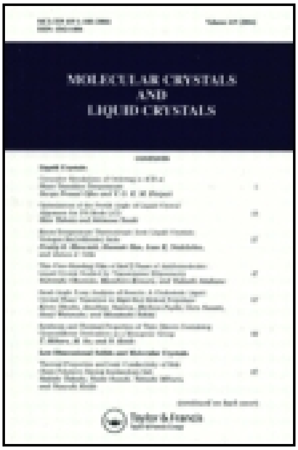

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The S_A-S_A Transition in a Homologous Series of 4(4-Alkoxyphenoxycarbonyl)phenyl 5-Nitro-2-furancarboxylates

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The S_A–S_A Transition in a Homologous Series of 4(4-Alkoxyphenoxycarbonyl)phenyl 5-Nitro-2-furancarboxylates

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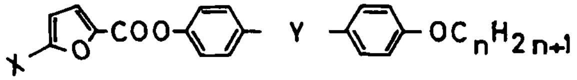
The thermal properties of a homologous series of 4(4-alkoxyphenoxycarbonyl)phenyl 5-nitro-2-furancarboxylates have been examined. The heptyloxy, octyloxy and nonyloxy homologs form two kinds of smectic A phases, where the lower phase has a bilayer arrangement of the molecules (S_{A2}) and the higher one the partially bilayer (S_{Ad}). The apparent S_A–S_A transitions can be detected by both differential scanning calorimeter and classical microscope.

It has been considered that in polar mesogens a dipole moment parallel to long molecular axis plays an important role in determining polymorphism of the mesophases, though the detailed mechanism of the dipole-dipole interaction has not been known.[1,2] When the dipole moments arising from the linkages and strongly polar terminal group direct opposite to each other and the dipole moment of the entire molecule parallel to the long molecular axis is weak, the molecules tend to form smectic A and C phases with bilayer arrangements, and sometimes experience a S_A–S_A transition.[1,2]

We have reported that nitrobenzophenone compounds form three kinds of smectic phases, in which two phases have been assigned to the smectic A with partially bilayer (S_{Ad}) and bilayer (S_{A2}) arrangements of the molecules.[3] Recently, we have also reported that cyanofuran compounds **2** form two kinds of smectic A phases, i. e., S_{Ad} and S_{A2} phases,[4] where the layer spacings are 1.4 and 2.0 times of the calculated molecular length.[5]

In this paper, we describe the thermal properties of the homologous series of 4(4-alkoxyphenoxycarbonyl)phenyl 5-nitro-2-furancarboxylates **1**, and the related compounds.



1 X = $-NO_2$ Y = $-COO-$
2 X = $-CN$ Y = $-COO-$
3 X = $-NO_2$ Y = $-OOC-$

The results will be discussed in terms of the geometrical and electric properties of the molecules.

EXPERIMENTAL

Materials: 4(4-Alkoxyphenoxycarbonyl)phenols were prepared by the method of van Meter et al.[6] 5-Nitro-2-furancarboxylic acid was purchased from Tokyo Kasei Co. Esterifications of the phenols and 5-Nitro-2-furancarboxylic acid were carried out by a usual manner.[7] Purification of the reaction product was carried out by column chromatography on silica-gel, where the elution solvent was a solvent mixture of n-hexane-ether (90:10), followed by recrystallization from absolute ethanol. The elementary analysis data are shown below.

n	formula		Calcd.(%)			Found(%)	
	compound **1**	C	H	N	C	H	N
6	$C_{24}H_{23}N_8O$	63.57	5.11	3.09	63.56	5.15	3.01
7	$C_{25}H_{25}N_8O$	64.23	5.39	3.00	64.21	5.45	2.93
8	$C_{26}H_{27}N_8O$	64.86	5.65	2.91	64.77	5.70	2.78
9	$C_{27}H_{29}N_8O$	65.44	5.90	2.83	65.36	5.92	2.69
Compound **3**							
8	$C_{26}H_{27}N_8O$	64.86	5.65	2.91	64.74	5.73	2.78
10	$C_{28}H_{31}N_8O$	66.00	6.13	2.75	65.97	6.12	2.70

Series **3** were prepared by a similar manner. 4(4-pentyl-(5DBCN) and 4(4-heptylphenoxycarbonyl)phenyl 4-cyanobenzoates (7DBCN) were prepared by the method of Haudouin et al.[8]

Method: Thermodynamical procedures were described in a previous paper.[7]

RESULTS

The transition temperatures and the latent heats for the homologous series **1** are summarized in Table I.

TABLE I

Thermal properties of series **1**

A) Transition temperatures (T/°C)

n	C	S_{A2}	S_{Ad}	N	I
6	. 146.6	—	—	— 171.6	.
7	. 139.7	(. 128.2)	. 140.8	. 168.6	.
8	. 139.0	(. 132.7)	. 164.7	. 172.6	.
9	. 137.6	(. 133.6)	. 172.5	—	.

B) Latent heats (kJ/mol)

n	ΔH_{mp}	$\Delta H_{SA2-SAd}$	ΔH_{SAdN}	ΔH_{N-I}
6	35.4	—	—	1.1
7	33.8	*1	0	1.4
8	33.5	1.7	0.1	2.2
9	38.5	1.3	—	2.7

*1 The transition could not be detected by DSC thermogram, since the phase transition and solidification occurred simultaneously. Parentheses indicate monotropic transitions.

The nitro compounds **1** have higher stability of the nematic phase than the cyano compounds **2**. Two smectic phases formed by the heptyloxy, octyloxy, and nonyloxy homologs are assigned to the partially bilayer (S_{Ad}) and bilayer (S_{A2}) smectic A phases by an examination of the phase diagram, which is shown in Figure 2a. The textures of both smectic A phases are similar to those for the homologous series **2**.[4] The smectic-nematic transitions could be observed only by microscopy, because the latent heats are too small to detect by DSC thermogram. On the other hand, the latent heats for the S_{A2}–S_{Ad} transitions are relatively large, and the transitions could be observed by both DSC and microscopic methods. In Figure 1, the transition temperatures are plotted against the carbon number.

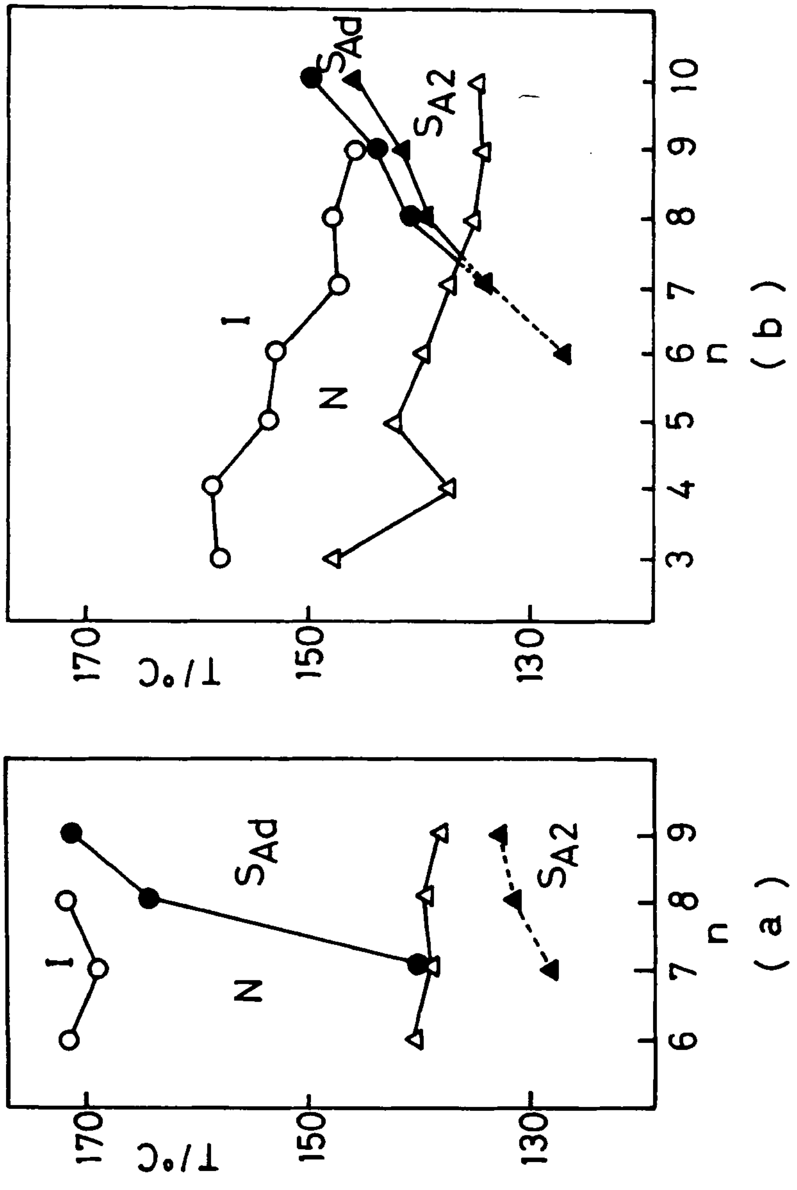


FIGURE 1 Plots of transition temperatures vs. carbon number, n. (a) series **1**, (b) series **2**. △ indicate solid-mesophase transitions.

For the comparative study, the plot for series **2**[4] is also illustrated in Figure 1b.

In series **2**, the nematic stabilities are relatively low, and the S_{A2}–S_{Ad}, and S_{Ad}–N transition temperatures tend to increase simultaneously, with increasing the carbon number, similar to benzophenone compounds.[3] As a result, series **2** produce quite narrow S_{Ad} phase. On the other hand, series **1** show higher stability of a nematic phase than series **2**, and the S_{A2}–S_{Ad} transition temperatures tend to become plateau in the range between n = 7 and 9, while the S_{Ad}–N transition temperatures rapidly increase in the range, producing a wide range S_{Ad} phase.

For the comparative study, we examined the thermal properties of 4(5-nitrofuran-2-carbonyloxy)phenyl 4-alkoxybenzoates **3**.

TABLE II

Transition temperatures of series **3** (T/°C)

n	C		S_{Ad}		N		I
8	.	157.2	.	160.4	.	173.1	.
10	.	154.4	.	171.4	—		.

Although these compounds have similar stabilities of mesophases, these exhibit only one smectic A phase, which is isomorphous with the S_{Ad} phase of series **1** (see Figure 2b).

We examined the thermal properties of the S_{Ad} and S_{A2} phases of the present series by means of binary phase diagrams.

For a binary mixture of the octyloxy homologs of **1** and **2** (Figure 2a), the S_{A2}–S_{Ad}, S_{Ad}–N, and N–I transition temperatures show ideal solution behavior, and the eutectic phenomenon does not follow the Schroeder-van Laar equation, indicating that these molecules have very similar structures.[9] On the other hand, the S_{Ad} phases for both octyloxy homologs of series **2** and **3** show an apparent discontinuous region in the isobaric diagram, while both S_{Ad} phases for both octyloxy homologs of series **1** and **3** are isomorphous (Figure 2b). 5DBCN and 7DBCN have been known to form the S_{A2}, and S_{Ad} and S_{A2} phases, respectively.[8,10] In Figure 3a, both S_{Ad} phase of **3** and S_{A2} phase of 5DBCN show remarkable depressions with increasing each component. Although both S_{Ad} phases are isomorphous (Figure 3b), the S_{Ad}–N transition temperatures show a minimum at ca. 75 mol% of 7DBCN and a broad maximum at ca. 30 mol% of 7DBCN. Thereby, the S_{A2}–S_{Ad} transition temperatures again decrease rapidly with decreasing the concentration of 7DBCN. These facts indicate that the

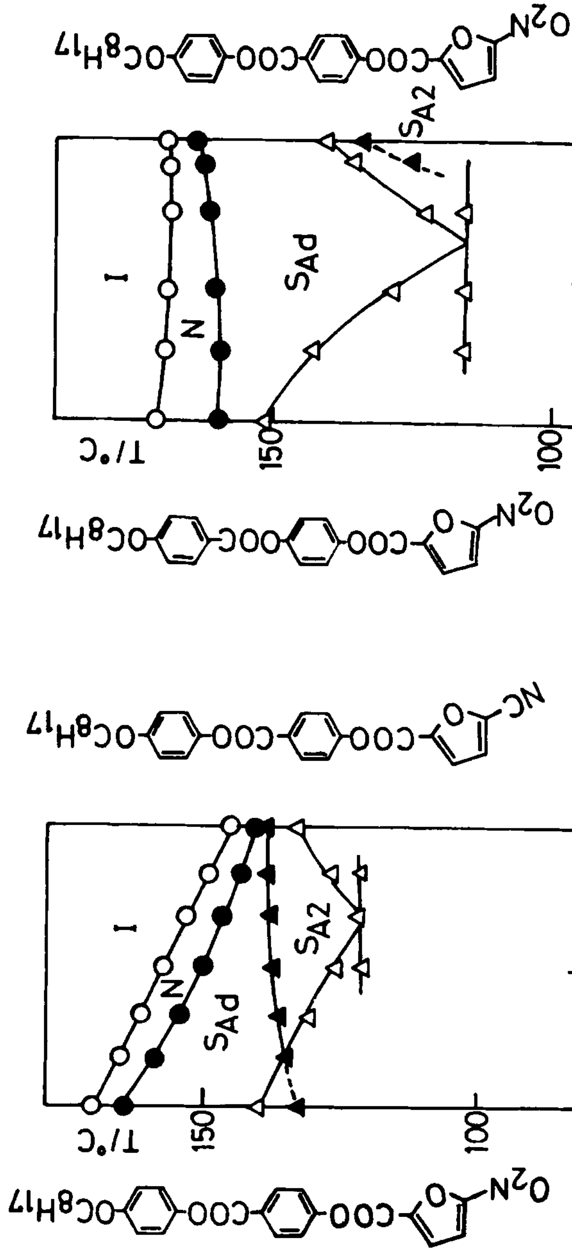


FIGURE 2 Isobaric diagrams

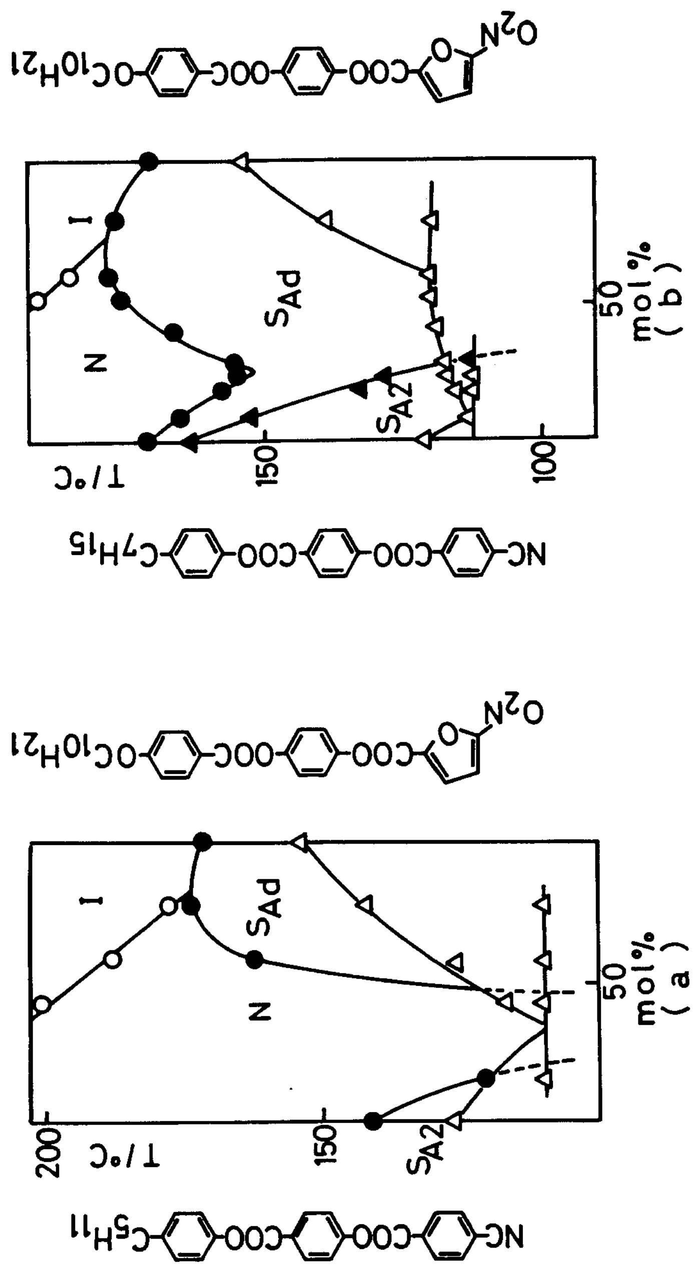


FIGURE 3 Isobaric diagrams

nitro compounds **3** have low affinity with the bilayer arrangement of the molecules.

In Figure 4, we examined the miscible relations between the S_{Ad} phase of **1** and **3** and the S_{Ad} phases of the reentrant compounds.[11,12] In Figure 4a, both S_{Ad} phases disappear in the middle region of the diagram, and the S_{Ad} phase of the octyloxy homolog shows a protruding feature. The binary mixture shows a reentrant phenomenon of S_{A2}–N–S_{Ad}–N–I type in the region between 30 and 50 mol% of the azomethine compound. On the other hand, both S_{Ad} phases are well miscible in Figure 4b.

DISCUSSION

It has been known that the S_{A2} phase is formed by polar mesogens, i.e., 4(4-alkylphenoxycarbonyl)phenyl 4-cyanobenzoates (**5**),[13,14] 4'-cyanobenzylidene-4-(4-alkoxyphenoxycarbonyl)anilines (**6**),[15] and 4(4-alkoxyphenoxycarbonyl)phenyl 4-cyanobenzoates (**7**).[16] In series **5** and **7**, the S_{A2} phase is formed by the homologs having a lateral substituent such as a methyl or a chloro group.[14,16]

Recently, we reported that 4(4-alkoxyphenoxycarbonyl)phenyl 4-(4-nitrobenzoyl)benzoates (**4**) show a C–S_{A2}–S(?)–S_{Ad}–N–I transition.[3] We have also reported that a homologous series of 4-(4-alkoxyphenoxycarbonyl)phenyl 5-cyano-2-furancarboxylates (**2**) experience S_{A2}–S_{Ad} transition.[4] The present series show the similar mesomorphic pathway to that of series **2**, though the transition temperatures are slightly different. Thereby, the thermal stabilities of the S_{Ad} and S_{A2} phases of series **2** and **4** are very close, giving the S_{Ad} phase with narrow range, while series **1** show a wide range S_{Ad} phase. A common fact is that these homologs have a mesomorphic pathway of the S_{A2}–S_{Ad}–N–I type, and do not show any tilt phase such as smectic C phase. In addition, the S_{A2} phase is formed by the low members (n = 5–7) and thereafter, indicating that these homologous series tend to form a bilayer arrangment of the molecules.

The molecular arrangements in the S_{A2} and S_{Ad} phases are illustrated in Figure 5, where 4(4-octyloxyphenoxycarbonyl)phenyl 5-nitro-2-furancarboxylate is refered.

A structural characteristic for series **1** and **2** is that the longitudinal components of the dipole moments arising from the linkages are opposite to that of the nitro group. These molecules have bent geometries due to the five membered ring, and the nitro group occurs at an angle with respect to the long molecular axis.

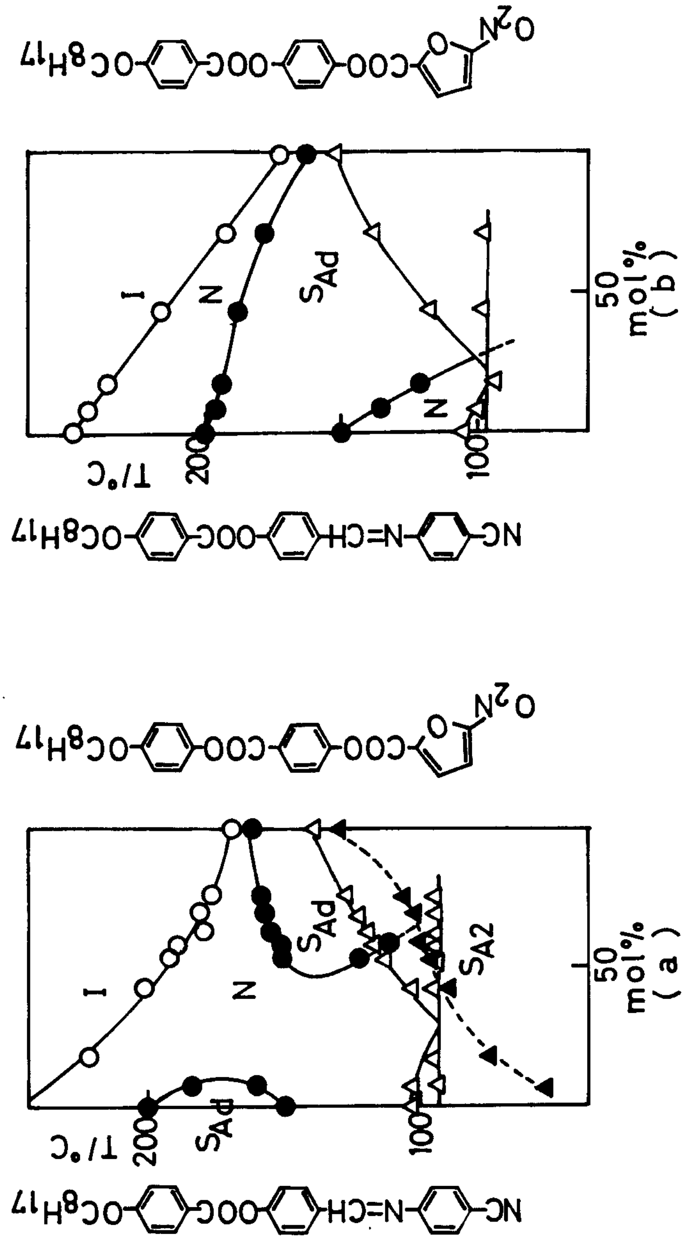


FIGURE 4 Isobaric diagrams

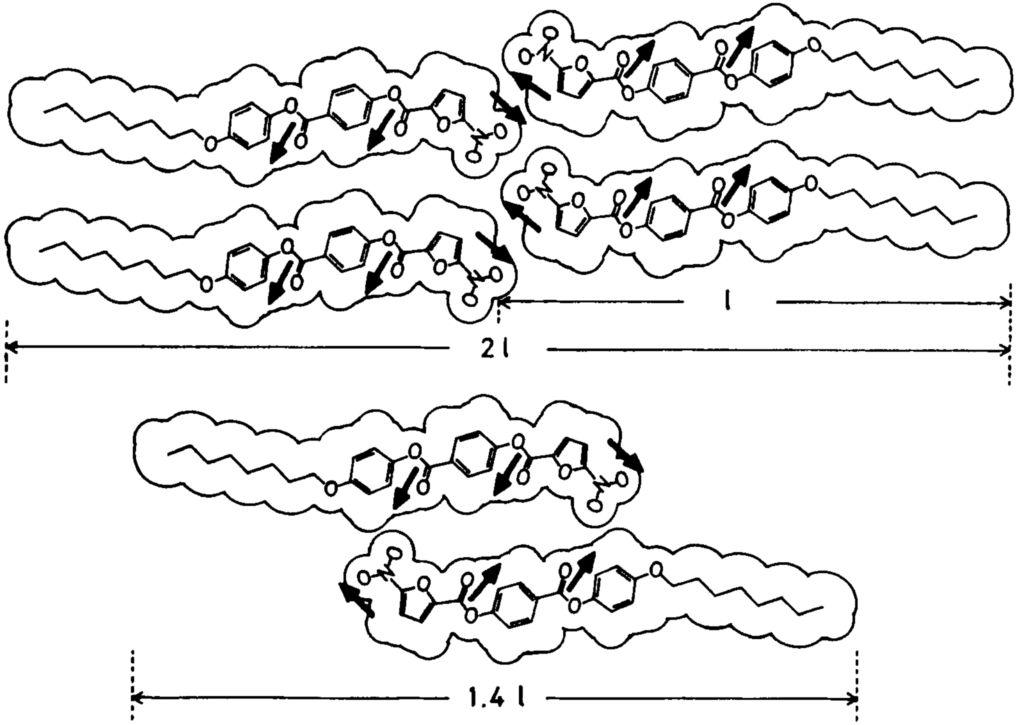


FIGURE 5 Models for molecular pairs in S_{A2} (upper) and S_{Ad} phases (lower). The arrows indicate the dipole moments arising from the functional groups.

As mentioned by several authors,[12] the dipole moments arising from the linkages play an important role in determining the mesomorphic pathway, i.e., the molecular arrangement in mesophases.

A dipole-dipole interaction is known to be proportional to the dipole moments and inversely proportional to the distance (R^{-3}). The dipole-dipole interaction is attractive, when dipoles arrange antiparallel, and repulsive, when they arrange parallel. The dipole-dipole interaction would be strongly dependent on an orientation and motion of dipoles, distance between dipoles, etc. The perpendicular components of the dipole moments arising from the linkages tend to cancel to each other due to an intramolecular rotation around the long molecular axis. Moreover, molecules in a disordered phase such as nematic and smectic A phases will rotate freely and the dipole moments will cancel intermolecularly, where the rotation around the long molecular axis is extremely fast (the relaxation time for the rotation is supposed to be an order of GHz). Therefore, the dipole-dipole interaction should be given by:

$$E = -\mu^4/R^6 + \dots..$$

where μ and R are dipole moments and the distance between dipoles, respectively. That is, the transverse component of the dipole-dipole interaction is always weakly attractive.

On the other hand, the longitudinal components of the dipole moments with respect to the long molecular axis is never cancelled by the intramolecular rotation. Furthermore, the molecular rotation around the perpendicular axis of the long molecular axis is relatively slow (the relaxation time for the rotation is usually supposed to be an order of kHz-MHz.). Therefore, the longitudinal component of the dipole-dipole interaction must affect on the molecular arrangement, when the molecule has large dipole moment.

In S_{A2} phase, as is evident from the model in Figure 5, the longitudinal components of the dipole moments arising from the linkages always arrange parallel to each other, irrespective of the orientation of the linkages. Therefore, it would be reasonable to assume that the dipole-dipole interaction arising from the linkages in pure substance is always repulsive in the S_{A2} phase, and never increases the thermal stability of the S_{A2} phase.

Here, we have to consider both dipole-dipole interaction of the entire molecules and local dipole-dipole interaction.

In the present series, the dipole moments of the entire molecules roughly estimated by a simple sum of group dipole moments.[17] The results are summarized in Table III.

TABLE III

Dipole moments of compounds

Compounds	Dipole moment (D) $\mu_{\parallel}$	$\mu_{\perp}$	$\Delta\mu$	Mesomorphic pathway
1	3.66	4.12	−0.46	S_{A2}–S_{Ad}–N–I
2	4.01	4.29	−0.18	S_{A2}–S_{Ad}–N–I
3	5.54	4.77	+0.77	S_{Ad}–N–I
4	4.91	5.96	−1.05	S_{A2}–S–S_{Ad}–N–I
5^{*1}	4.41	3.48	+0.93	S_{A2}–S_{Ad}–N–I
6	5.04	3.72	+0.13	S_{A2}–S_C–S_{A1}–N–I
7^{*1}	4.55	3.75	+0.80	S_{A2}–S_{Ad}–N–I

^{*1}: These compounds have a methyl or a chloro group at the lateral direction of the molecules.

Series **3** do not show the S_{A2} phase, and that these remarkably decrease the thermal stability of the S_{A2} phase in binary mixtures (Figures 3b and 4 b). As is evident from the table, the longitudinal component of the dipole moment is relatively large. For series **1** and **2**, the longitudinal components of the dipole moments are relatively small, while these have very polar group at the terminal position. Furthermore, the bent geometries increase their molecular breadthes. It would be reasonable to assume that these factors reduce the repulsive dipole-dipole interaction in the S_{A2} phase (Figure 5). For series **4**, the longitudinal component of the dipole moment is relatively large. However, the quite large molecular breadth (ca. 10 Å) will separate the molecules in the S_{A2} phase, and reduce the repulsive dipole-dipole interaction. A similar argument is applicable to the formation of the S_{A2} phase in compounds **5** and **7**.

Although these molecules have relatively large dipole moments, the substituents at the lateral position increase the molecular breadthes, and weaken the dipole-dipole interaction. Compound **6** also has relatively large dipole moment, while it also produces the S_{A2} phase.

On the other hand, the local dipole-dipole interaction may affect on the mesophase stability. As is evident from Figure 5, the dipole-dipole interaction in the S_{Ad} type's arrangements of the molecules is attractive for series **3**, and partially attractive for series **1**. The attractive dipole-dipole interaction may give rise to stable interdigited dimers in series **3** (Figure 5). Certainly, series **3** produce more stable N and S_{Ad} phases than series **1**, while series **1** should have more rigid core than series **3**.

We conclusively assume that strong dipole moment of entire molecule along the long molecular axis is quite unfavorable for the formation of layer arrangement of molecules in S_{A2} and also S_{C2} phases.

The effect of dipole-dipole interaction is also recognized in isobaric diagrams of binary mixtures. In general, so-called "polar-nonpolar" mixtures display a remarkably enhanced or an injected smectic A phase,[18–22] in which the smectic A phase always has a monolayer arrangement of molecules.[23,24] This is explicable in terms of an increase in the thermal stability of the monolayer arrangement of molecules, perhaps due to reduction in repulsive dipole-dipole interaction by solvating polar molecules by nonpolar molecules. In binary mixtures shown in Figures 2–5, however, we can not expect such phenomena, because both components are polar. Rather, we can expect that the isobaric diagrams become complex, because a mixing of polar molecules must give rise to the crossed pairs, in addition to the respective pairs. As is evident from Figure 2a and isobaric diagram for a mixture of 5DBCN and the octyloxy homolog of **2**[4] where all dipole moments arising from the linkages in both components have the same orientation, the S_{A2}–S_{Ad} transition temperatures show an ideal solution behavior.

When the orientation of the dipole moments arising from the functional groups is different, the isobaric diagrams become complex (refer to Figures 2b, 3a, and 3b). In Figure 2b, the S_{A2}–S_{Ad} transition temperatures rapidly decrease with increasing the concentration of **3**, while the S_{Ad}–N transition temperatures show an ideal solution behavior. On the other hand, the thermal stabilities of both S_{Ad} and S_{A2} phases in Figure 3a rapidly decrease by mixing each component. In these mixtures, the complicated pairs in addition to the original pairs would be formed, and destabilize the original molecular arrangements, i.e., the S_{Ad} and S_{A2} phases of the components. In Figure 3b, both S_{Ad} phases of both components are isomorphous with dispaying a minimum, though the S_{A2} phase disappears in the diagram. An increase in the alkyl chain length would increase the molecular breadth, and reduce repulsive dipole-dipole interaction. This is assumed to be an origin of increase in affinity between both S_{Ad} phases.

The abnormal behavior in the S_{Ad} phase is also apparent in Figures 4a and 4b, where both S_{Ad} phases show an apparent discontinuity in the former, while these are completely miscible in the latter. A possible explanation is that the dipole-dipole interactions of the components in Figure 4a are rather repulsive in the S_{Ad} phase, while the interactions in Figure 4b are rather attractive in the S_{Ad} phase (refer to Figure 5).

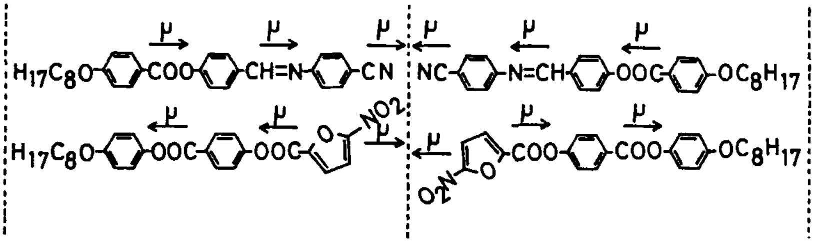


FIGURE 6 A possible model for a 1:1 pair of 4(4-octyloxybenzoyloxy)benzylidene-4'cyanoaniline and the octyloxy homolog of **1**. The arrows indicate the dipole moments arising from the functional groups.

An interesting fact in Figure 4a is that the S_{A2}–S_{Ad} or –N transition temperatures show remarkable upward convexed trend in the center of the diagrams. The similar enhanced S_{A2} and S_{C2} phases in the diagrams are observed in the binary mixtures of 4-cyanophenyl 4(4-alkoxybenzoyloxy)benzoates and 4(4-alkylphenoxycarbonyl)phenyl 4-cyanobenzoates.[26] This must indicate that the 1:1 complexes of the components are formed, and show relatively stable S_{A2} phase, since the dipole moments arising from the linkages in both components direct just opposite to each other, and the interaction should be attractive, as shown in Figure 6.

Conclusively, the S_{A2} phase is stably formed, when the longitudinal component of dipole moment is small, and that the molecule have a polar terminal group, just like compounds **1**–**2**, and **4**. The molecular arrangements in N and S_{Ad} phase in binary mixture are affected by the dipole moment of the molecules.

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