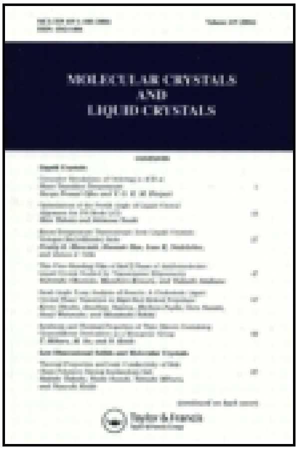

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Thermal and X-Ray Diffraction Studies of Some Liquid Crystals Having a Nitro Group at the Lateral Position

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Thermal and X-Ray Diffraction Studies of Some Liquid Crystals Having a Nitro Group at the Lateral Position

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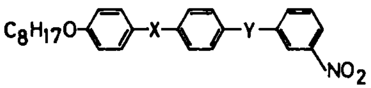
3-Nitrophenyl 4-(4-octyloxy- and 4-(4-nonyloxybenzoyloxy)-benzoates(compound **1**), 4-(4-octyloxyphenoxycarbonyl)phenyl 3-nitrobenzoate(compound **2**), 4-(4-octyloxy- and 4-(4-decyloxybenzoyloxy)phenyl 3-nitrobenzoates(compound **3**), and 3-nitrophenyl 4-(4-octyloxy- and 4-(4-nonyloxyphenoxycarbonyl)benzoates (compound **4**) have been prepared. All the compounds show smectic A and nematic phases, where the molecular arrangement in the smectic A phase is dependent on the orientation of the ester linkages. The smectic A phase for compounds **1** and **3** has a monolayer arrangement of the molecules, while the smectic A phase for compound **3** also involves a small contribution of a partially bilayer nature near the smectic A-nematic transition. The smectic A phase for compound **2** has a bilayer arrangement, and compounds **4** probably the bilayer one. A dipole correlation within the smectic A phases has been discussed.

Keywords: polar liquid crystals, smectic A modification, x-ray diffraction, lateral substituent effect

INTRODUCTION

It is well known that many polar liquid crystals having a nitro or a cyano group at the terminal position form four kinds of smectic A phases which are classified according to the molecular arrangements; that is, monolayer (S_{A1}), bilayer (S_{A2}), partially bilayer (S_{Ad}), and antiphase ($S_{\tilde{A}}$), and show interesting polymesomorphisms involving a smectic A-smectic A transition and a reentrant phenomenon.[1] The diversity of the molecular arrangement has been frequently discussed in terms of attractive interactions of dipoles arising from the linkages and the terminal polar substituents.[2] On the other hand, the polar substituents attached at the lateral position of a molecule tend to enhance the smectic properties, though the substituents do not alter the molecular arrangement.[3-5] The remarkable change has been also attributed to the attractive interactions involving the dipoles.

We are interested in the thermal properties of four related liquid crystals having a nitro group at the meta position with respect to the ester linkage.



1	-COO-	-COO-
2	-OOC-	-OOC-
3	-COO-	-OOC-
4	-OOC-	-COO-

n = 8 ~ 10

The nitro group locates at the terminal and lateral position in a geometrical point of view. In addition, the nitro group lacks a direct conjucative interaction with the ester group, since both substituents locate at the meta position to each other. Therefore, we can expect that the electrostatic effect of the nitro group is different from that of the usual polar terminal groups and the lateral ones.

In this paper, we describe the thermal properties of the four related compounds and the molecular arrangements in the smectic A phase, and the diversity of the molecular arrangements will be discussed in terms of the dipoles arising from the ester and nitro groups.

Experimentals

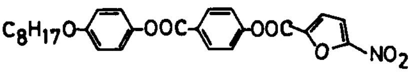
Materials: 3-Nitrophenyl 4-(4-octyloxybenzoyloxy)benzoate: 4-Octyloxy benzoyl chloride which was prepared by the reaction of 4-octyloxy benzoic acid (10 g, 0.04 mol) and thionyl chloride (10 ml), and benzyl 4-hydroxybenzoate (9.3 g) in a solvent mixture of anhydrous pyridine and toluene (1:1 w/w, 50 ml) were heated at 80°C for 5 hrs. The reaction mixture was evaporated to dryness, and the residue was extracted with ether. The ether extract was purified by column chromatography on silica-gel, where chloroform was used as an elution solvent. The eluent was recrystallized from light petroleum ether, giving benzyl 4-(4-octyloxybenzoyloxy)benzoate, as colorless needles: 16.2 g (yield: 88%), mp. 63°C. Benzyl 4-(4-octyloxybenzoyloxy)benzoate (10 g, 0.022 mol) were hyrogenated in toluene and ethanol (1:1 w/w, 300 ml) under the presence of Pd-C (10%, 1 g). After removing the catalyst, the reaction mixture was concentrated to dryness, and the residue was purified by column chromatography on silica-gel, where chloroform containing ethanol (2%) was used as an elution solvent. 4-(4-Octyloxybenzoyloxy)benzoic acid was recrystallized from ethanol: 7.6 g (yield: 95%). Crystal.172.nematic.236. isotropic(T/°C). Anal. Found: C, 71.28%; H, 7.00%; Calcd for $C_{22}H_{26}O_5$: C, 71.33%; H, 7.08%.

4-(4-Octyloxybenzoyloxy)benzoic acid (0.5 g, 1.3 mmol) was chlorinated with phosphorous pentachloride (0.3 g) in thionyl chloride (1 ml) at room temperature. After removing thionyl chloride and phosphorous trichloroxide, the acid chloride and 3-nitrophenol (0.19 g) in a solvent mixture of dry pyridine and toluene (1:1, 10 ml) were heated at 80°C for 5 hrs. The reaction mixture was evaporated to dryness, and the residue was extracted with ether. The extract was purified by column chromatography on silica-gel, where chloroform was used as an elution solvent. The eluent was recrystallized from a solvent mixture of ether-petroleum ether, giving 3-nitrophenyl 4-(4-octyloxybenzoyloxy)benzoate as colorless needles: 0.48 g (yield: 75%). Anal. Found: C, 68.39%; H, 5.88%; N, 2.79%. Calcd for $C_{28}H_{29}NO_7$: C, 68.42%, H, 5.95%; N, 2.85%. The purity was also checked by thin layer chromatography on silica-gel, where ether was used as a developing solvent.

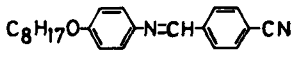
Compounds **2** and **3** were obtained by a similar method, where the hyroxy group of 4-hydroxybenzoic acid was protected by a benzyl group, and the protecting group was also removed by catalytic hydrogenation. 4-Octyloxyhenyl 4-benzyloxybenzoate: mp. 123°C. 4-Benzyloxyphenyl 4-octyloxybenzoate: Crystal.94 .nematic.99.isotropic(T/°C). 4-(4-Octyloxyphenoxycarbonyl)phenol: mp. 157°C. 4-(4-Octyloxybenzoyloxy)phenol: mp. 111°C. On the other hand, 4-phenoxycarbonylbenzoic acid, the material of compound **4**, was not easy to obtain by a partial esterification of terephthaloyl chloride.[6] In the present work, 4-(4-octyloxyphenoxycarbonyl)benzoic acid was prepared according to the following way. Dibenzyl terephthalate (10 g, 0.029 mol) obtained by an esterification of terephthaloyl chloride with phenol, was hydrogenated with Pd-C (10 W%, 1 g) in a solvent mixture of toluene and ethanol (1:1, 300 ml). After uptaking hyhdrogen (37% of the theoretical amount), the catalyst was filtered off, and the residual solution was concentrated to dryness. The product was purified by column chromatography on silica-gel. The second eluent was recrystallized from ethanol, giving 4-benzyloxycarbonylbenzoic acid as colorless needles: 2 g (yield: 27%). mp. 181°C. A 6 g of dibenzyl terephthalate was recovered as the first eluent. 4-Benzyloxycarbonylbenzoic acid chloride prepared by the reaction of 4-benzyloxycarbonylbenzoic acid (10 g, 0.039 mol) and phosphorous pentachloride (8.4 g) in thionyl chloride (10 ml), and 4-octyloxyphenol (8.9 g, 0.04 mol) in a solvent mixture of anhydrous pyridine and toluene (1:1, 50 ml) were heated at 80°C for 5 hrs. 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 light petroleum ether and ether, giving benzyl 4-octyloxyphenyl terephthalate as colorless needles: 15.5 g (yield: 86%). mp. 84°C.

The benzyl group was removed by a method similar to that mentioned above, giving 4-(4-octyloxyphenoxycarbonyl)benzoic acid which was recrystallized from ethanol. The yield of de-benzylation was 85%. Crystal.172.nematic.236. isotropic(T/°C). Anal. Found: C, 71.26%, H, 7.00%. Calcd for $C_{22}H_{26}O_5$: C, 71.33%; H, 7.08%. The final esterification was carried out by a method similar to that of compound **1**.

4-Cyanobenzylidene-4-octyloxyaniline (CBOOA) was purchased from Tokyo-kasei C. 4-(4-Octyloxyphenoxycarbonyl)phenyl 4-nitrofuran-2-carboxylate (OPPNF) was prepared according to the method of Takenaka *et al.*[7]



OPPNF



CBOOA

Method: Transition temperatures were determined by using a Nikon Model POH polarizing microscope fitted with a Mettler FP-52 heating stage, where the apparatus was operated by a heating rate of 5°C/min. Transition enthalpies were measured with a Daini-Seikosha SSC-560 differential scanning calorimeter, where indium (99.9%) was used as a calibration standard with a heating rate of 5°C/min (mp. 156.6°C, ΔH, 6.8 mcal/mg).

X-ray diffraction: The sample sealed in a square cell (5×5 mm^2) was gradually cooled from the isotropic liquid under a ca. 1 kG magnetic field in order to obtain a single domain in the cell. The cell temperature was controlled automatically within ±0.05°C by a micro-computer. A CuK radiation monochromatized by a pyrolytic graphite crystal was employed as an X-ray source (35–40 kV, – 80 mA, focus size: 0.5×5 mm^2). The X-ray beam scattered from the sample was directed to the scintillation counter through two receiving slits.

Results

Thermal Studies: The transition temperatures and latent heats for the present compounds are summarized in Table I.

Although the octyloxy homologs of compounds **1**, **3**, and **4** show a monotropic S_A phase, these were inadequate for the subject materials for the X-ray study because of recrystallization. Therefore, we also prepared some higher members.

All the octyloxy derivatives show the S_A phase as well as the N one. The ratios of the smectic A-nematic transition temperature ($T_{S_A\text{-}N}$) to the nematic-isotropic one ($T_{N\text{-}I}$)[8] are considerably high (0.95–0.99), indicating that these derivatives favor the layer arrangement. The S_A–N transition for the octyloxy derivative of compound **2** is accompanied by a large latent heat.

In order to characterize the S_A phases, some binary phase diagrams were examined, and the results are shown in Figures 1 and 2.

TABLE I

Transition temperatures (T/°C) and latent heats (kJ/mol) for compounds **1–4**

Compounds	n	X	Y	C	S_A	N	I	$\Delta H_{S_A\text{-}N}$	$\Delta H_{N\text{-}I}$
1	8	—COO—	—COO—	. 119(	. 106)	. 120	.	0.9	0.7
	9			. 103	. 111	. 119	.	1.0	0.9
2	8	—OOC—	—OOC—	. 106	. 112	. 131	.	2.8	0.8
3	8	—COO—	—OOC—	. 113(	. 82)	. 134	.	*1	0.7
	10			. 101	. 101	. 132	.	0.6	1.1
4	8	—OOC—	—COO—	. 119(	. 109)	. 123	.	0.7	1.0
	9			. 120	. 120	. 124	.	0.6	1.1

Parentheses indicate monotropic transitions.

*1 The Phase transition accompanied by solidification.

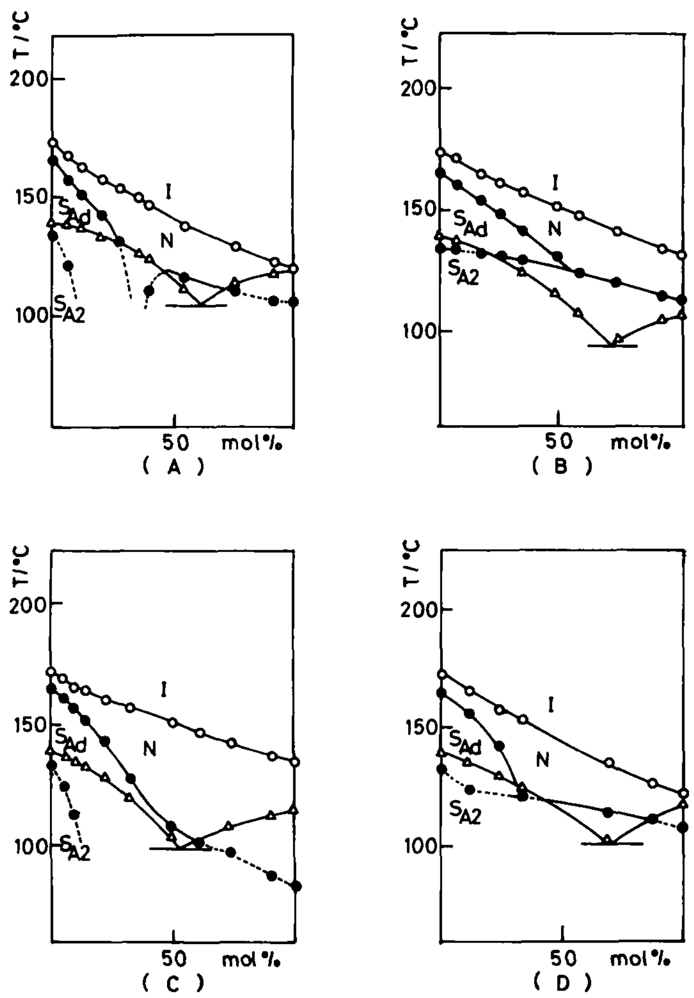


FIGURE 1 Binary phase diagrams for the mixtures of OPPNF (on left) and the octyloxy derivatives of: A; compound **1** (on right), B; compound **2**, C; compound **3**, and D; compound **4**. ○ nematic-isotropic, ●; smectic A-nematic (smectic A), □; crystal-mesophase transitions. Dashed lines indicate monotropic transitions.

In Figure 1, OPPNF, showing the polymesomorphism of a S_{A2}–S_{Ad}–N–I type, was used as a reference material. In Figure 1A, the S_A phases of both compounds have no affinity. A sharp discontinuity occurs at ca. 70 mol% of OPPNF. The S_A phase for the octyloxy homolog of compound **1** is miscible with the S_{Ad} phase of CBOOA in Figure 2A, where S_A–N transition temperature shows a linear correlation with the molar composition.

In Figure 1B, the S_A phase of the octyloxy homolog is miscible with the lower S_A phase of OPPNF, and the S_A–S_A(N) transition temperature shows a linear correlation with the molar composition. In the figure, the S_{Ad}–N transition temperature disappears in the middle of the diagram. The S_A phase of th octyloxy

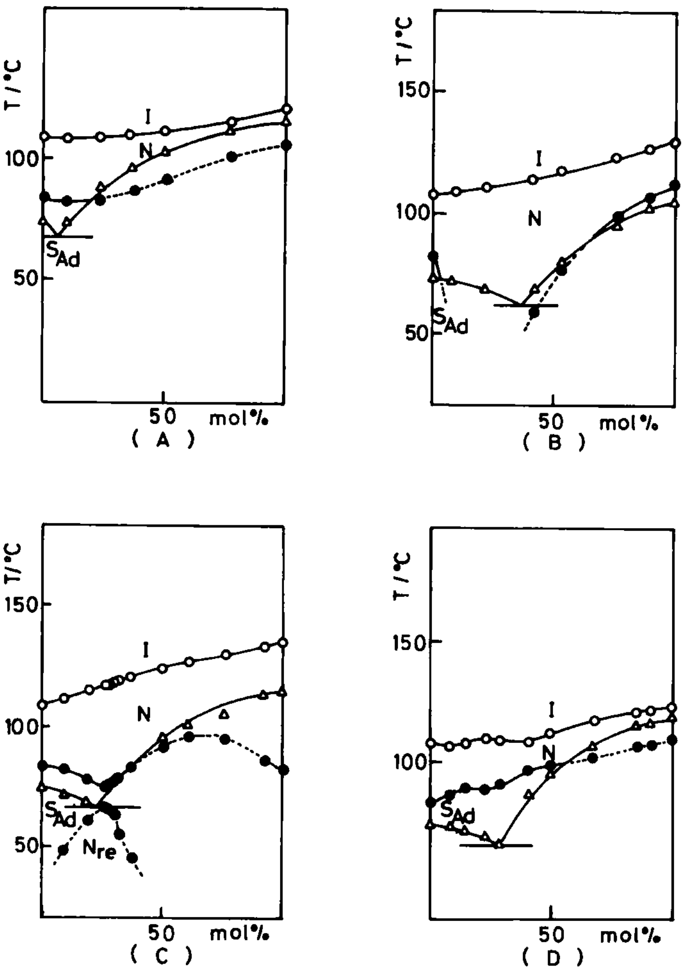


FIGURE 2 Binary phase diagrams for the mixtures of CBOOA (on left) and the octyloxy derivatives of: A; compound **1** (on right), B; compound **2**, C; compound **3**, and D; compound **4**. Refer to the caption in Figure 1.

homolog has no affinity with the S_{Ad} phase of CBOOA in Figure 2B. These facts suggest that the S_A phase of compound **2** has a bilayer nature.

The S_A phase of the octyloxy homolog of compound **3** has an affinity with the S_{Ad} phase of OPPNF, while the S_A–N transition temperature shows weak downward convexity, as shown in Figure 1C. In Figure 2C, the S_A–N transition temperature for the mixture of the octyloxy homolog and CBOOA shows a remarkable non-linear behavior with composition, and the diagram shows a reentrant nematic phase in the range between 95 and 65 mol% of CBOOA. In general, the characteristic constriction can be observed when both S_A phases have a partially bilayer nature. From these results, we can assume that the S_A phase has a partially bilayer nature. The binary phase diagram for the octyloxy homolog of compound **4** and OPPNF (Figure 1D) is very similar to that for the octyloxy homolog of compound **2** and OPPNF (Figure 1B). However, the S_A phase for the octyloxy homolog has an affinity with the S_{Ad} phase of CBOOA (Figure 2D). An interesting fact is that both S_A–N and N–I transition temperatures show a non-linear behavior in the range between 90 and 70 mol% of CBOOA. These facts indicate that in both the N and S_A phases, some molecular rearrangement occurs in this range. Therefore, we can assume that the S_A phase of compound **2** has a bilayer nature.

In Figure 3, the relative miscibilities of these S_A phases are shown.

The S_A phases for the octyloxy derivatives are well miscible to each oher, while the S_A–N transition temperature sometimes shows a non-linear behavior with molar composition. Especially, the non-linear behavior is observed in the mixtures of **1** and **2** (Figure 3A), **1** and **4** (Figure 3C), **3** and **2** (Figure 3D), and **3** and **4** (Figure 3F), indicating that the S_A phases for compounds **2** and **4** have different thermal properties from those for compounds **1** and **3**.

X-ray diffraction studies: The X-ray profiles for compounds **1–4** are shown in Figure 4.

The nonyloxy derivative of compound **1** shows a maximum at $2\theta = 2.68°$ (32.9 Å) at 106°C (T_{S_A-N}–5°C), and the maximal position becomes a little shorter at a lower temperature. These facts indicate that the S_A phase has a monolayer arrangement.

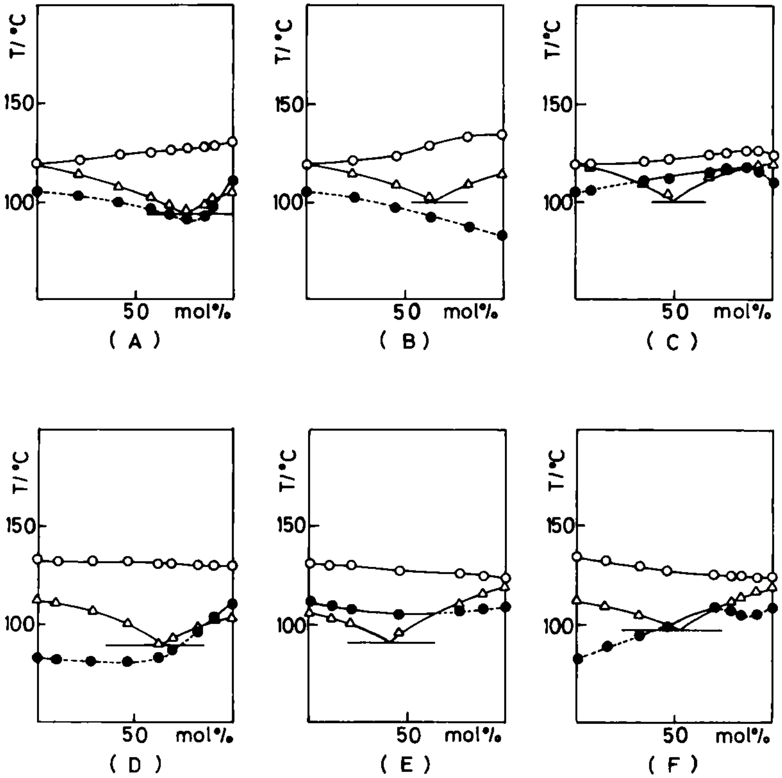


FIGURE 3 Binary phase diagrams for the mixtures of the octyloxy derivatives of: A; compounds **1** (on left) and **2** (on right), B; compounds **1** (on left) and **3** (on right), C; compounds **1** (on left) and **4** (on right), D; compounds **3** (on left) and **2** (on right), E; compounds **2** (on left) and **4** (on right), F; compounds **3** (on left) and **4** (on right). Refer to the caption in Figure 1.

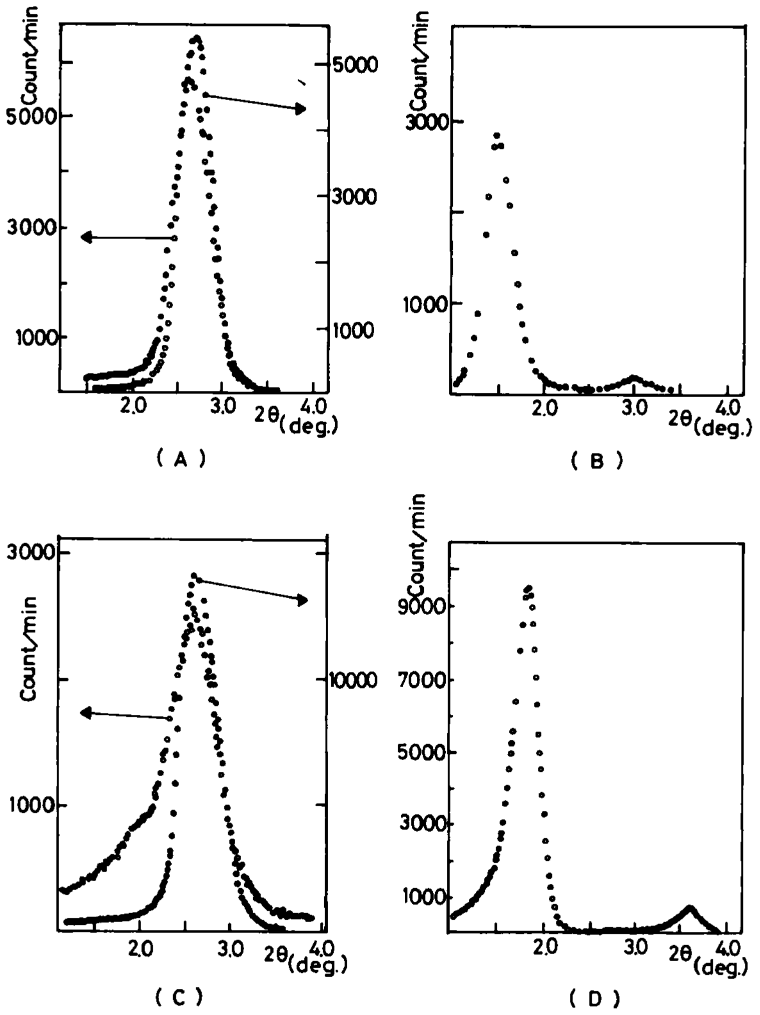


FIGURE 4 The plots of scattered X-ray intensities (count/min) against 2θ (deg) for: A; the nonyloxy derivative of compound **1**, B; the octyloxy derivative of compound **2**, C; the decyloxy derivative of compound **3**, D; the nonyloxy derivative of compound **4**, ○; at $T_{S_A\text{-}N}$–5°C and ●; at $T_{S_A\text{-}N}$–10°C.

The octyloxy derivative of compound **2** shows a weak maximum at 2θ = 2.98° (29.6 Å) and a sharp one at 2θ = 1.47° (60.0 Å) at 107°C ($T_{S_A\text{-}N}$–5°C), indicating that the S_A phase of compound **2** has a bilayer arrangement. The temperature dependency of the X-ray diffraction was impossible to examine because the monotropic S_A phase recrystallized very easily.

The decyloxy derivative of compound **3** shows a maximum at 2θ = 2.58° (34.2 Å) at 96°C ($T_{S_A\text{-}}$–5°C). The layer spacing corresponds to the monolayer arrangement. As is evident from Figure 4C, the profile also shows a shoulder at 2θ = 1.8 – 2.0° (ca. 45 Å). The layer spacing corresponds to 1.3 times the fully extended molecular length. This fact indicates that the S_A phase of compound **3** also has a

S_{Ad} nature near the S_A–N transition. Of course, the shoulder disappears at a lower temperature, as shown in Figure 4C.

The nonyloxy derivative of compound **4** shows an enantiotropic S_A phase. However, the solidification occurred so easily that X-ray examination was not possible. Figure 3D shows an X-ray profile at 115°C (T_{S_A-N}–5°C), which is not in the S_A phase but in the solid phase. The profile shows two peaks at $2\theta = 3.60°$ (24.5 Å) an $2\theta = 1.79°$ (49.3 Å). The former value is far shorter than the fully extended molecular length, and the latter is also shorter than two times the length. The abnormal diffraction must arise from the solid phase as a paramorphosis from the S_A phase. Therefore, we conclusively assume that the S_A phase of compound **4** has a bilayer arrangement.

Discussion

It is known that in many liquid crystals having a nitro or a cyano group at the terminal position, the molecular arrangements in the smectic A phase are correlated with the orientation of the linkages with respect to the polar group, where the dipoles arising from the linkages and the polar terminal group are considered to play some important role.[1] Although the nitro group for the present compounds locates at the meta position with respect to the ester linkage at position *Y*, the molecular arrangements in the S_A phases are also concerned with the relative orientation of the ester linkages. The present results can be summarized in Table II.

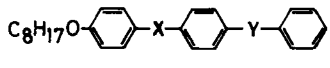
It is also known that lateral nitro and cyano groups increase the smectic properties due to polar interactions around the substituent.[3–5] Certainly, the nito group remarkably enhances smectic properties in compounds **2** and **3**. However, the effect of the nitro group is not recognized in compounds **1** and **4**. Rather, the nitro group in compound **4** decreases the smectic properties. With regard to the effect of the

TABLE II

Smectic properties for the octyloxy homologs of compounds **1–4**

Compounds	Linkages *X*	Linkages *Y*	Molecular arrangements	T_{S_A-N}/T_{N-I}	T_{S_A-N}/T_{N-I}[*1]
1	—COO—	—COO—	S_{A1}	0.96	0.95
2	—OOC—	—OOC—	S_{A2}	0.95	[0.78]
3	—COO—	—OOC—	S_{A1}-(S_{Ad})	0.87	[0.82]
4	—OOC—	—COO—	S_{A2}[*2]	0.96	[0.98]

[*1] The values for the following compounds:[13]



The un-nitrated derivatives of compounds **2** and **3** do not show any smectic phase even in higher members such as the tetradecyl homologs, and the values in the table were calculated from the extrapolated S_A–N transition temperatures. For the un-nitrated derivative of compound **4** the S_A phase could not be observed because of recrystallization, but the S_A–N transition temperature extrapolated from the binary phase diagrams was as high as compound **1**. The value in the table was also calculated from the extrapolated S_A–N transition temperature.

[*2] The molecular arrangement was deduced from the thermal properties in the binary phase diagrams.

nitro group, we have to pay attention to the fact that the un-nitrated derivatives of compounds **2** and **3** are quite poor in the smectic properties compared with compounds **1** and **4**, and the introduction of the nitro group dissolves the difference in the smectic properties. In the present compounds, compounds **1** and **3** mainly form the monolayer arrangement, and compound **2** form the bilayer one, and compound **4** is probably also.

It is well known that a dipole-dipole interaction plays an important role in determining the molecular arrangement in the S_A phases.[1] The dipole correlations for the present compounds in the monolayer, partially bilayer, and bilayer arrangements are roughly illustrated in Figure 5.

We can assume that the molecular arrangement in the S_{A1} phase for compound **1** is a statistical average of two extreme arrangements, A and B, where the layer spacing is 32.9 A. In model B, all the dipoles arising from the linkages and the nitro group are concentrated in a specific area within the layer, and the longitudinal

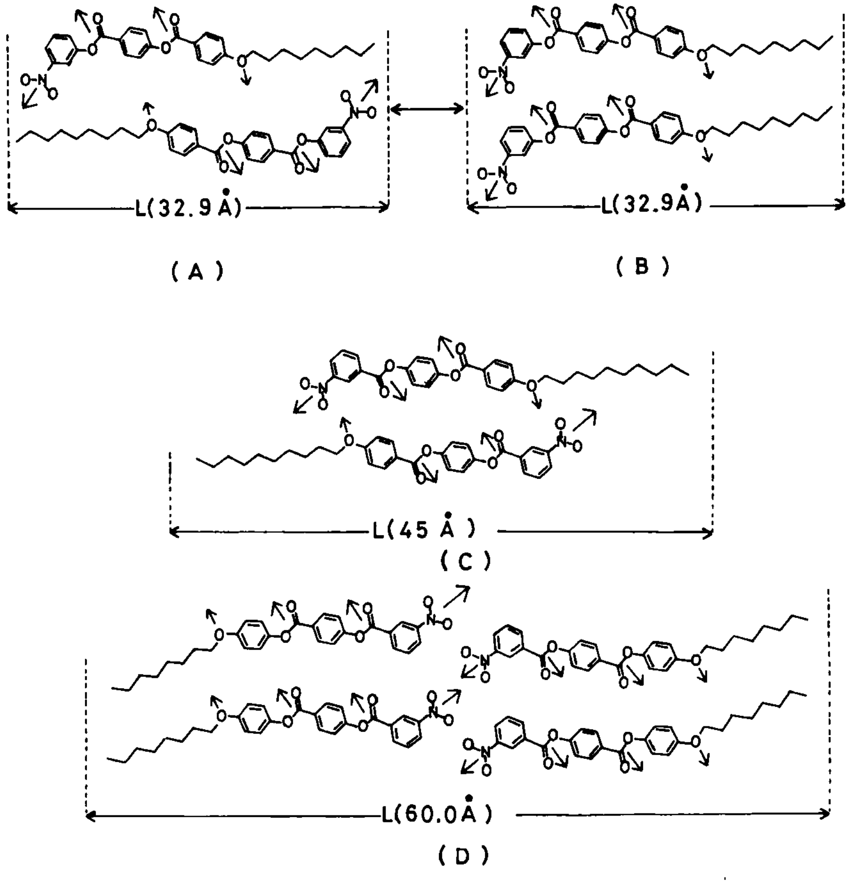


FIGURE 5 The molecular arrangements and dipole correlation in the S_{A1}, S_{Ad}, and S_{A2} phases. The molecular structures for models A and B are substituted by the nonyloxy derivative of compound **1**. Model C indicates the partially bilayer arrangement of the decyloxy derivative of compound **3**. Model D indicates the bilayer arrangement of the octyloxy derivative of compound **2**. Arrows indicate the dipole moments arising from the ester and nitro groups. L indicates the layer spacing in the S_A phases.

components of the dipoles always arrange parallel. In the arrangement, the dipole-dipole interaction ($W_{\mu\mu p}$) is someway proportional to $\mu^2/125$ supposing that the distance between the adjacent molecules in the mesophases is ca. 5 Å,[10] and the dipole-dipole interaction is inversely proportional to the third power of distance between participant dipoles.

In model A, on the other hand, all the dipoles arising from the linkages and the nitro group arrange antiparallel in the pair so that the interaction is attractive to the layer arrangement. However, the distance between each dipole is a function of the alkoxy chain length at the terminal position. As we can assume from the figure, the distance between the nitro groups in the pair is ca. 30 Å when the alkoxy chain is in the nonyloxy group. In the arrangement, the dipole-dipole interaction around the nitro group ($W_{\mu\mu ap}$) is proportional to $\mu^2/27000$. Considering thus, $W_{\mu\mu ap}$ would be far smaller than $W_{\mu\mu p}$, and the former interaction would be of primary importance in determining the thermal stability and molecular arrangement in the smectic A phase. There is an interesting molecular arrangement; a similar arrangement to model C. In the pair model, all the dipoles arising from the functional groups arrange close and antiparallel so that the interaction involving the dipoles is considered to be attractive for the monolayer arrangement.[11] However, the model is inapplicable to compound **1** since the layer spacing does not agree with the X-ray results. In fact, a similar antiparallel correlation model is frequently used as a dimer model in the S_{Ad} phase.[12]

Compound **2** form a bilayer arrangement (model D), where the layer spacing is 60.0 Å. In the arrangement, all the dipoles arising from the ether and ester groups arrange close and parallel while the dipoles arising from the nitro groups arrange antiparallel. Only the dipole-dipole interaction around the nitro groups would be attractive for the layer arrangement.

Compound **3** mainly forms a monolayer arrangement, where the layer spacing is 34.2 Å. The average molecular arrangement and the dipole correlation are similar to models A and B. The X-ray studies suggest that an interdigited molecular arrangement (model C) is also present near the S_A–N transition. The layer spacing (ca. 45 Å) corresponds to 1.3 times the fully extended molecular length. In the antiparallel pair (model C), the dipoles arising from the ester groups arrange parallel. Although the dipoles arising from the nitro group arrange antiparallel, the nitro groups are too apart to interact each other. Therefore, the attractive interaction between the nitro groups in the pair may not be so important.

Compound **4** may have a similar molecular arrangement to model D, though we could not obtain the evidence. In the arrangement, the ester and ether groups also arrange close and parallel. It is well known that the dipole-dipole interaction is attractive when the participant dipoles arrange antiparallel, and repulsive when parallel. As mentioned above, most of the dipoles in the smectic A phases arrange parallel. Even if the dipoles arrange antiparallel (for example, models A and C), the interaction should be weak since the functional groups locate apart each other. Therefore, we are difficult to explain the diversity of the molecular arrangements for compounds **1–4** in terms of the attractive interaction involving the dipoles.

In an earlier paper, we described the geometrical and electrostatic characteristics for compounds **1–4** having no nitro group, and concluded that the molecular geometries are of primary importance in determining the smectic properties of the molecules, and a strong dipole-dipole intraction is not always favorable for the layer arrangement of the molecules.[13]

For the present compounds the molecular structures involving the long alkoxy chain are fairly different due to the difference in the orientation of the ester groups with respect to the long alkoxy chain. That is, the gross molecular structures of compounds **2** and **4** are linear, while the long alkoxy chain increases the molecular breadth. On the other hand, compounds **1** and **3** intrinsically have bent geometries, and the long alkoxy chain increases not only the molecular breadth but also the geometrical bend.[13]

Furthermore, the nitro group at the terminal position decreases the charge on the carbonyl group at position *Y* due to the electron-withdrawing nature of the nitro group. For compounds **2** and **3** the remarkable enhancement of the smectic properties would be concerned with the reduction of the charge of the carbonyl group at position *Y*.

CONCLUSION

The diversity of the molecular arrangement in the smectic A phase is fundamentally impossible to explain in terms of the attractive interactions involving dipoles. Rather, we have to pay much attention to the geometrical factor in connection with the packing effect in the smectic A phase, and repulsive dipole-dipole interaction in the parallel arrangement of the molecules. For the formation of the S_{A2} phase, on the other hand, the inter-layer dipole-dipole interaction around the nitro groups at the terminal position is indispensable.

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