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The substituent effect on mesomorphic properties of 4-octyloxyphenyl 4-(4-*R*-3-nitrobenzoyloxy)benzoates and 4-(4-octyloxybenzoyloxy)phenyl 4-*R*-3-nitrobenzoates

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The substituent effect on mesomorphic properties of 4-octyloxyphenyl 4-(4-*R*-3-nitrobenzoyloxy)benzoates and 4-(4-octyloxybenzoyloxy)phenyl 4-*R*-3-nitrobenzoates

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The thermal properties of 4-octyloxyphenyl 4-(4-*R*-3-nitrobenzoyloxy) benzoates (**1**) and 4-(4-octyloxybenzoyloxy)phenyl 4-*R*-3-nitrobenzoates (**2**) have been examined, where R = hydrogen, halogens, alkyl and alkoxy groups. The derivatives of compound **1** incorporating hydrogen, halogens, methoxy and nitro groups show a smectic A phase having a bilayer arrangement, and the others with a long alkoxy group show the S_A phase with the monolayer arrangement. The derivatives of compound **2** incorporating halogens, and the nitro group show the S_A phase with the monolayer arrangement. The alkoxy derivatives show a smectic C phase as well as the nematic phase. The nitro group at the lateral position tends to increase the ratio of the S_A–N transition temperature to the N–I. The effect of the nitro group on the smectic properties has been discussed in terms of the structural and electrostatic nature of the nitro group.

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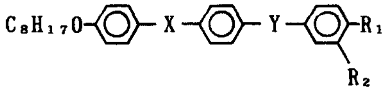
1. Introduction

The effect of a lateral substituent on mesomorphic properties has been examined by several authors. Generally, a lateral substituent is known to be unfavourable for the mesomorphic phenomena [1, 2] since it decreases the polarizable anisotropy as well as the geometrical anisotropy of molecules. Gray *et al.*, for example, found that the nematic–isotropic (N–I) transition temperature has a good correlation with the van der Waal's radii for the substituents attached at the lateral position of the molecules [3]. On the other hand, the effect of the lateral substituent on the thermal properties of S_A and S_C is fairly complex. Generally, the lateral substituents also decrease the transition temperatures, but these sometimes increase remarkably the smectic properties due to polar interactions [4–6]. The nitro and cyano groups at the lateral position are of special interest for mesomorphic phenomena.

In this paper, we describe the effect of a terminal substituent on the thermal properties of N, S_A and S_C phases for 4-octyloxyphenyl 4-(3-nitro-4-*R*-benzoyloxy) benzoates (**1**) and 4-(4-octyloxyphenoxycarbonyl)phenyl 3-nitro-4-*R*-benzoates (**2**), shown below.



The results will be discussed in terms of the change in the electrostatic nature of the cores and the polar interactions around the nitro group, and clarify the effect of the nitro group on the smectic properties of the molecules.

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Compound	X	Y	R_2
1	OOC	OOC	$-NO_2$
2	COO	OOC	$-NO_2$
3	OOC	OOC	-H
4	COO	OOC	-H
5	COO	COO	-H

$R_1 = H, F, Cl, CH_3, NO_2, OC_nH_{2n+1}$ ($n = 1$–9).

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2. Experimental

Materials: 3-Nitro-4-*R*-benzoic acids ($R = F$, Cl, CH_3, OCH_3, NO_2) were commercially available, and 4-alkoxy-3-nitrobenzoic acids were obtained by the alkylation of methyl 4-hydroxy-3-nitrobenzoate with corresponding *n*-alkylbromides in 3-pentanone, followed by hydrolysis with alcoholic sodium hydroxide. Compound **1** was obtained by the reaction of 4-(4-octyloxyphenoxycarbonyl)phenol and 3-nitro-4-*R*-benzoyl chlorides in dry pyridine. Compound **2** was obtained by the reaction of 4-(4-octyloxybenzoyloxy)phenol with 3-nitro-4-*R*-benzoyl chlorides in dry pyridine. The purification of the products was achieved by column chromatography on silica gel. The materials were identified by elementary analysis and N.M.R. Compounds **3** and **4** were prepared according to the method of Takenaka *et al.* [7]. 4-*N*-(4-Cyanobenzylidene)-4-octyloxyaniline (CBOOA) was purchased from Tokyo Kasei Co., and was purified by recrystallization from absolute ethanol. 4-(4-Octyloxyphenoxycarbonyl)phenyl 5-cyanofuran-2-carboxylate (OPPNF) was prepared by the method of Takenaka *et al.* [8].

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 Daini-Seikosha SSC-5200 differential scanning calorimeter (DSC), where indium (99·9 per cent) was used as a calibration standard (mp = 156·6°C, $\Delta H = 6{\cdot}8$ mcal/mg). The DSC thermogram was operated by heating and cooling rates of 5°C/min.

3. Results

Transition temperatures for compounds **1** and **2** are summarized in tables 1 and 2. For the comparative study, the transition temperatures of compounds **3** and **4** are also indicated. The transition temperatures for the alkoxy derivatives of compounds **1** and **2** are plotted against the carbon number (n) in figure 1. The thermal properties of the smectic phases were examined by binary phase diagrams, and the results are shown in figures 2–4.

The S_A phase of the hydrogen derivative **1a** is identified to a bilayer arrangement (S_{A_2}) by the X-ray diffraction study [9]. As we can see from figures 2 (*a*), (*b*) the S_{A_2} phase is immiscible with the partially bilary (S_{Ad}) phase of CBOOA and OPPNF, and is miscible with the S_{A_2} phase of OPPNF. In order to know the virtual S_A–N transition temperature for derivative **1f**, the binary phase diagrams for the mixtures of **1f** and **1a** and **1f** and **1g** were examined, as shown in figure 2 (*c*). In figure 2 (*c*), the solid phase for the mixture of derivatives **1f** and **1a** shows an eutectic feature, while that for **1f** and **1g** shows a mixed crystal type feature. These facts indicate that from the structural point of view derivative **1f** is similar to **1g** rather than **1a**. On the other hand, the S_A–N transition for the mixture of derivatives **1f** and **1a** shows a linear correlation against the molar

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Table 1. Transition temperatures (T/°C) for compounds **1** and **3**.

Compound		**1**											**3**						
	R	C		S_{C_1}		S_{A_2}		S_{A_1}		N		I	S_{C_1}		S_{A_1}		N		I
a	H	●	106	—		●	112	—		●	131	●	—		—		●	135	●
b	CH_3	●	114	—		●	122	—		●	145	●	—		—		●	189	●
c	F	●	115	—		●	128	—		●	134	●	—		●	122	●	185	●
d	Cl	●	100	—		●	141	—		●	*1	●	—		●	185	●	214	●
e	NO_2	●	101	—		●	141	—		●		●	—		●	129*2	●	228	●
f	OCH_3	●	141	—		●	[117]	—		●	166	●	—		—		●	214	●
g	OC_2H_5	●	122	—		—		●	154	●	177	●	—		—		●	213	●
h	OC_3H_7	●	96	—		—		●	160	●	173	●	—		—		●	209	●
i	OC_4H_9	●	85	●	(*3)	—		●	173	●	179	●	●	65	—		●	207	●
j	OC_5H_{11}	●	87	●	(56)	—		●	179	●		●	●	101	—		●	201	●
k	OC_6H_{13}	●	82	●	(69)	—		●	181	●		●	●	132	●	144	●	198	●
l	OC_7H_{15}	●	75	●	113	—		●	180	●		●	●	142	●	155	●	193	●
m	OC_8H_{17}	●	76	●	128	—		●	179	●		●	●	142	●	163	●	188	●
n	OC_9H_{19}	●	71	●	142	—		●	176	●		●							

C, S_A, N, and I indicate crystal, smectic A, nematic phases, and isotropic solution, respectively. Parentheses indicate a monotropic transition. *1, a nematic phase is observed before the transition from the S_A to I phase. *2, S_{A_2} phase [11]. *3, an S_C phase could be observed before recrystallization.

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Table 2. Transition temperatures (T/°C) for compounds **2** and **4**.

Compound		**2**									**4**						
	R	C		S_{C_1}		S_{A_1}		N		I	S_{C_1}		S_{A_1}		N		I
a	H	●	113	—		●	(82)	●	134	●	—		●	[60]	●	141	●
b	CH_3^{*1}	●	133	—		●	(90)	●	147	●	—		—		●	199	●
c	F	●	112	—		●	142	—		●	—		—		●	193	●
d	Cl	●	130	—		●	155	—		●	—		—		●	217	●
e	NO_2	●	101	—		●	156	—		●	—		●	239*2	●	246	●
f	OCH_3	●	118	—		●	[75]	●	171	●	—		—		●	224	●
g	OC_2H_5	●	116	—		—		●	178	●							
h	OC_3H_7	●	101	●	106	—		●	175	●							
i	OC_4H_9		76	●	114	—		●	172	●							
j	OC_5H_{11}	●	63	●	123	—		●	168	●	—		—		●	205	●
k	OC_6H_{13}	●	87	●	139	—		●	169	●	●	109	—		●	200	●
l	OC_7H_{15}	●	55	●	144	—		●	165	●	●	119	—		●	197	●
m	OC_8H_{17}	●	64	●	150	—		●	164	●	●	126	—		●	194	●
n	OC_9H_{19}	●	59	●	152	—		●	161	●	●						

Parentheses indicate a monotropic transition. Brackets indicate a virtual transition extrapolated from the binary phase diagram (see text). *1, a S(tilted)–S_A transition occurs at 77°C. *2, S_{A_d} phase.

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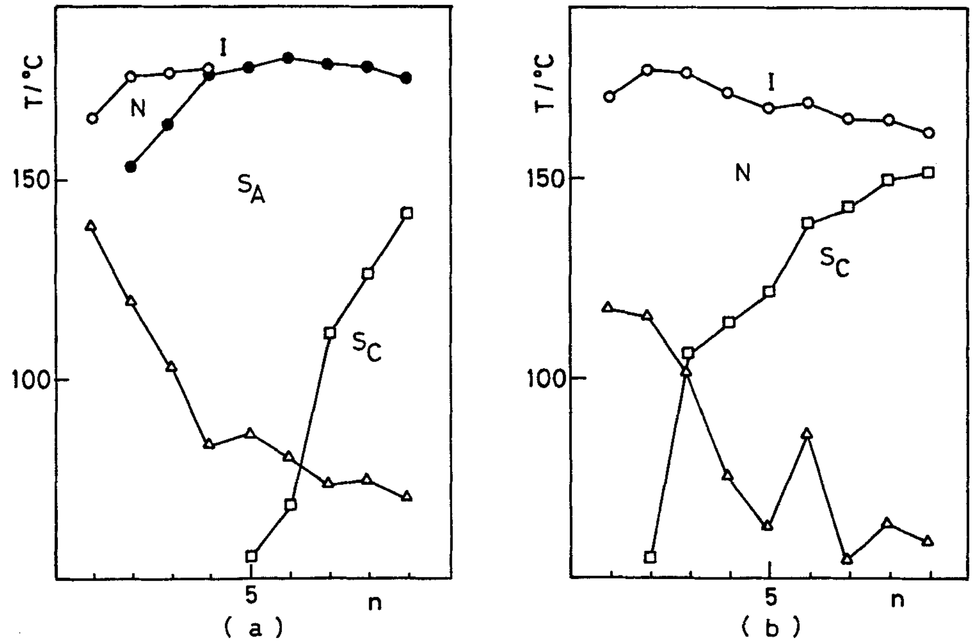

Figure 1. Plots of the transition temperatures against the carbon number (*n*) for compounds: (*a*) **1**, (*b*) **2**. △, melting points.

concentration and intersects the left side axis at 117°C, while that for the mixture of **1f** and **1g** shows non-linear behaviour, and the extrapolated transition temperature for **1f** is far lower than 117°C. These facts indicate that the S_A phase for derivative **1f** has the same molecular arrangement as that for **1a**, but is different from that for **1g**. That is, the smectic phase for derivatives **1f** and **1a** is a S_{A_2} phase, and that for **1g** is a S_{A_1} phase.

The S_A phase of the hydrogen derivative **2a** is assigned to the monolayer type (S_{A_1}) from the X-ray diffraction study [9]. As shown in figure 3 (*a*), however, the S_A phase in the binary mixture of CBOOA and derivative **2a** is miscible with the S_{A_d} phase of the reference compound, where the S_{A_d} phase has a narrow part at *c*. 75 mol% of the reference compound, and the mixtures at both sides show the reentrant mesomorphism of a N_{re}–S_A–N–I type. These facts indicate that both S_A phases at the boundary (75 mol% of CBOOA) are S_{A_d} phases. In fact, the S_A phase of derivative **2a** is miscible with the S_{A_d} phase of OPPNF in figure 3 (*b*). Although the S_A phase of derivative **2a** has the S_{A_d} nature in point of the thermal properties, it is assigned to the S_{A_1} phase according to the X-ray results. Figures 3 (*c*), (*d*) show the phase diagrams for the mixtures of OPPNF and derivatives **1d** and **2d**, respectively. The S_{A_2}–S_{A_d} (N) transition in figure 3 (*c*) shows an interesting feature, where the mixture of 75 mol% of OPPNF shows the mesomorphism of a S_{A_2}–N_{re}–S_{A_d}–N–I type. Figure 4 (*a*) shows the phase diagram for the mixture of derivatives **1c** and **2c**. At 62 mol% of derivative **1c** in the figure, both S_A–N and N–I transitions show minima. Probably, the $S_{A_d}S_{A_2}$ transition occurs around the region, for example, of the dotted line with the arrow. Figures 4 (*b*), (*c*) show the phase diagrams for the mixtures of derivatives **1c** and **2i** and **2c** and **2n**. In the diagrams the S_A–N transitions show an upward convexity, and the S_C–S_A transitions show a rapid reduction at corresponding concentrations.

Figure 4 (*d*) shows the phase diagram for the mixture of derivatives **1j** and **2j**, where both S_C phases of the components are miscible with each other, though the S_C–S_A (N) transition shows a remarkable non-linear feature against the concentration.

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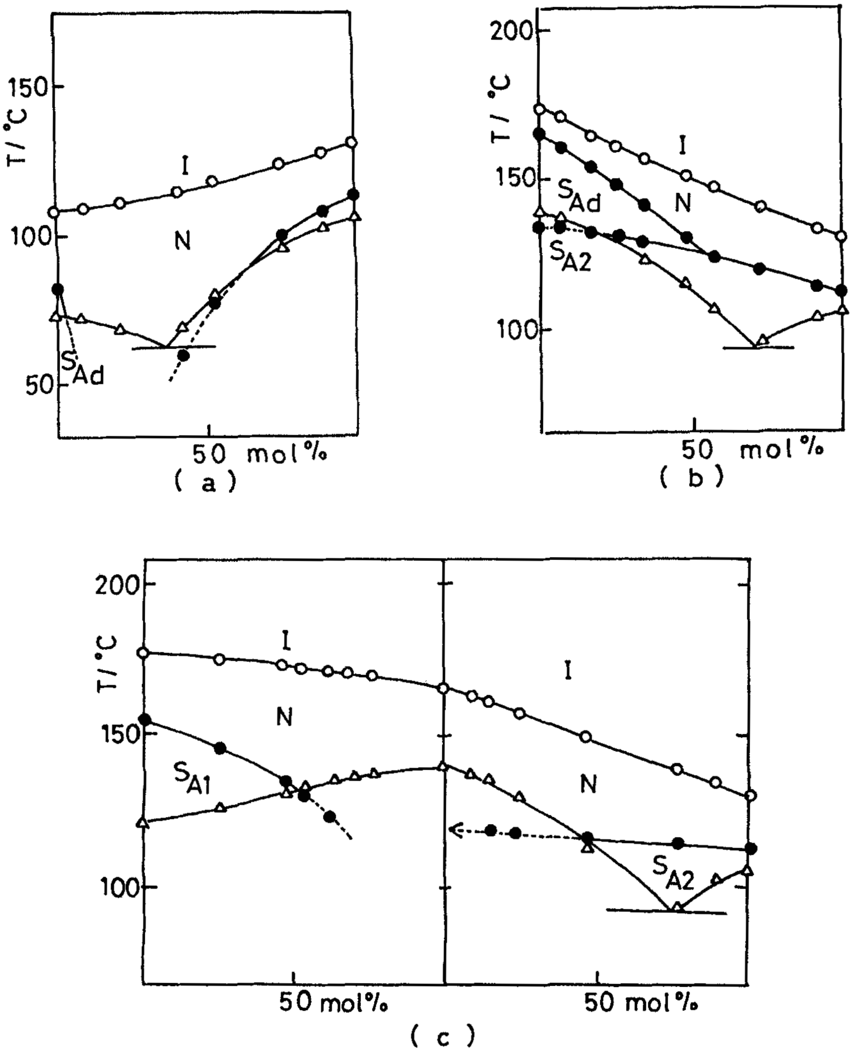

Figure 2. Binary phase diagrams for the mixtures of: (*a*) CBOOA (left) and **1a** (right), (*b*) OPPNF (left) and **1a** (right), (*c*) **1g** (left), **1f** (centre) and **1a** (right). △, melting points. Dashed lines indicate monotropic transitions.

For comparative studies the $\mathrm{S_A}$–N, $\mathrm{S_C}$–$\mathrm{S_A}$ and $\mathrm{S_C}$–N transition temperatures for compounds **1** and **2** are plotted against $\mathrm{S_A}$–N transitions for compound **5** [7] in figure 5.

4. Discussion

The substituent effect on the mesomorphic properties has been frequently discussed in terms of the effectiveness for mesophase transition temperatures such as N–I and $\mathrm{S_A}$–N ($T_{\mathrm{S_A-N}}$ and $T_{\mathrm{N-I}}$ respectively) transitions [2]. The substituent effect on the mesomorphic properties for compounds **3**, **4** and **5** has been investigated, and is discussed in connection with the charge on the ester groups and the substituents [10]. In another paper, we also examined the effect of a nitro group on the mesomorphic properties for compounds **3** and **4** [9], and a part of the results are shown in tables 1 and

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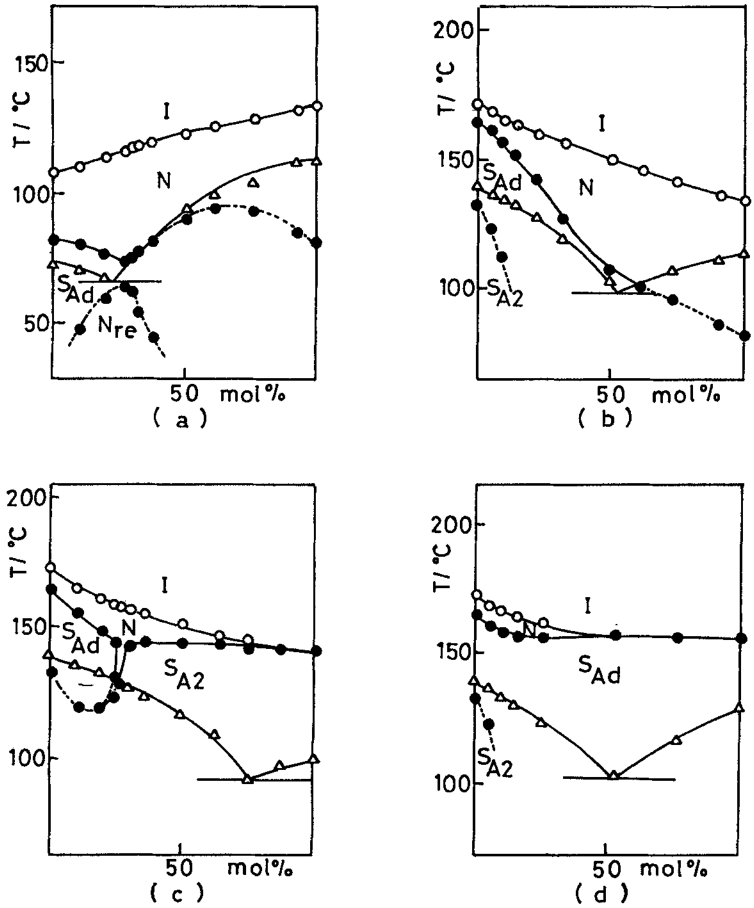

Figure 3. Binary phase diagrams for the mixtures of: (*a*) CBOOA (left) and **2a** (right), (*b*) OPPNF (left) and **2a** (right), (*c*) OPPNF (left) and **1d** (right), (*d*) OPPNF (left) and **2d** (right). △, melting points. Dashed lines indicate monotropic transitions.

2. There is no doubt that the mesomorphic properties are strongly influenced by the nitro group at position 3.

For compound **1**, the nitro group at position 3 apparently increases T_{S_A-N}, but decreases T_{S_C-N} and $T_{S_C-S_A}$. This trend is apparent in the transition temperatures for the alkoxy derivatives, **1g**–**1n**. In order to evaluate the effect of the lateral nitro group on the mesomorphic properties, the transition temperatures for compounds **1** and **2** are plotted against T_{S_A-N} for compound **5** in figure 5.

Although the orientation of the ester groups of compound **1** is opposite to that of **5**, we decided to use **5** as a reference since most of the derivatives form a S_A phase.

If the structural and electrostatic effects of the lateral nitro group on the mesomorphic properties are constant through the derivatives, we can expect that the plots for both compounds should have some good correlations. T_{S_A-N}s for derivatives **1g**–**1n** show a good correlation (line A in figure 5), and the slope appears to be a close one, though the line shows an upward shift (*c*. 30°C). As mentioned in the result section,

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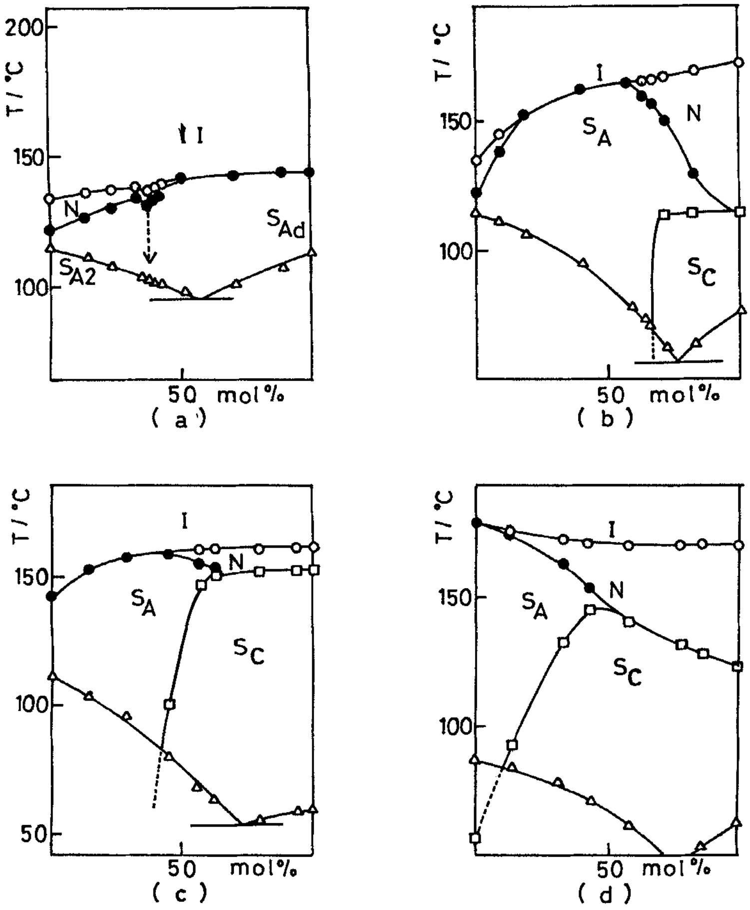

Figure 4. Binary phase diagrams for the mixtures of: (*a*) **1c** (left) and **2c** (right), (*b*) **1c** (left) and **2i** (right), (*c*) **2c** (left) and **2n** (right), (*d*) **1j** (left) and **2j** (right). △, melting points. Dashed lines indicate monotropic transitions.

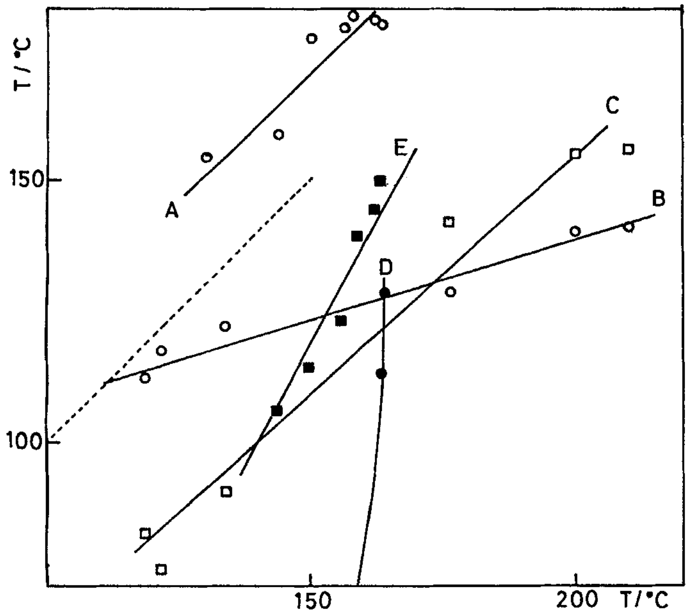

Figure 5. Plots of transition temperatures for compounds **1** and **2** (vertical axis) and **5** (horizontal

except for **1f**, the S_A phase for the alkoxy derivatives has a monolayer arrangement. These facts indicate that the nitro group at the lateral position uniformly enhances T_{S_A-N} of the monolayer S_A phase through the homologous series. As we can see from figure 5, the plots for derivatives **1a**–**1e** as well as **1f** are out of the line, and form another line. In an earlier paper [9] we clarified that derivative **1a** forms the S_{A_2} phase. Figure 3 (*c*) shows that derivatives **1d** and **1c** show the S_{A_2} phase, and figure 2 (*c*) suggests that **1f** also forms the S_{A_2} phase. These facts suggest that the plots belonging to line B correspond to the S_{A_2}–N transition. Interestingly, the slope of line B is considerably smaller than one. Furthermore, line B is far apart from A at around 120°C. The following can be assumed from these results. The first is that the substituent effect on the S_{A_2}–N transition temperature is less sensitive than that on the S_{A_1}–N transition. The second is that the thermal properties of both phases should be different since the transition temperatures are fairly different, so that both phases in binary mixtures should be immiscible, for example, figures 2 (*c*) and 4 (*a*).

4-(4-Octyloxybenzoyloxy)phenyl benzoate derivatives **4** scarcely show smectic phases. The nitro derivative **4e** shows the S_A phase having a partially bilayer arrangement [11] and the long alkoxy derivatives **4k**–**4m** show the S_C phase. In contrast, the corresponding nitro derivatives **2a**–**2e** form the S_A phase. As mentioned in the result section, the S_A phase of **2a** is assigned to the S_{A_1} phase, while the S_A phase is miscible with the S_{Ad} phase of CBOOA (figure 3 (*a*)). The S_A phases for derivatives **2c**–**2e** are miscible with that of **2a** so that these are assigned to the S_{A_1} phase. Interestingly, the T_{S_A-N}s and the reduced T_{S_A-N} for **2c**–**2e** are higher than those for derivatives **1c**–**1e**.

T_{S_A-N}s for compound **2** are plotted against those for compound **5** in figure 5. The plots for derivatives **2a**–**2e** are rather more dispersive than those for derivatives **1a**–**1e**, and the slope (line C) is apparently larger than that of line B and close slopes. A possible explanation for the difference is that $T_{S_{A_2}-N}$s for derivatives **1a**, **1b** and **1f** are enhanced by the nitro group, where polarity of the nitro group is increased by the electron-donating substituents such as methoxy and methyl groups. On the other hand, the nitro group of compound **1** decrease $T_{S_{A_1}-N}$.

$T_{S_C-S_A}$s for derivatives **1l** and **1m** and **2h**–**2m** are plotted against T_{S_A-N}s for the corresponding derivatives of compound **5** in figure 5. The slopes of lines D and E are apparently larger than one, indicating that the S_C phase is formed by a different mechanism from that of the S_A phase. Interestingly, line E for derivatives **2h**–**2m** intersects line B at *c*. 130°C near the plot for **2b**. In fact, derivative **2b** forms a tilted smectic phase at the cooling stage.

The smectic properties of compounds **1** and **2** are compared by binary phase diagrams. In figures 4 (*b*), (*c*), the mixtures show the enhancement of the $S_{A-N(I)}$ transition temperatures. Apparently, the enhancement is irrespective of the orientation of the ester group at position X and the nitro group at the meta position.

The S_C–S_A (N) transitions in these diagrams show a somewhat interesting trend. In figures 4 (*b*), (*c*), the S_C–S_A (N) transitions show a linear correlation against the molar concentration of each component near the right-side axes, but these show a rapid reduction at *c*. 70 mol % of **2i** and 60 mol % of **2n**, respectively. The rapid reduction may be concerned with the reduction of the tilt angle due to an increase in the concentration of **1c** or **2c**.

Although the S_C–S_A (N) transition for the mixture of derivatives **1j** and **2j** (figure 4 (*d*)) shows a non-ideal solution behaviour, we can assume that the molecular arrangements of both S_C phases are fundamentally the same, and both phases are miscible.

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5. Conclusion

The nitro group at position 3 enhances T_{S_A-N} for the alkoxy derivatives of compound **1**, and gives rise to the formation of the S_{A_2} phase for **1a–1e** and **1f**. However, the nitro group reduces the S_C–S_A (N) transition temperature. The nitro group at position 3 for compound **2** enhances $T_{S_A-N(I)}$ and T_{S_C-N}, but it is impossible to form the S_A phase in the alkoxy derivatives.

References

[1] Gray, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), p. 263 and references cited therein.

[2] Gray, G. W., 1962, *Molecular Structure and the Properties of Liquid Crystals*, edited by G. W. Gray (Academic Press).

[3] de Jew, W. H., and van der Veen, J., 1977, *Molec. Crystals liq. Crystals*, **40**, 1.

[4] Nguyen, Huu Hinh, Zann, A., and Dubois, J. C., 1979, *Molec. Crystals liq. Crystals*, **53**, 29.

[5] Schroeder, J. P., 1980, *Molec. Crystals liq. Crystals*, **61**, 229.

[6] Kelly, S. M., and Schad, Hp., 1984, *Molec. Crystals liq. Crystals*, **110**, 239.

[7] Takenaka, S., Sakurai, Y., Takeda, H., Ikemoto, T., Miyake, H., Kusabayashi, S., and Takagi, T., 1990, *Molec. Crystals liq. Crystals*, **178**, 102.

[8] Takenaka, S., Miyake, S., and Kusabayashi, S., 1984, *Molec. Crystals liq. Crystals*, **126**, 211, 1985, *Ibid.*, **131**, 257.

[9] Takenaka, S., Sakurai, Y., Takeda, S., Kusabayashi, S., Sugiura, H. Morita, H., Terauchi, H., and Nishihata, Y., 1989, *Molec. Crystals liq. Crystals*, **177**, 59.

[10] Sakurai, Y., Takenaka, S., Miyake, H., Morita, H., and Ikemoto, T., 1989, *J. chem. Soc. Perkin II*, p. 1199.

[11] Nguyen Huu Tinh, and Destrade, C., 1981, *Nouv. J. Chim.*, **5**, 337.

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