy)benzylidene-4'-cyanoaniline show a similar behavior. The S_{Ad} phases of these homologs are not miscible with that of the cyanoaniline compound.

DISCUSSION

It has been reported that a homologous series of nitrobenzene[4,6] and benzonitrile[6,14] compounds (**II** and **III**) show two kinds of smectic A phases. In a previous paper, we have reported that a homologous series of 4-nitrobenzophenone compounds **IV** also showed two kinds of smectic A phases and a smectic A-like phase.[8]



These molecules belong to a class [B], and a common in structures for series **II**–**III** and the present series (**I**) is that these have a polar group as the terminal function and the ester groups as the linkage. However, the dipole moments arising from these groups orient opposite to each other, and set off. As a result, the dipole moment of the entire molecule parallel to the long molecular axis will be smaller than that of class [A]. The homologous series of **II** and **III** have linear structures, so that these form highly stable nematic and smectic A phases. On the other hand, the homologous series of **I** and **IV** have large molecular breadths because of the nitrobenzoyl or the cyanofuran group. The increased molecular breadth is proposed to account for the low nematic stability. Inspite of the structural demerit, series **I** and **IV** form considerably stable smectic A phases.

		T_{N-I}	$T_{S_{Ad}-N}$	$T_{S_{A2}-S_{Ad}}$	$T_{S_{Ad}-N}/T_{N-I}$	$T_{S_{A2}-S_{Ad}}/T_{N-I}$
I	(n = 8)	147.4	140.5	140.2	0.98	0.98
II	(n = 8)	207	118.2	91.7	0.82	0.76
III	(n = 7)	233	172	168	0.88	0.87
IV	(n = 8)	196	155.5	145.5	0.92	0.89

Indeed, the $T_{S_{Ad}-N}$ and $T_{S_{A2}-S_{Ad}}/T_{N-I}$ values for series **I** and **IV** are considerably larger than those for series **II** and **III**. This fact indicates that a lateral separation of molecules does not always decrease the smectic A stability. Especially, the thermal stabilities of the S_{A2} phases for series **I** and **IV** are relatively higher than those for series **II** and **III**. A possible explanation is that a lateral separation of the molecules in the smectic A phases reduces a repulsive interaction of the dipole moments parallel to the long molecular axis, and makes easy of the parallel arrangement of the molecules, increasing the thermal stability of the S_{A2} phase.

We can recognize some interesting facts from the comparison of the thermal properties among these series. The one is that the latent heats for the S_{Ad}–N transitions are very small, while the $T_{S_{Ad}-N}/T_{N-I}$ is

relatively large. On the other hand, the latent heats for the S_{A2}–S_{Ad} (N) transitions are considerably large, and tend to decrease with increasing the chain length of the alkoxy group.

We can assume that the S_{Ad} - N transition is close to a second order nature, when the alkoxy chain is short, i.e., the thermal stability of the S_{Ad} phase is low. On the other hand, the S_{A2}–S_{ad} (N) transition essentially has a first order nature. The other interesting fact is recognized in the dependence of the smectic stabilities on the chain length in the alkyl or the alkoxyl group. In series **II**, the S_{Ad}–N transition temperatures rapidly increase with increasing the chain length, and the S_{Ad} range is considerably wide. In series **I** and **IV**, on the other hand, an increment of the S_{Ad}–N transition temperature is moderate and the S_{Ad} range is quite narrow. In series **I**–**III**, the S_{Ad} range tends to increase with increasing the chain length, while the range in series **IV** tends to decrease with increasing the chain length. We can assume that the bend of the molecules tends to decrease the thermal stabilities of the nematic and S_{Ad} phase, while the thermal stability of the S_{Ad} phase is less sensible to the bent geometry of the molecules.

Some noteworthy facts are recognized in the isobaric diagrams, in connection with the bent geometry of the present series. The first is that the S_{A2} phases appear to be isomorphous, irrespective of their molecular geometries, though the S_{A2}–S_{Ad} ($S_{\tilde{C}}$ or N) transition temperatures show weak non-ideal solution behaviour. The second is that the S_{Ad}–N transition temperatures show remarkable deviation from the linearity, indicating that the thermal stability of the S_{Ad} phase is strongly dependent on their molecular geometries. The third is that an affinity between S_{A2} and S_{Ad} phases appears to be low (see Figure 6b). In this case, the geometrical difference may be important. The forth is that the S_{A2} phase is immiscible with the S_{A1} phase in Figure 5a, while the S_{A1} or S_{A2}–nematic (isotropic) transition temperatures show an ideal solution behaviour, except for the discontinuous region. This fact indicates that the S_{A1} and S_{A2} phases have low affinity, while these two phases should have very similar arrangement of the molecules. Further studies on the miscible relation between the S_{A1} and S_{A2} phases are now in progress.

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