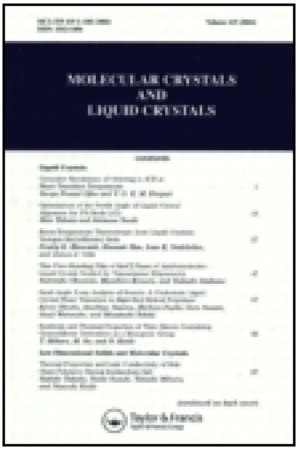

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Molecular Structure and Smectic Properties: Thermal Properties of Some Liquid Crystals Having a Nitro Group at the Terminal Position

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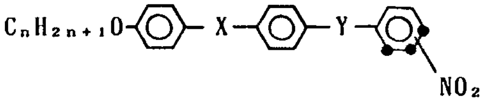
Summary: The thermal properties of ortho (*o*)-, meta (*m*)-, and para(*p*)-nitrophenyl 4-(4-alkoxybenzoyloxy)benzoates (**1**), 4-(4-alkoxyphenoxycarbonyl)phenyl *o*-, *m*-, *p*-nitrobenzoates (**2**), 4-(4-alkoxybenzoyloxy)phenyl *o*-, *m*-, *p*-nitrobenzoates (**3**), *o*-, *m*-, *p*-nitrophenyl 4-(4-alkoxyphenoxycarbonyl)benzoates (**4**), and some related compounds have been reported. For the *p*-nitro derivatives of compounds **1**–**4** the smectic *A* phase having a partially bilayer arrangement (S_{Ad}) commences from the hexyloxy, nonyloxy, pentyloxy, and nonyloxy homologs, respectively, where the smectic *A*-nematic transition temperatures are almost independent of the orientation of the ester linkages. The *p*-nitro derivatives of compounds **2** and **3** also show two kinds of smectic *A* phases having bilayer (S_{A2}) and/or monolayer (S_{A1}) arrangements at low temperature. All the *m*-nitro derivatives show smectic *A* phases, where **2** and probably **4** have the S_{A2} phase, and **1** and **3** show the S_{A1} one. The *o*-nitro derivatives fof compounds **2** and **4** show the S_{A2} phase which commences from the nonyloxy homologs. The dielectric properties for *m*- and *o*-nitro derivatives have been examined. The results are discussed in terms of polar interactions around the substituents and linkages.

INTRODUCTION

It is known that liquid crystals having a nitro group or a cyano group at the terminal position form associated dimers, and show very complex mesomorphisms involving re-entrant phenomena.[1,2] The strong attractive interactions involving dipole-dipole and dipole-induced dipole ones are supposed to play some important role in the phenomena. The associated dimers form monolayer (S_{A1}), bilayer (S_{A2}), partially bilayer (S_{Ad}), and antiphase ($S_{\tilde{A}}$) arrangements in the smectic A phase, and corresponding tilted arrangements in the smectic C one. For the modification in the smectic phases the dipoles arising from the linkages such as ester and azomethine groups are considered to play some important role.[2–5] In these papers, the participation of the dipoles arising from the polar functional groups has been emphasized.

For practical purposes, a lot of liquid crystals having a nitro or a cyano group at the lateral position of a molecule have been prepared, and some of them show abnormal smectic properties.[6–8] These phenomena have also been discussed in terms of the attractive polar interactions between the substituents.

In this paper, we want to reexamine in more detail the effect of dipoles on the smectic properties. For this purpose, we prepared four related ester compounds incorporating a nitro group at the *o*-, *m*-, and *p*-positions of the terminal aromatic ring, as shown below.



Compound	X	Y
1	-COO-	-COO-
2	-OOC-	-OOC-
3	-COO-	-OOC-
4	-OOC-	-COO-

Some compounds having chlorine, methoxy, and acetyl groups instead of the nitro group were also prepared. The difference in the smectic properties has been discussed in terms of polar interactions around the ester groups and the terminal substituents.

EXPERIMENTAL

Materials: The method of preparation has been reported.[9] The molecular structures were confirmed by elementary analysis and NMR spectroscopy.

N-[4-(4-Heptyloxybenzoyloxy)benzylidene]-4-cyanoaniline (HBBCA) was prepared according to the method of Weissflog *et al.*[10] 4-(4-Octyloxyphenoxycarbonyl)phenyl 5-nitrofuran-2-carboxylate (OPPNF) was prepared according to the method of Takenaka *et al.*[4] OPPNF shows the mesomorphic sequence of a $C \cdot 139$ $(\cdot\ S_{A2} \cdot 133) \cdot S_{Ad} \cdot 165 \cdot N \cdot 170 \cdot I$ (T/°C), where the layer spacings for the S_{A2} and S_{Ad} phases are 2.0 and 1.4 times of the molecular length, respectively. 4-Alkoxybiphenyl-4′-yl 4-cyanobenzoates were prepared according to the method of Goodby *et al.*[11]

Method: Phase transitions were observed by using a Nikon Model *POH* polarizing microscope fitted with a Mettler FP-52 heating stage. Transition temperatures and the latent heats were determined with a Seiko-denshi SSC-5200 differential scanning calorimeter (DSC), where indium (99.9%) was used as a calibration standard (mp. = 156.6°C, $\Delta H = 6.8$ mcal/mg). The DSC thermogram was operated by heating and cooling rates of 5°C/min.

Dielectric constants were measured by using an Ando-denki TR-10 precision capacitance measurement system. The capacitor cell consisted of two indium-coated glass electrodes separated by a 10 μm spacer. The cell temperature was controlled by means of 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.

RESULTS

Transition temperatures and latent heats for the homologs of compounds **1**–**4** are summarized in Tables I–IV.

The *p*-nitro derivatives of compounds **1**–**4** show the *N* phase, where the average *N-I* transition temperatures for **1a**, **2a**, **3a**, and **4a** (from the heptyloxy to nonyloxy homologs) are 225, 228, 244, and 221°C, respectively. All the *p*-nitro derivatives show the S_A phase, though the beginning is different.

In order to characterize the thermal properties of the S_A phases, we examined the binary phase diagrams, as shown in Figure 1.

It has been known that the S_A phase for the homologs of compound **1a** has a

TABLE I

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

Compounds	Position of nitro group	n	C	S_A	N	I	$\Delta H_{S_A\text{-}N}$	$\Delta H_{N\text{-}I}$
1a	*p*	5	· 122	—	· 240	·		0.6
		6*¹	· 118	· 152	· 238	·	0	0.7
		7	· 121	· 199	· 228	·	0.1	0.5
		8	· 114	· 210	· 224	·	0.4	0.7
		9	· 116	· 218	· 222	·	2.0	1.7
1b	*m*	4	· 129	(· 98	· 127)	·	1.2	0.5
		5	· 105	(· 98)	· 122	·	1.4	0.5
		6	· 114	(· 100)	· 123	·	0.8	0.5
		7	· 114	(· 101)	· 122	·	0.8	0.7
		8	· 119	(· 106)	· 120	·	0.9	0.7
		9	· 103	· 111	· 119	·	1.0	0.9
1c	*o*	7	· 118	—	(· 112)	·		0.7
		8	· 120	—	(· 110)	·		0.7
		9	· 112	—	(· 108)	·		1.0

C, S_A, *N*, and *I* indicate crystal, smectic *A*, nematic phases, and isotropic solution, respectively. Parentheses indicate monotropoic transitions.

*¹Reference 12.

TABLE II

Transition temperatures (T/°C) and latent heats (kJ/mol) for compound **2**

Compounds	Position of nitro group	n	C	S_A	N	I	$\Delta H_{SA\text{-}N}$	$\Delta H_{N\text{-}I}$
2a	*p*	4	· 141	—	· 254	·		0.9
		5	· 130	(· 100)	· 244	·	0	0.8
		6	· 120	· 120	· 241	·	0	0.8
		7*1	· 111	· 131	· 233	·	0.2	1.0
		8*1	· 101	· 129	· 228	·	0.1	0.7
		9*2	· 116	· 195	· 224	·	2.0	1.7
2b	*m*	5	· 103	(· 74)	· 133	·	*3	0.7
		6	· 105	(· 93)	· 135	·	2.4	0.7
		7	· 106	(· 104)	· 133	·	2.8	0.6
		8	· 106	· 112	· 131	·	2.8	0.8
		9	· 104	· 115	· 128	·	3.3	0.9
2c	*o*	7	· 101	—	(· 97)	·		0.6
		8	· 94	—	· 98	·		0.8
		9	· 96	(· 84)	· 108	·	6.4	0.8

*1These compounds underwent a smectic *A*-smectic *A* transition at 109°C (the latent heats were less than 0.1 kJ/mol).

*2Reference 13.

*3The latent heat was not measured because of recrystallization.

TABLE III

Transition temperatures (T/°C) and latent heats (kJ/mol) for compound **3**

Compounds	Position of nitro group	n	C	S_A	N	I	$\Delta H_{SA\text{-}N}$	$\Delta H_{N\text{-}I}$
3a	*p*	3	· 201	—	· 283	·		0.9
		4	· 189	(· 172)	· 274	·	0	0.7
		5	· 169	· 204	· 262	·	0.1	0.7
		6*1	· 165	· 217	· 257	·	0.1	0.7
		7	· 166	· 233	· 250	·	0.4	0.6
		8	· 165	· 239	· 246	·	0.8	0.9
		9	· 165	· 242	· 243	·	4.5*2	
3b	*m*	7	· 122	—	· 137	·		0.7
		8	· 113	(· 82)	· 134	·	*3	0.7
		9	· 106	(· 92)	· 133	·	1.0	0.9
3c	*0*	7	· 110	—	(· 96)	·		0.6
		8	· 95	—	· 95	·		0.6
		9	· 95	—	(· 94)	·		0.7

*1Reference 14. The data in this table are our values.

*2The value is the sum of the smectic *A*-nematic and nematic-isotropic transitions.

*3The latent heat was not measured because of recrystallization.

partially bilayer arrangement.[12] In Figure 1a, the S_A phase for the reference compound has been assigned to the S_{A1} one.[11] In the diagram, both S_A phases are discontinuous in the range between 15 and 30 mol% of OBCB, and the mixture containing 9 mol% of OBCB shows the mesomorphism of an N_{re}-S_A-N-I type, indicating that the S_A phase of the octyloxy homolog has a partially bilayer ar-

TABLE IV

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

Compounds	Position of nitro group	n	C	S_A	N	I	$\Delta H_{SA\text{-}N}$	$\Delta H_{N\text{-}I}$
4b	p	7	· 153	—	· 223	·		0.6
		8^{*1}	· 153	[· 100]	· 224	·		0.7
		9^{*2}	· 156	· 198	· 219	·	1.7	0.7
4b	m	7	· 121	—	· 123	·		1.6
		8	· 119	(· 109)	· 123	·	0.7	1.0
		9	· 120	· 120	· 124	·	0.6	1.1
4c	o	7	· 105	—	(· 104)	·		0.9
		8	· 107	—	(· 101)	·		1.1
		9	· 108	(· 60	· 102)	·	^{*3}	1.4

^{*1}A virtual transition (see text).
^{*2}Reference 15.
^{*3}The latent heat could not be measured because of recrystallization.

rangement. An important fact in the diagram is that the hexyloxy homolog has no other S_A phase in the low temperature region.

It is known that the S_{Ad} phase for compound **2a** commences from the nonyloxy homolog, and the nonyloxy homolog shows the mesomorphism of a $C \cdot 109$ $(\cdot\ S_{c2} \cdot 90) \cdot S_{\tilde{c}} \cdot 118 \cdot S_{A1} \cdot 124 \cdot N_{re} \cdot 127 \cdot S_{Ad} \cdot 138 \cdot N_{re} \cdot 156 \cdot S_{Ad} \cdot 195 \cdot N$ $\cdot\ 224 \cdot I$ type.[13] As we can see from Table II, the lower members show two kinds of S_A phases. In Figure 1b, the S_{Ad} phase of OPPNF disappears at around 65 mol% of the reference compound, and the S_{A2} phase is miscible with the lower S_A phase of the octyloxy homolog. The upper S_A phase of the octyloxy homolog disappears at 60 mol% of the octyloxy homolog. From these results, the lower and upper S_A phases of the octyloxy homolog can be assigned to the S_{A2} and S_{A1} ones, respectively.

The S_A phase of compound **3a** has been assigned to the S_{Ad} one.[14] In Figure 1c, the S_A-N transition shows a remarkable non-linear feature, and the re-entrant sequence of an S_{A1}-N_{re}-S_A-N-I type is shown in the range between 56 and 70 mol% of OBCB. Although the re-entrant mesomorphism disappears below 56 mol% of OBCB, no S_A-S_A transition could be observed in the range between 0 and 56 mol% of OBCB.

The S_A-N transition for the mixtures of OBCB and the pentyloxy and butoxy homologs are also indicated in Figure 1c. In the diagram, the S_A-N transition shows a straight line in the range between 45 and 100 mol% of OBCB, and shows an upward convexity in the other region. On the other hand, the S_A-N transition for the mixture of OBCB and the butoxy homolog in Figure 1c shows a straight line over the whole range. These facts indicate that the S_A phase for the butoxy homolog has the monolayer arrangement, and the pentyloxy and the after members form two S_A phases having the partially bilayer and monolayer arrangements at higher and lower temperature regions, respectively. In Figure 1c, the S_{A1}-S_{Ad} transition for the pentyloxy homolog occurs at ca. 170°C, though the transition was impossible to detect by both DSC and microscopy. Therefore, the homologous series of **3a**

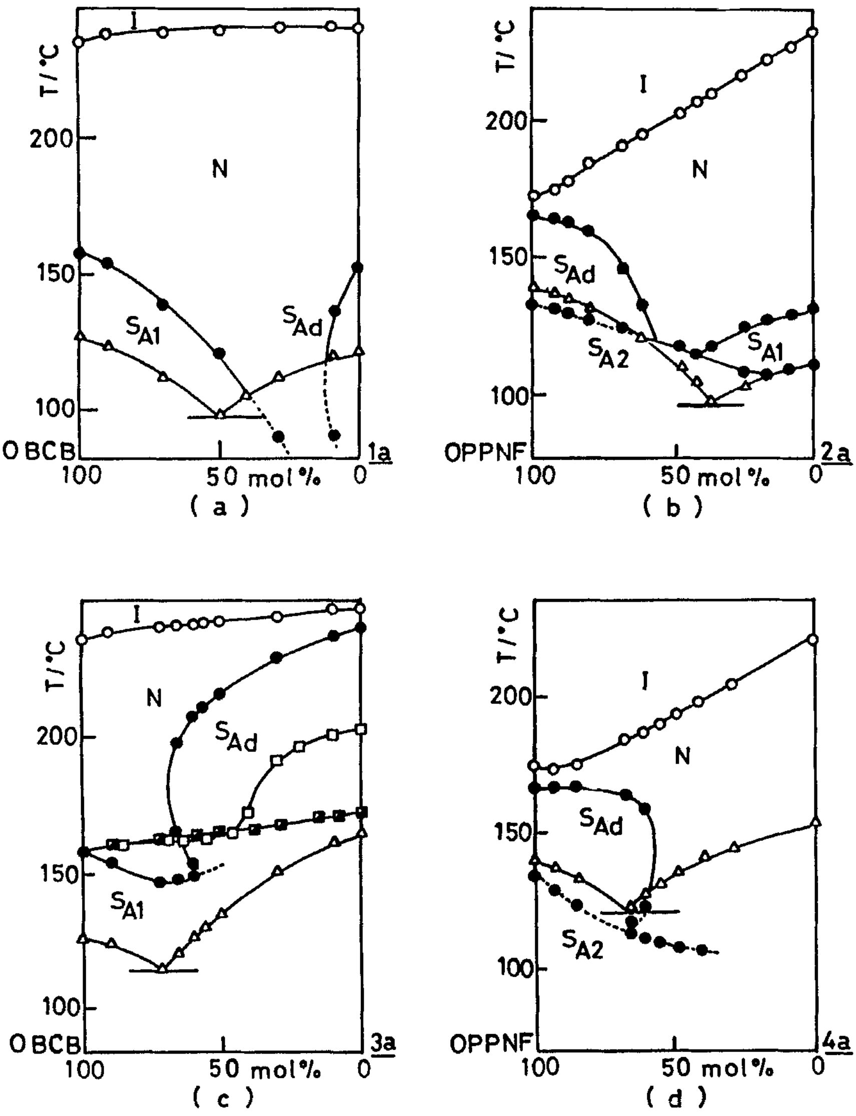


FIGURE 1 Binary phase diagrams for the mixtures of: a; OBCB (on left) and the octyloxy homolog of compound **1a** (on right) b; OPPNF and the octyloxy one of **2a**, c; OBCB and the octyloxy one of **3a**, and d; OPPNF and the octyloxy one of **4a**. In Figure 1c, □ and ▨ indicate the S_A-N transitions for the mixtures of OBCB and the pentyloxy homolog of compound **3a**, and OBCB and the butoxy one, respectively. △; melting points.

show both S_{A1} and S_{Ad} phases, where the S_{Ad} phase commences from the pentyloxy homolog, and the S_{A1}-S_{Ad} transition occurs at ca. 170°C. This phase sequence does not agree with the X-ray results.[14]

It has been reported that the S_{Ad} phase for compound **4a** commences from the nonyloxy homolog. In Figure 1d, the S_{Ad} phase of the reference compound disappears at 55 mol%, and the re-entrant mesomorphism of an S_{A2}-N_{re}-S_{Ad}-N-I type is observed in the range between 55 and 64 mol% of OPPNF. An interesting fact is that the S_{A2}-$S_{Ad}(N)$ transition gradually decreases on an increase in the concentration of the octyloxy homolog. The extrapolated S_{A1}-S_{Ad} transition intersects with the right side axis at ca. 100°C, indicating that for the octyloxy homolog of compound **4a** the S_{A2}-N transition occurs at the temperature.

The transition temperatures are plotted against the carbon number (n) in Figure 2.

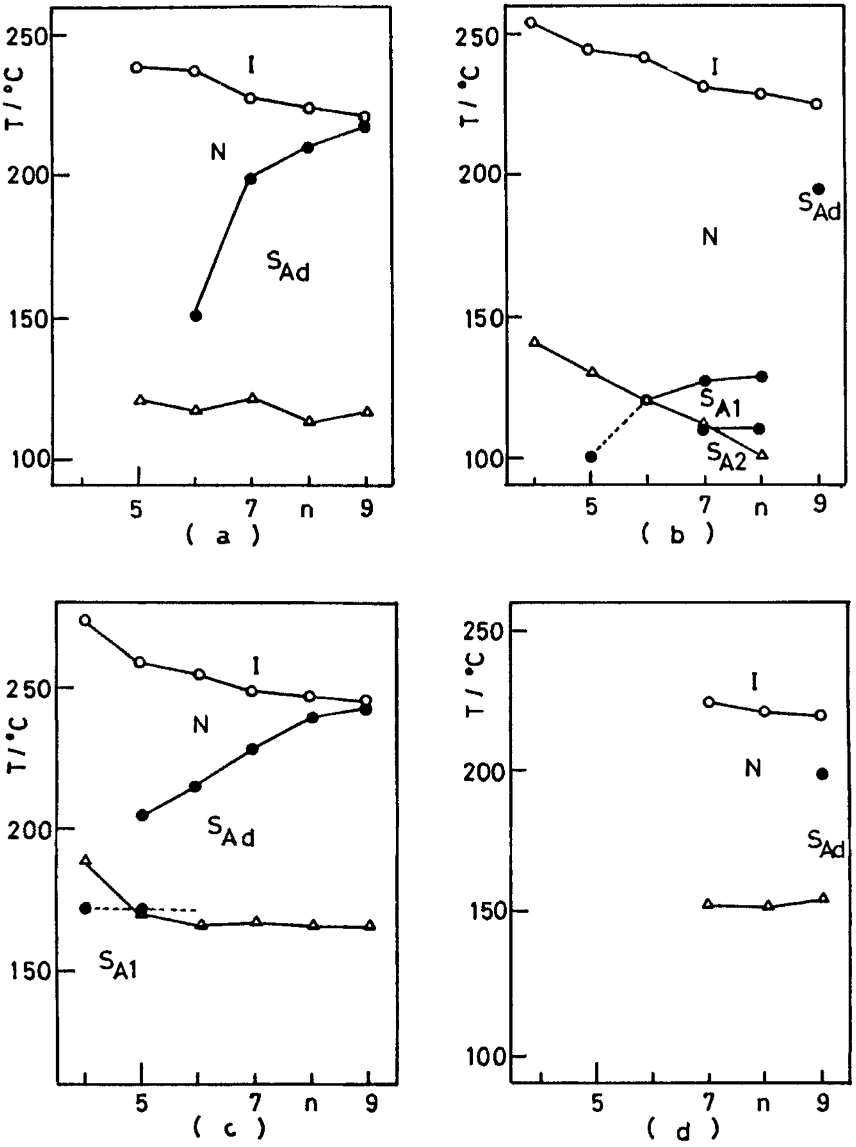


FIGURE 2 Plots of transition temperatures against the carbon number (n) for compounds: a; **1a**, b; **2a**, c; **3a**, and d; **4a**. △; melting points.

The *m*-nitro compounds show the S_A phase as well as the N one. In an earlier paper,[16] the S_A phases for compounds **1b**, **2b**, and **3b** were assigned to the S_{A1}, S_{A2}, and S_{A1} ones based on the X-ray diffraction study, respectively, and the S_A phase for compound **4b** was assumed to be the S_{A2} one from the examination of the thermal properties in binary phase diagrams. The thermal behavior of these S_A phases in binary mixtures is shown in Figure 3.

As we can see from the Figure, these S_A phases are miscible with each other. The S_A-N transitions for the mixtures of compounds **1b** and **3b** (Figure 3b) and compounds **2b** and **4b** (Figure 3e) show a linear correlation against the molar concentration. On the other hand, the S_A-N transitions in the other mixtures show a non-linear correlation against the molar concentration. The non-linear feature always occurs in the region between 70 and 100 mol% of compounds **2b** and **4b**. In the diagrams, the S_A-S_A transition could be observed neither by DSC nor microscopy. These facts indicate that both S_{A1} and S_{A2} phases are miscible probably

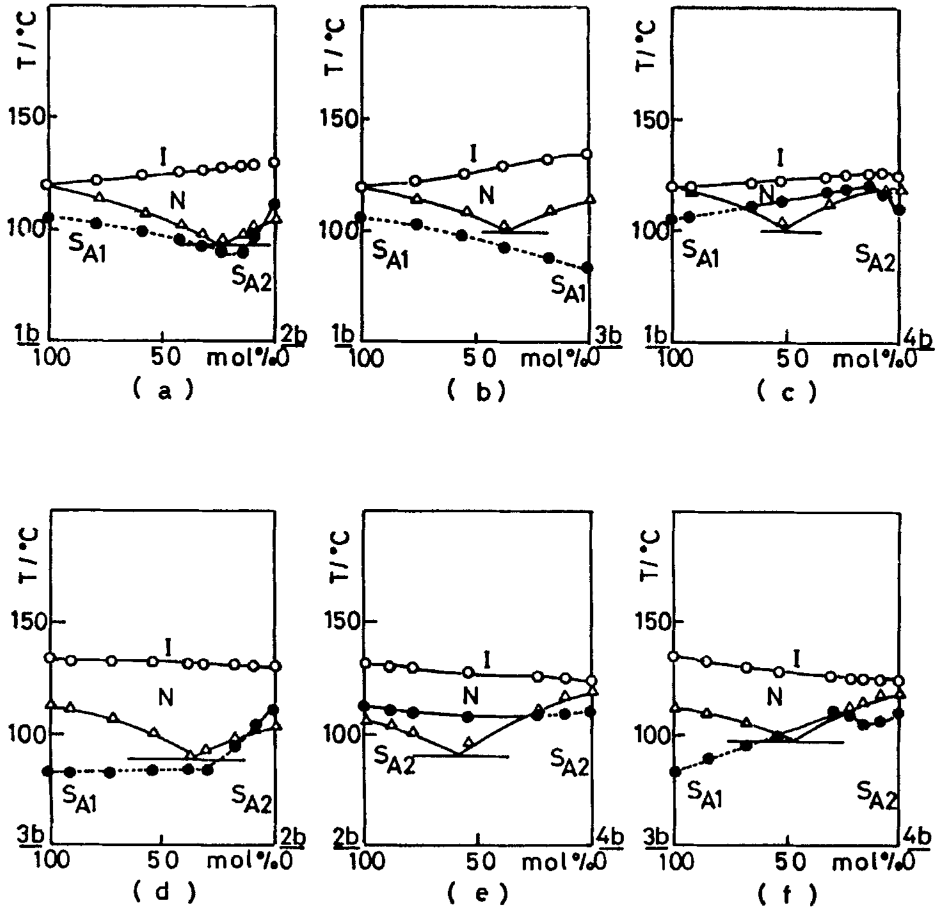


FIGURE 3 Binary phase diagrams for the mixtures of the octyloxy homologs of compounds: a; **1b** (on left) and **2b** (on right), b; **1b** and **3b**, c; **1b** and **4b**, d; **3b** and **2b**, e; **2b** and **4b**, and f; **3b** and **4b**. △; melting points.

due to their structural similarity, though the $S_{A1}(S_{A2})$-N transition shows a non-linear correlation against the molar concentration.

For *o*-nitro derivatives the S_A phase is formed by the nonyloxy homologs of compounds **2c** and **4c**. The layer spacing in the S_A phase for compound **2c** is 63 Å, indicating that the S_A phase has a bilayer arrangement. The X-ray experiment for compound **4c** was impossible because of recrystallization. The binary phase diagrams for the mixtures are shown in Figure 4.

In Figure 4a, the S_{A2}-$S_{Ad}(N)$ transition show a linear correlation against the molar concentration, and the S_A phase of the nonyloxy homolog is miscible with the S_{A2} phase. The S_A phase of the nonyloxy homolog is also miscible with the S_{A2} phase of the nonyloxy one of compound **2c**. From these results, we assumed that the S_A phase of compound **4c** has a bilayer arrangement.

In Figure 4b, the S_{Ad}-N and S_{A2}-S_{Ad} transition temperatures steeply decrease with an increase in the concentration of the nonyloxy homolog, indicating that the S_A-N transition temperature for the nonyloxy homolog is fairly low.

For a comparative study, the thermal properties of some related compounds were also examined,[16] and the results are shown in Table V.

For hydrogen derivatives the S_A phase is formed only by compound **1d**. Interestingly, the virtual S_A-N transition temperature for compound **4d** is the highest of all.

An introduction of a substituent at the terminal position increases the N-I transition temperature. On the other hand, the S_A-N transition temperature is strongly dependent on the electric nature of the substituent and the orientation of the ester linkages. Apparently, the electron-withdrawing substituents tend to enhance the S_A-N transition temperature, while the electron-donating substituent (methoxy group) rather decreases it. As we can see from the table, compounds **1** and **4** intrinsically favor the layer arrangement of the molecules. In compound **2**, the

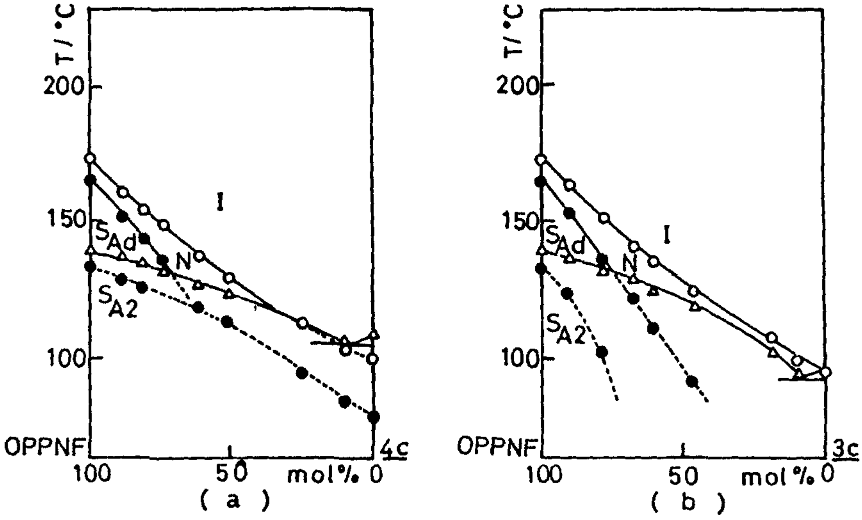
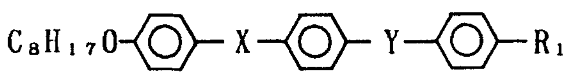


FIGURE 4 Binary phase diagrams for the mixtures of OPPNF (on left) and: a; the nonyloxy homolog of compound **4c** (on right) and b; **3c**. △; melting points.

TABLE V

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



Compounds	R_1			C	S_A	N	I	$\Delta H_{SA\text{-}N}$ or $\Delta H_{SA\text{-}I}$	$\Delta H_{N\text{-}I}$
1d	H	COO	COO	· 118	· 119	· 140	·	1.6	0.7
1e	OCH_3			· 107	· 122	· 226	·	0	0.6
1f	Cl			· 123	· 200	· 209	·	1.8	0.8
1g	$COCH_3$			· 131	· 210	· 227	·	1.3	0.7
2d	H	OOC	OOC	· 118	[· 45]	· 135	·		0.7
2e	OCH_3			· 101	—	· 214	·		0.8
2f	Cl			· 119	· 185	· 214	·	0.3	0.7
2g	$COCH_3$			· 147	· 211	· 231	·	0.3	0.9
3d	H	COO	OOC	· 117	[· 60]	· 141	·		1.0
3e	OCH_3			· 124	—	· 224	·		1.2
3f	Cl			· 168	—	· 217	·		0.7
3g	$COCH_3$			· 162	—	· 236	·		0.8
4d	H	OOC	COO	· 154	[· 130]	(· 140)	·		*1
4e	OCH_3			· 167	[· 125]	· 226	·		0.6
4f	Cl			· 198	· 222	—	·	2.4*2	
4g	$COCH_3$			· 204	· 235	· 235	·	2.7*2	

Brackets indicate a virtual transition.

*1 The latent heat was not measured because of recrystallization.

*2 The sum of S_A-N and N-I transitions.

hydrogen compound is nematogenic, but the electron-withdrawing substituents facilitate the layer arrangement. On the other hand, all of compound **3** are nematogenic, except for **3a**. In order to clarify the smectic properties of compound **3**, we examined some binary phase diagrams, and the results are shown in Figure 5.

In the diagrams, *N*-[4-(4-heptyloxybenzoyloxy)benzylidene]-4-cyanoaniline (HBBCA) was used as a reference compound. HBBCA shows only an *N* phase, though the octyloxy homolog and the higher members show a re-entrant mesomorphism.[10] Although the induction of the S_A phase occurs in all the mixtures, and the maximal S_A-N transition temperatures are almost independent of the electric nature of the substituents (213–218°C), the range of the induced S_A phase is fairly different from system to system. For example, the induction of the S_A phase at 100°C for the mixture of HBBCA and **3g** occurs in the range between 5 and 97 mol% of **3g**, while for the mixture of HBBCA and **3e** it occurs in the range between 5 and 68 mol% of **3e**.

Dielectric studies of *m*- and *o*-nitro compounds: The dielectric constants for compounds **1b–4c** are plotted against temperature in Figure 6.

In the figure, the dielectric constants for the S_A phase are not reliable since the molecular alignment in the cell was disturbed by the formed fan texture.

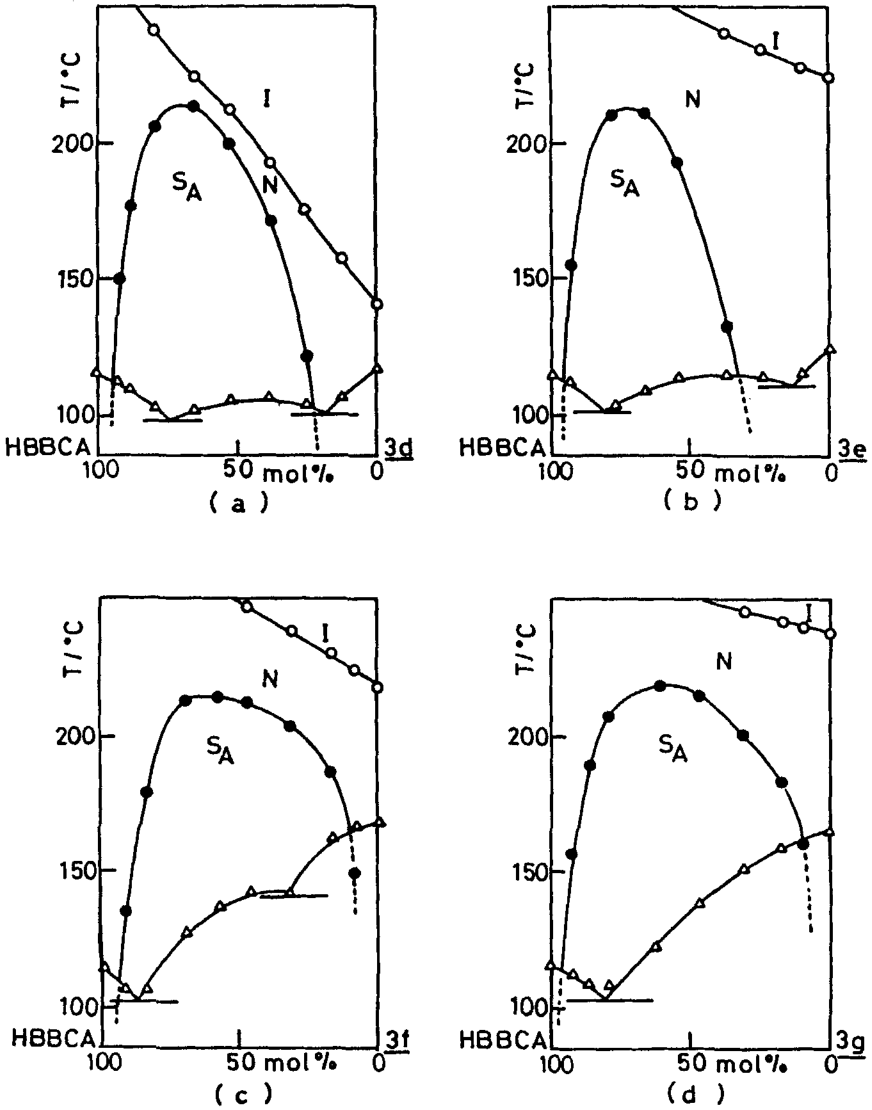


FIGURE 5 Binary phase diagrams for the mixtures of HBBCA (on left) and compounds: a; **3d** (on right), b; **3e**, c; **3f**, and d; **3g**. △; melting points.

The dielectric anisotropies, $\Delta\varepsilon$ ($=\varepsilon_{\parallel}$ (the longitudinal component of dielectric constant) $-$ $\varepsilon_{\perp}$ (the transverse one)), for compounds **1b** and **2c** are 2.2 at $T_{N\text{-}I}$ $-$ 10°C. The dielectric anisotropies for compounds **3b** and **4b** are positive (0.8 and 0.9, respectively, while the anisotropic dipole moments calculated from the Maier-Meier Equation[17] are negative. The dielectric anisotropy for compound **3c** is -1.9 at $T_{N\text{-}I}$ $-$ 10°C. The dielectric anisotropy for compound **4c** is almost zero. In fact, compound **4c** in the *N* phase is insensible to the electric field.

Interestingly, both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for compounds **1b** and **2c** steeply increase in the *N*

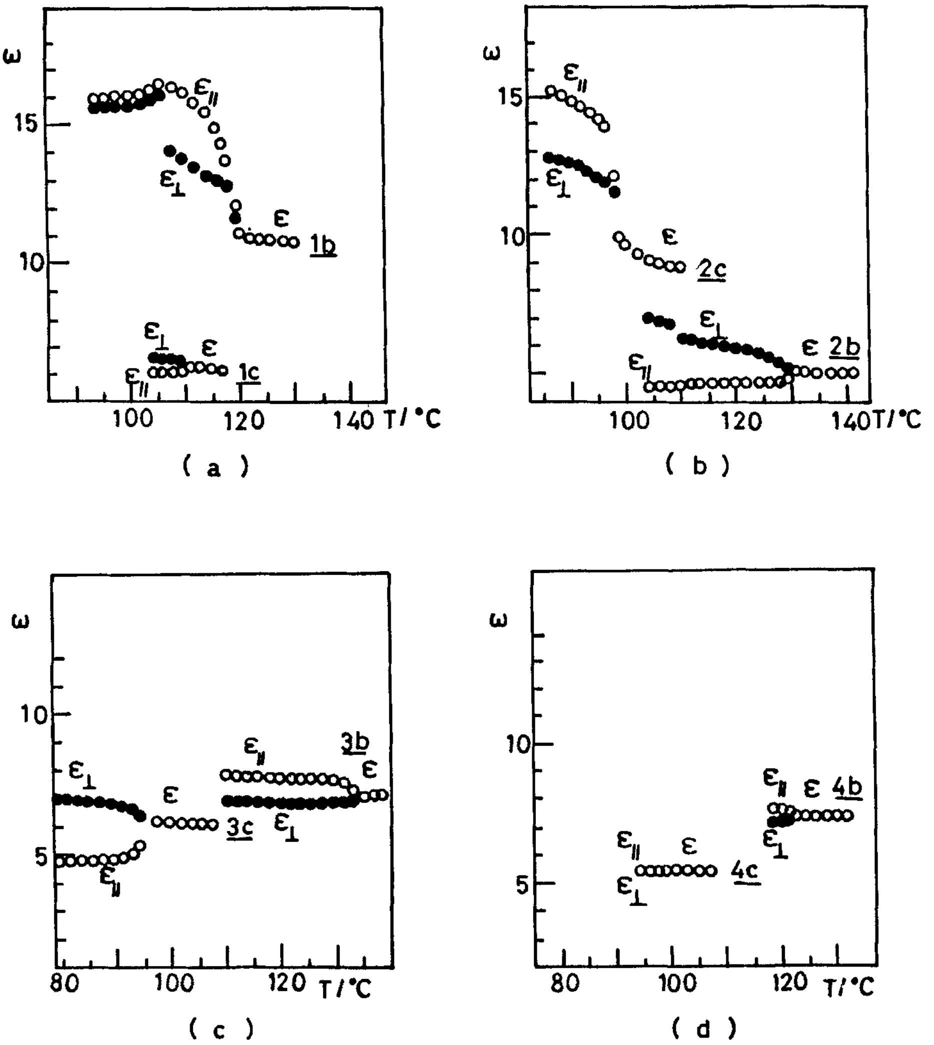


FIGURE 6 Plots of dielectric constants against temperature for compounds: a; **1b** and **1c**, b; **2b** and **2c**, c; **3b** and **3c**, d; **4b** and **4c**. $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ indicate the longitudinal and transverse components of the dielectric constants (ε), respectively.

phase, where the mean dielectric constants $((\varepsilon_{\parallel} + 2\ \varepsilon_{\perp})/3$ at $T_{N\text{-}I}$ − 10°C) for compounds **1b** and **2c** are larger by 3 than the dielectric constants in the isotropic solution. On the other hand, the difference in these dielectric constants in the *N* phase and the isotropic solution is almost zero in the other compounds.

MO calculation: In order to estimate the electric circumstances of the ester and terminal groups, the molecular orbital calculation of the present compounds has been done by the *AM*-1 method.[18,19] Although the present compounds have an octyloxy group at the terminal position, a methoxy group was substituted for the octyloxy group for convenience' sake. The electric circumstances around the core should be irrespective of the substitution. The twist angle between the phenyl groups calculated by *AM*-1[19] was in the range between 42 and 46° so that an angle of 44° was used as an average in the calculation. The calculated charges and total dipole moments are summarized in Table VI.

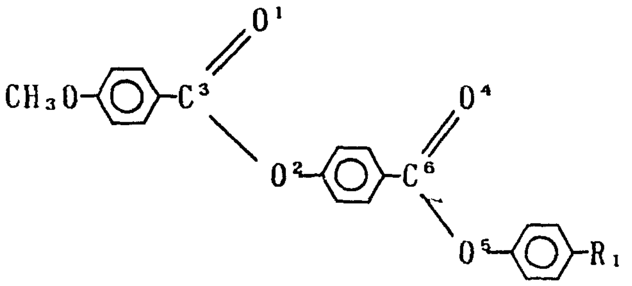
DISCUSSION

In this work, we examined the substituent effect on smectic properties, especially the effect of the nitro group. As shown in Table V, the mesomorphism and transition temperatures are apparently affected by the electric properties of the substituents and the orientation of the ester linkages at positions *X* and *Y*. The results are summarized in Table VII.

TABLE VI

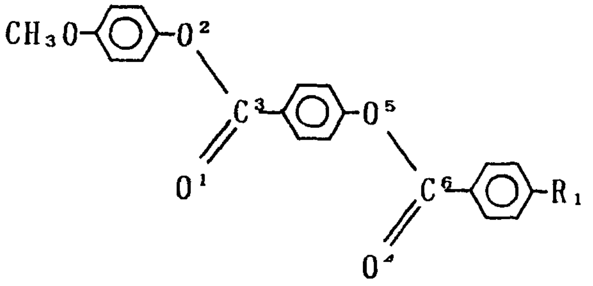
Charges and dipole moments (*D*) of compounds **1–4**

Compound **1**



Substituent R₁	O-1	O-2	Charge C-3	O-4	O-5	C-6	Dipole moment
H	−0.3605	−0.1653	0.3673	−0.3566	−0.1651	0.3569	3.09
OCH_3	−0.3604	−0.1655	0.3673	−0.3586	−0.1622	0.3554	3.95
NO_2	−0.3597	−0.1650	0.3674	−0.3488	−0.1641	0.3573	8.04

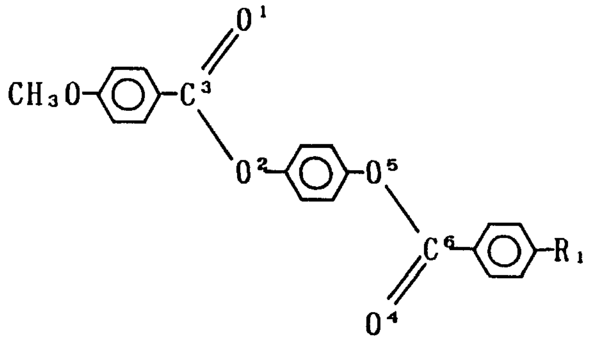
Compound **2**



Substituent R₁	O-1	O-2	Charge C-3	O-4	O-5	C-6	Dipole moment
H	−0.3577	−0.1626	0.3554	−0.3547	−0.1650	0.3561	5.13
OCH_3	−0.3577	−0.1622	0.3554	−0.3604	−0.1655	0.3573	3.95
NO_2	−0.3553	−0.1626	0.3549	−0.3408	−0.1646	0.3529	5.84

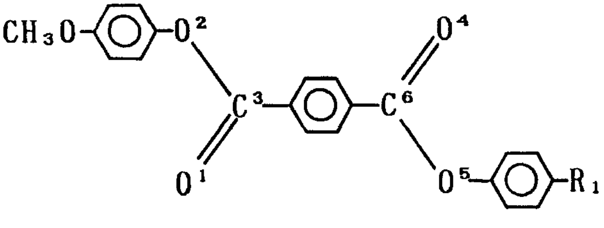
TABLE VI (*continued*)

Compound **3**



Substituent			Charge				Dipole
R_1	O-1	O-2	C-3	O-4	O-5	C-6	moment
H	−0.3652	−0.1629	0.3601	−0.3595	−0.1611	0.3557	1.72
OCH_3	−0.3651	−0.1630	0.3600	−0.3651	−0.1630	0.3600	0.0
NO_2	−0.3642	−0.1627	0.3601	−0.3456	−0.1605	0.3524	6.37

Compound **4**



Substituent			Charge				Dipole
R_1	O-1	O-2	C-3	O-4	O-5	C-6	moment
H	−0.3533	−0.1553	0.3509	−0.3538	−0.1627	0.3531	1.61
OCH_3	−0.3536	−0.1553	0.3510	−0.3536	−0.1653	0.3510	0.0
NO_2	−0.3508	−0.1552	0.3503	−0.3458	−0.1618	0.3536	6.35

It would be reasonable to assume that the smectic A phases for compounds d – g have a monolayer arrangement. For the S_{A1} phase McMillan has introduced a new parameter, R (S_A-N transition temperature to the N-I one), as a criterion of the layer formation of molecules.[20] In this work, we are interested in the R value rather than the S_A-N transition temperature, since the N-I transition temperatures for compounds **1d**–**4d** are fairly different from those for the other derivatives.

Based on the fundamental aspect for the mesomorphism of the compounds, the effect of the nitro group on the mesomorphism is arranged in Table VIII.

The change in the smectic polymorphism in Tables VII and VIII is summarized as:

1) Hydrogen compounds **1d**–**4d** are the fundamental materials of the present compounds. Phenyl 4-benzoyloxybenzoate, the core of compounds **1**, intrinsically favors the layer arrangement, displaying the S_{A1} phase with high R value. Diphenyl

TABLE VII

The substituent effect on the mesomorphism

Compound	Substituent			
	$OCH_3(e)$	H(*d*)	Cl(*f*)	$COCH_3(g)$
1	S_{A1}-*N*-*I* 0.79	S_{A1}-*N*-*I* 0.95	S_{A1}-*N*-*I* 0.98	S_{A1}-*N*-*I* 0.97
2	*N*-*I* —	*N*-*I* [0.78]	S_{A1}-*N*-*I* 0.94	S_{A1}-*N*-*I* 0.96
3	*N*-*I* —	*N*-*I* [0.82]	*N*-*I* —	*N*-*I* —
4	[S_{A1}]-*N*-*I* [0.81]	[S_{A1}]-*N*-*I* [0.98]	S_{A1}-*I* 1.0	S_{A1}-*N*-*I* 1.0

Brackets indicate the virtual formation. The low column indicates the ratio of the S_{A1}-*N* transition temperature (T/°C) to the *N*-*I* one.[19]

TABLE VIII

The effect of nitro group on the mesomorphism

Compound	Position of nitro group		
	para(**a**)	meta(**b**)	orth(**c**)
1	S_{Ad}-*N*-*I*	S_{A1}-*N*-*I*	*N*-*I*
2[*1]	S_{A2}-S_{A1}-S_{Ad}-*N*-*I*	S_{A2}-*N*-*I*	S_{A2}-*N*-*I*
3	S_{A1}-S_{Ad}-*N*-*I*	S_{A1}-*N*-*I*	*N*-*I*
4[*2]	[S_{A2}]-S_{Ad}-*N*-*I*	S_{A2}-*N*-*I*	S_{A2}-*N*-*I*

Brackets indicate the virtual formation.

[*1] Although the nonyloxy homolog of **2a** is known to show a very complex mesomorphism involving tilted phases,[13] these are neglected in the table.

[*2] The molecular arrangement for compounds **4b** and **4c** was assumed from the thermal properties in the phase diagrams and the X-ray experiments.[16]

terephthalate, the core of compound 4, also has high *R* value, though the formation of the S_{A1} phase is virtual because of high melting point. On the other hand, phenyl 4-benzoyloxybenzoate and 4-benzoyloxyphenyl benzoate, the cores of compounds **2** and **3**, form the layer arrangement with difficulty, while the former has the same core as compound **1d**. The *R* value involving the virtual transition decreases in the order of **4d** > **1d** > **3d** > **2d**. These facts indicate that the electric and structural properties of the cores determine the smectic nature. The *MO* calculation in Table VI shows that the charge of the ester group at position *Y* decreases in the order:

$$\text{For derivatives } d\ (R = H)\ \mathbf{3d} > \mathbf{1d} > \mathbf{2d} > \mathbf{4d} \qquad (1)$$

As is evident from the comparison of **1d** and **2d**, in addition, the octyloxy group of compound **1d** plays very important role in displaying the S_{A1} phase. The difference in smectic properties between **1d**–**2d** has been discussed in terms of the structural difference.[21]

2) An introduction of the methoxy group having an electron-donating nature at the terminal position, is expected to increase the polarizable anisotropy of the molecules and increase the *N*-*I* transition temperature.[22] In fact, the methoxy group

increases the N-I transition temperature by 82°C on average. However, the S_A-N transition temperatures increase a little. As a result, the methoxy group fairly decreases the R values in compounds **1** and **4**. Compounds **2e** and **3e** are nematogenic, and the virtial S_A-N transition temperatures were too low to evaluate. These results indicate that the methoxy group makes difficulty of the layer arrangement of the molecules. As shown in Table VI, the methoxy group increases the charge of the ester group at position Y, and the charge decreases in the order of:

$$\text{For derivatives } e\ (OCH_3)\ \mathbf{3e} > \mathbf{2e} > \mathbf{1e} > \mathbf{4e} \qquad (2)$$

Interestingly, the R value decreases in the inverse order, that is, **4e** > **1e** > **2e**, **3e**.

3) Chlorine and the acetyl group at the terminal position also increase the polarizable anisotropy, enhancing the N-I transition temperatures, 75 and 93°C on average, respectively. These substituents also enhance the S_A-N transition temperatures in compounds **1f** and **4f**. The chlorine atom induces the S_A phase in **2f**. The R values for compounds **1f**, **2f**, and **4f** are higher than those for the corresponding hydrogen (*d*) and methoxy (*e*) compounds. The acetyl compounds **1g**, **2g**, and **4g** have high S_A-N transition temperatures, and R values are comparable with those for compounds **1f**–**4f**. Interestingly, compound **3g** still shows no S_A phase. The layer spacings in the S_A phase for compounds **1g**, **2g**, and **4g** agree with the fully extended molecular length, indicating that the molecules form the monolayer arrangement.

These substituents have an electron-withdrawing nature, so that these would decrease the charge of the ester group at position Y. A noteworthy fact is that the acetyl group itself has a dipole moment of 2.9 D (for acetophenone) which is larger than the chlorine atom of 1.6 D (for chlorobenzene).[23] Interestingly, the R value of compound **1g** is smaller than that of **1f**, while the R value of **2g** is larger than that of **2f**.

4) When the nitro group is introduced at the terminal position, the smectic properties show remarkable change. Interestingly, the S_{A1} phase is formed by compounds **2a** and **3a**, where the R values for the octyloxy homolog of the former and the butoxy one of the latter are 0.80 and 0.81, respectively. On the other hand, the S_{A1} phase formed by compounds **1d**–**1g** and **4d**–**4g** disappears in **1a** and **4a**. The charge of the ester group at position Y decreases in the order:

$$\text{For derivative } a\ (NO_2)\ \mathbf{1a} > \mathbf{4a} > \mathbf{3a} > \mathbf{2a} \qquad (3)$$

There is no doubt from the comparison of Equations (1)–(3) that the formation of the S_{A1} phase is closely related to the charge of the ester group at position Y, that is, the increase in the charge of the ester group is unfavorable for the formation of the S_{A1} phase. All the nitro derivatives show the S_{Ad} phase, while the beginning of the formation is different from system to system. Sometimes, the formation of the S_{Ad} phase is discussed in terms of the antiparallel correlation of dipoles arising from the terminal polar group and the linkages.[1] However, the present results suggest that such antiparallel correlation of dipoles is not indispensable for the formation. As discussed in a previous paper, the polar interactions around the terminal polar group (repulsive and/or attractive) and the molecular structure in connection with the closed packing of molecules within the smectic layer are assumed to be important factors for the formation.[9]

The S_{A2} phase is formed by the nitro derivatives, **2a** and probably **4a** and is not formed by **1a** and **3a**, and hydrogen, chlorine, methoxy, and acetyl derivatives. As mentioned in an earlier paper,[24] in order to form the S_{A2} phase the polar group having larger dipole moment than 3 D (the nitro group = 4.2 D) is indispensable. In addition, the linearity of the molecular structure is also important in connection with the packing effect in the S_{A2} phase.

As mentioned in an earlier paper,[21] the molecular structures of compound **1d**–**4d** are strongly dependent on the relative orientation of the terminal octyloxy group with respect to the ester ones, because the bond angle of the ester groups (—CO—O— = 110°) is less than that of the aromatic ring (—C═C— = 120°), and compounds **2d** and **4d** are superior in linearity to **1d** and **3d**.

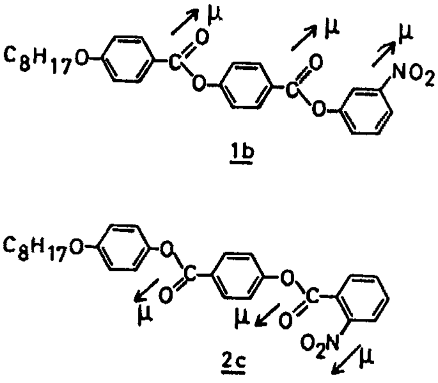
5) The molecular arrangements in the S_A phase for the *m*- and *o*-nitro derivatives are fundamentally same as those for the *p*-nitro one, though the S_{Ad} phase is not formed in every system. All the *m*-nitro derivatives show the S_A phase. The R values (ca. 0.96 on average for the octyloxy homologs, except for compound **3b**) are higher than those of **2a** and **3a**, and are almost independent of the orientation of the ester linkages, indicating that the nitro group at *m*-position weakens the local interactions around the linkages, and facilitates the layer arrangement of the molecules. For *o*-nitro derivatives compounds **2c** and **4c** show the S_{A2} phase, and **1c** and **3c** are nematogenic. There is no doubt that the smectic properties have the same trend as those of *m*- and *p*-nitro derivatives. These facts indicate that the electric and structural characterics of the core determine the molecular arrangement in the S_A phase.

6) The dipole moments of the entirety of the molecules have no correlation with smectic properties such as S_A-N transition temperature and molecular arrangement. For example, the dipole moments of compounds **3e** and **4e** should be very small in practice, while the S_A-N transition temperatures are different.

7) In polar liquid crystals, the nematic and smectic properties are frequently discussed in terms of the antiparallel correlation model.[1,2]

As we can see from Figure 6, the temperature dependency of the dielectric constants in the N phase for compounds **1b** and **2c** shows an abnormal behavior. The orientation of the dipoles arising from the nitro and ester groups of these two is shown in Figure 7.

As we can assume from the Figure, the longitudinal components of all the dipoles arising from the ester and nitro groups orient parallel. The remarkable increase in the dielectric constants suggests that the formation of the nematic arrangement reduces the dipole correlation, that is, the antiparallel correlation of the dipoles is less favorable in the N phase than in the isotropic solution. Inspite of the abnormal behavior of the dielectric properties for compounds **1b** and **2c**, in addition, the S_A-N transition temperatures and the R values are quite similar to those of the other derivatives, indicating that there has no direct correlation between the thermal and dielectric properties.



1b

2c

FIGURE 7 Orientation of dipoles arising from the functional groups for compounds **1b** and **2c**. Arrows indicate dipole moments (μ) arising from the ester and nitro groups.

8) Figure 5 shows the binary phase diagrams, where an induced S_A phase is observed in every system. Such phenomena are sometimes interpreted in terms of the formation of an electron donor-acceptor complex (EDA).[1] The binary mixture of compound **3e** and HBBCA may correspond to this case. However, it is impossible to expect such interaction in the other mixtures, while the phase diagrams show a similar feature. These facts indicate that such interaction is not indispensable for the induction of the S_A phase. As we can see from Figure 5, the substituent effect is recognized in the range of the induced S_A phase, and the range becomes narrow in the order of **3g** > **3f** > **3d** > **3e**. Of course, the binary mixture of HBBCA and **3a** does not show the induced S_A phase. Therefore, the most important thing for the phenomena is not why the induction of the S_A phase occurs in the binary mixtures, but why compound **3**, the methoxy and nitro derivatives of **1–4** show the S_A phase with difficulty in the pure state.

CONCLUSION

In the present systems, the polar interactions around the functional groups and the terminal substituents and the molecular structure involving the long alkoxy group are very important factors in determining the smectic properties. The increase in the polarity around the linkages decreases the R value. The increase in the polarity at the terminal position also decreases the R value, and results in the alternation of molecular arrangement. The polar interactions are also very important in determining the smectic properties in binary mixtures, and sometimes causes of the abnormal behavior of the S_A-N transition temperature.

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