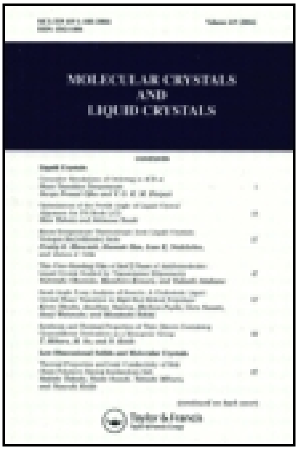

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The Substituent Effect on the Thermal Stability of the Smectic A Phase in para- Phenylene Systems Incorporating Ester Linkages

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The Substituent Effect on the Thermal Stability of the Smectic A Phase in para-Phenylene Systems Incorporating Ester Linkages

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Summary: The thermal properties of 4-Z-phenyl 4-(4-octyloxybenzoyloxy)benzoates (**1**), 4-octyloxyphenyl 4-(4-Z-benzoyloxy) benzoates (**2**), 4-(4-octyloxybenzoyloxy) phenyl 4-Z-benzoates (**3**) and 4-octyloxyphenyl 4-(4-Z-phenoxycarbonyl)benzoates (**4**) have been examined, where the substituents (Z) are halogens, alkoxy, alkyl, formyl, acetyl, cyano, and nitro groups, etc. The smectic properties are strongly dependent on the orientation of the ester linkages. Compounds **1** and **4** having alkoxy and alkyl groups tend to show smectic A and C phases. Compounds **2** and **3** are intrinsically poor in smectic properties, and only a smectic C phase is formed by the long-alkoxy and alkyl derivatives. Throughout the compounds, the thermal stability of the smectic A phase is strongly dependent on the electrostatic nature of the substituents; that is, both electron-donating substituents such as the methoxy and methyl groups and electron-withdrawing ones such as the cyano and nitro groups, steeply lower the smectic A thermal stability, and the halogens, acetyl and formyl groups enhance it. The substituent effect on the smectic A thermal stability is correlated with the charges around the functional groups calculated by the MNDO method. The ratios of the smectic A-nematic transition temperature to the nematic-isotropic one show an interesting correlation with Hammett's constants, σ_p.

INTRODUCTION

Generally, the nematic properties of molecules have been discussed in terms of geometrical and polarizable anisotropies.[1] The smectic properties, on the other hand, have been frequently discussed in terms of local lateral interactions, where the dipole-dipole and dipole-induced dipole interactions play an important role in promoting smectic thermal stabilities.[1] In practice, however, the thermal stabilities of the smectic A and C(S_A and S_C, respectively) phases are not easy to correlate to the electrostatic nature of molecules. A typical example is that both electron-withdrawing substituents such as the nitro and cyano groups, and electron-donating ones such as the methyl and methoxy groups enhance the S_A thermal stability,

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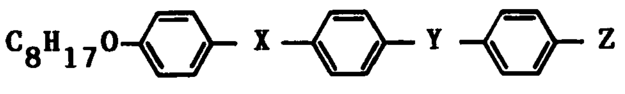
while the two types of substituents have an opposite electrostatic nature. The substituent effect of these two kinds on chemical reactions, of course, gives opposite results,[2] and some kinetic parameters have a linear correlation with the substituent parameters, such as Hammett's constant. If the electrostatic interactions around the cores of molecules play some important roles in promoting the S_A thermal stability, the S_A–N transition temperature is expected to have some correlations with electrostatic circumstances around the core, and also with the substituent parameters, such as Hammett's constant, σ_p.[2]

In this paper, we try to reexamine the substituent effect on the thermal stabilities of S_A and S_C phases. For this purpose, we prepared four types of compounds, as shown below.



Compounds	X	Y
1	—COO—	—COO—
2	—OOC—	—OOC—
3	—COO—	—OOC—
4	—OOC—	—COO—

$Z = —OC_nH_{2n+1}, —C_nH_{2n+1}, —F, —Cl, —Br, —CF_3,$

$—CHO, —COCH_3, —CN, —NO_2$

As mentioned in a previous paper,[3] compound **1** intrinsically has a bent geometry and has a rich smectic nature due to the packing effect of the bent molecule. Compounds **2** and **3** have a poor smectic nature due to electrostatic interactions around the ester groups, and show only a smectic C phase when the alkoxy and alkyl groups are sufficiently long. Compound **4** has a linear geometry and is rich in smectic properties.

In this work, we want to correlate the smectic properties with the change in the electrostatic circumstances around the ester group at position Y due to the electrostatic interactions between the ester group and the substituents, and extend our new empirical model for the formation of the S_A and S_C phases.

EXPERIMENTAL

Materials

The preparation of the materials has been reported in a previous paper.[3] The identification of the materials was carried out by elementary analysis and thin layer chromatography on silica-gel.

Method

Transition temperatures were determined by using a Nikon Model POH polarizing microscope fitted with a Mettler FP 52 heating stage. The apparatus was operated with a heating rate of 5°C/min. Transition enthalpies were measured with a Daini-Seikosha SSC-560 differential scanning calorimeter, and 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).

RESULTS

The transition temperatures and latent heats for the present compounds are summarized in Tables I–IV. Thereby, the ratios of the smectic A-nematic transition temperature (T_{S_A-N}) to the nematic-isotropic one (T_{N-I}) are also indicated. Some of materials in the tables have already been prepared.[4]

The alkoxy and alkyl derivatives of compound **1** show N and S_A phases, and the S_A–N transition temperatures gradually increase on ascending the series. The S_C phase commences from the propoxy and propyl derivatives, and the S_C–S_A transition temperatures show maxima at the hexyloxy and hexyl homologs.[9] The halogenated, acetyl, cyano, and nitro derivatives also show the S_A phase, where the S_A–N transition temperatures are higher than those for the alkoxy and alkyl derivatives. However, these derivatives do not show the S_C phase. In order to estimate the S_C nature of the halogenated derivatives, some binary phase diagrams were examined, and the results are shown in Figure 1.

Figure 1a shows the binary phase diagram for the mixture of the octyloxy and fluoro derivatives of **1**. In the diagram, both S_A phases are miscible, though the

TABLE I

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

Substituent	C		S_C		S_A		N		I	$\Delta H_{S_C-S_A}$	ΔH_{S_A-N}	ΔH_{N-I}	T_{S_A-N}/T_{N-I}
H	.	118	–		.	119	.	140	.	–	1.6	0.7	0.95
OCH_3	.	107	–		.	122	.	226	.	–	0	0.6	0.79
OC_2H_5	.	110	–		.	130	.	213	.	–	0.2	1.3	0.83
OC_3H_7	.	100	.	106	.	144	.	206	.	0	0.2	1.3	0.87
OC_8H_{17}	.	84	.	141	.	163	.	188	.	0	1.5	1.8	0.95
CH_3	.	109	–		.	134	.	195	.	–	0.4	1.3	0.87
C_2H_5	.	97	–		.	138	.	185	.	–	0.5	1.2	0.89
C_5H_{11}	.	85	.	99	.	149	.	184	.	0	0.3	1.1	0.93
C_8H_{17}	.	84	.	88	.	160	.	174	.	0	0.8	1.4	0.97
F	.	120	–		.	176	.	185	.	–	2.1	1.0	0.98
Cl	.	123	–		.	200	.	209	.	–	1.8	0.8	0.98
Br	.	126	–		.	206	.	214	.	–	1.7	0.6	0.98
$COCH_3$	.	131	–		.	210	.	227	.	–	1.3	0.7	0.97
NO_2	.	114	–		.	210	.	224	.	–	0.4	0.7	0.97
CN[a]	.	116	–		–		.	229	.		–		

[a] Reference 5.

TABLE II

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

Substituent	C		S_C		S_A		N		I	$\Delta H_{S_C-S_A}$ or $-N$	ΔH_{S_A-N} or $-I$	ΔH_{N-I}	T_{S_A-N}/T_{N-I}
H[a]	.	118	–		[.	45]	.	135	.	–	–	0.7	0.78
OCH_3	.	101	–		–		.	214	.	–	–	0.8	<0.74
OC_5H_{11}	.	97	.	101	–		.	201	.	–	–	1.3	–
OC_6H_{13}	.	96	.	132	.	144	.	198	.	0	0	1.5	0.98
OC_8H_{17}	.	84	.	141	.	163	.	188	.	0	1.5	1.8	0.95
CH_3	.	112	–		–	(>20)	.	189	.	–	–	0.7	<0.63
C_6H_{13}	.	89	.	95	–		.	180	.	0	–	1.4	–
C_8H_{17}	.	93	.	126	–		.	175	.	0.3	–	1.6	–
F	.	114	–		.	122	.	185	.	–	0	0.8	0.86
Cl	.	119	–		.	185	.	214	.	–	0.3	0.7	0.94
Br	.	128	–		.	192	.	222	.	–	0.3	0.7	0.94
CHO[b]	.	126	–		.	167	.	226	.	–	0	0.4	0.88
$COCH_3$	.	147	–		.	211	.	231	.	–	0.3	0.9	0.90
CF_3	.	128	–		.	210	–		.	–	3.0	–	1.0
NO_2[c]	.	101	.	109	.	129	.	228	.	–	0.1	0.7	0.80
CN[d]	.		–	180	.	200	.	240	.				0.92

[a]The value in brackets is a virtual transition temperature. [b]This compound underwent an S_A-S_A transition at 145°C. [c]The transition at 109°C is an S_A-S_A one. [d]The transition temperatures were evaluated from Figure 1 in Reference 6. Two smectic A phases were assigned to the partially bilayer (S_{Ad}) and bilayer (S_{A2}) ones.

S_A–N transition temperature shows a weak upward convexity. On the other hand, the S_C–S_A transition temperature shows a steep depression in the range between 90 and 84 mol% of the octyloxy derivative, giving rise to the reentrant phenomenon of the S_A–S_C–S_A–*N*–I type. This trend is also observed in the mixtures involving the other halogenated derivatives.

Compound **2** has a relatively poor smectic nature. The alkoxy and alkyl derivatives preferentially form the S_C phase, and the S_A phase is formed by the higher

TABLE III

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

Substituent	C		S_C		S_A		N		I	$\Delta H_{S_C-S_A}$	ΔH_{S_A-N}	ΔH_{N-I}	T_{S_A-N}/T_{N-I}
H[a]	.	117	–		[.	60]	.	141	.	–	–	1.0	0.82
OCH_3	.	124	–		–		.	224	.	–	–	1.2	<0.75
OC_8H_{17}	.	122	.	126	–		.	194	.	3.2	–	2.1	–
CH_3	.	102	–		–		.	199	.	–	–	1.1	<0.76
C_6H_{13}	.	103	.	106	–		.	184	.	2.0	–	1.6	–
C_8H_{17}	.	101	.	118	–		.	176	.	2.5	–	1.7	–
F	.	122	–		–		.	193	.	–	–	1.0	–
Cl	.	168	–		–		.	217	.	–	–	0.7	–
Br	.	175	–		–		.	217	.	–	–	0.8	–
CHO	.	143	–		–		.	232	.	–	–	0.7	–
$COCH_3$	.	162	–		–		.	236	.	–	–	0.8	–
NO_2	.	165	–		.	239	.	246	.	–	0.8	0.9	0.99
CN[b]	.	140	–		.	193	.	255	.				0.88

[a]The value in brackets is the virtual transition temperature. [b]Reference 7.

TABLE IV

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

Substituent	C	S_C	S_A	N	I	$\Delta H_{S_C-S_A}$	ΔH_{S_A-N}	ΔH_{N-I}	T_{S_A-N}/T_{N-I}
H^a	. 154	−	[. 130]	. (140)	.	−	−	−	0.98
OCH_3^{a}	. 167	−	[. 125]	. 218	.	−	−	0.6	0.81
OC_5H_{11}	. 142	. 176	. 183	. 200	.	0.2	0.4	1.6	0.96
OC_8H_{17}	. 144	. 180	. 183	. 191	.	0.5	0.6	2.1	0.98
CH_3^{a}	. 140	−	[. 131]	. 187	.	−	−	0.8	0.88
C_5H_{11}	. 133	. 150	. 160	. 182	.	0	0.5	1.5	0.96
C_8H_{17}	. 138	. 158	. 167	. 175	.	0.4	1.1	2.0	0.98
F	. 173	−	. 196	−	.	−	2.1	−	1.0
Cl	. 195	−	. 222	−	.	−	2.4	−	1.0
Br	. 206	−	. 228	−	.	−	3.7	−	1.0
$COCH_3$	. 204	−	. 235	. 235	.	−		2.7^b	1.0
NO_2	. 153	−	−	. 220	.	−	−	0.7	−
CN^c	. 148	−	. 158	. 233	.				0.85

[a]The values in brackets are the virtual transition temperatures. [b]The latent heats for the S_A–N and N–I transitions. [c]Reference 8.

members of the alkoxy derivatives, and the halogenated, acetyl, cyano, and nitro derivatives. The virtual S_A–N transition temperature for the unsubstituted derivative is ca. 45°C($T_{S_A-N}/T_{N-I} = 0.78$).[3] The virtual S_A–N transition temperatures for the methyl and methoxy derivatives were estimated from the binary phase diagrams shown in Figure 2.

As is evident from Figures 2a and 2b, the S_A–N transition temperatures steeply decrease with an increase in the concentration of the methoxy and methyl derivatives, so the extrapolation was difficult. However, there is no doubt that the S_A–N transition temperatures for these derivatives are far lower than that for the unsubstituted derivative.

The halogenated, acetyl, cyano, and nitro derivatives have a rich S_A nature, though the derivatives do not show any tilt phase. The S_C nature of these derivatives were examined by binary phase diagrams, and the example is shown in Figure 1b. In the figure, both S_A phases are miscible, though the S_A–N transition temperature shows a remarkable enhancement (ca. 50°C). The S_C–S_A transition temperature, on the other hand, shows a rapid reduction with an increase in the concentration of the fluoro derivative, indicating that the fluoro derivative has a very poor S_C nature. A similar phase diagram was observed in the other halogenated derivatives and in the acetyl one.

Compound **3** is also very poor in smectic properties. The virtual S_A–N transition temperature for the unsubstituted derivative is ca. 60°C($T_{S_A-N}/T_{N-I} = 0.82$).[3] The virtual S_A–N transition temperatures for the methoxy and methyl derivatives were also difficult to estimate from the binary phase diagrams (which are similar to those in Figures 2a and 2b). The S_A phase is formed only by the nitro and cyano derivatives. However, the S_A phase does not have a monolayer arrangement but a partially bilayer one. As shown in Figure 1c, the fluoro derivative has a very poor S_C nature, similar to the fluoro derivative of compound **2**.

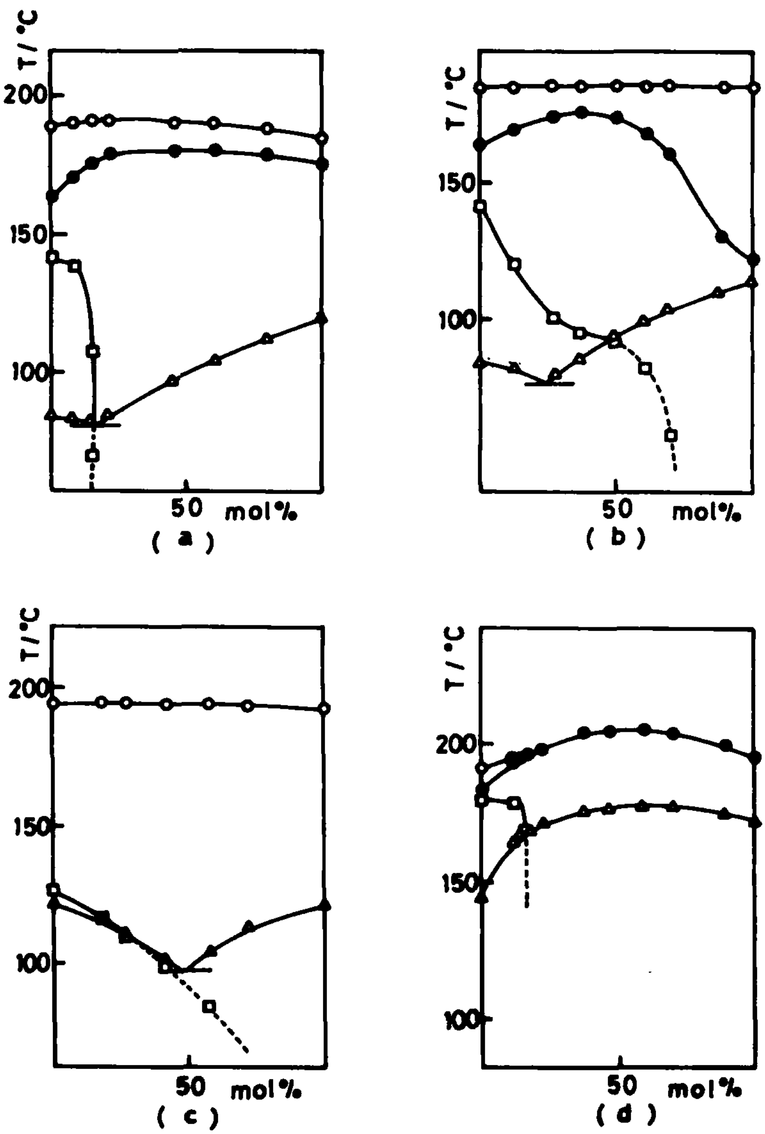


FIGURE 1 Phase diagrams for the binary mixtures of the octyloxy (on left) and fluoro (on right) derivatives of compounds: (a) **1**, (b) **2**, (c) **3**, and (d) **4**. Dashed lines indicate monotropic transitions. ○; nematic–isotropic, ●; smectic A–nematic(isotropic), □; smectic C–smectic A(nematic) and smectic A–smectic C, and △; crystal–mesophase transitions.

Compound **4** has an intrinsically rich smectic nature. The virtual S_A–N transition temperature for the unsubstituted derivative is 130°C(T_{S_A-N}/T_{N-I} = 0.98).[3] The binary phase diagrams for the mixtures of the methoxy derivatives of **1** and **4** (Figure 2c) and the methyl ones (Figure 2d), show an ideal solution behavior. The virtual S_A–N transition temperatures for the methoxy and methyl derivatives were

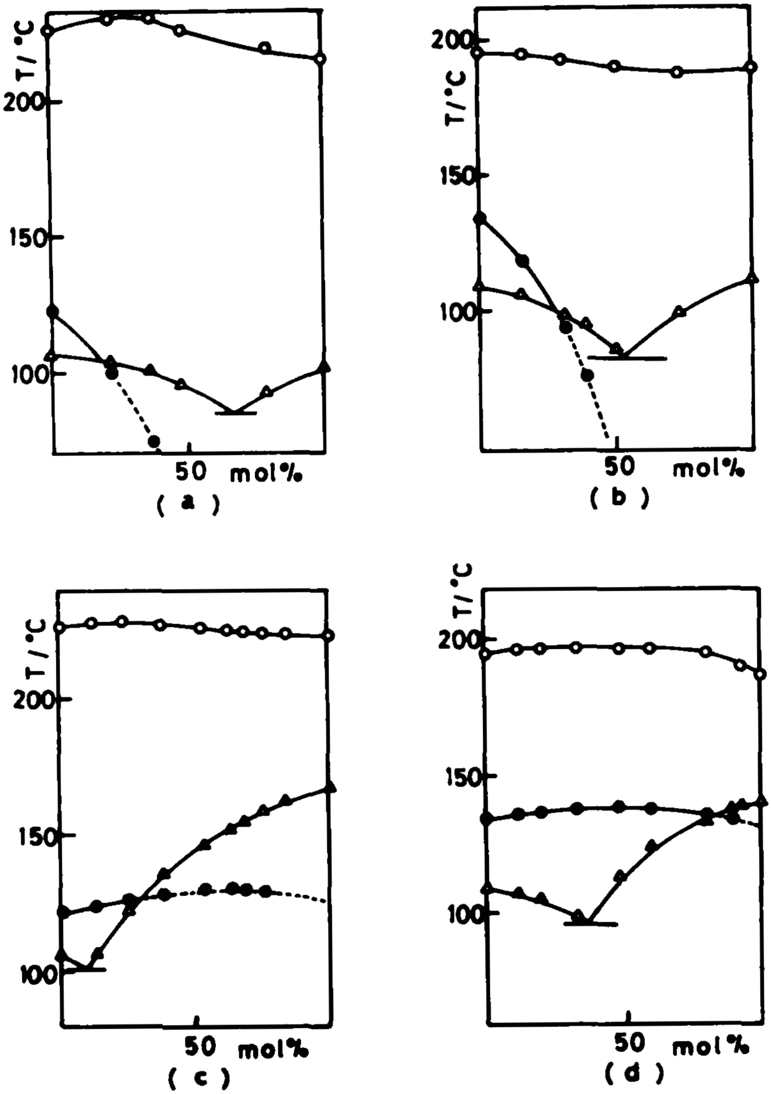


FIGURE 2 Phase diagrams for the binary mixtures of: (a) the methoxy derivatives of **1** (on left) and **2** (on right), (b) the methyl derivatives of **1** (on left) and **2** (on right), (c) the methoxy derivatives of **1** (on left) and **4** (on right), (d) the methyl derivatives of **1** (on left) and **4** (on right). Refer to the caption in Figure 1.

evaluated to be 125 and 131°C, respectively. The practical S_A phase commences from the propoxy and propyl derivatives. The S_C phase commences from the pentyloxy and pentyl derivatives. The halogenated derivatives show only an S_A phase. The acetyl derivative shows the N phase just before the S_A–I transition. The nitro derivative shows no S_A phase. The S_A phase for the cyano derivative is known to have a partially bilayer arrangement.[8]

Molecular orbital calculation: In order to estimate the local polarity around the ester groups and substituents, we calculated the charges of the functional groups and the dipole moments of the entirety of the molecules by the MNDO method.[10] The geometrical parameters used in the calculation were described in an earlier paper.[3] The twisted angles between the phenyl groups are supposed to be 50°.[11] In order to simplify the calculation, the octyloxy group was replaced by a methoxy one. The results are summarized in Table V.

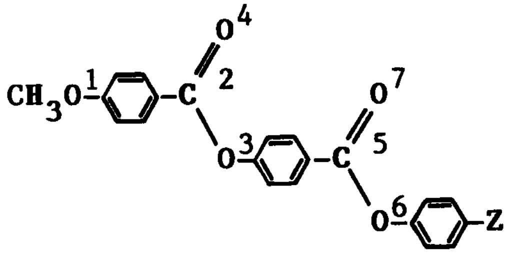
The total dipole moments are in good agreement with the values calculated by the method of Klingbiel *et al.*,[12] indicating that the calculation gives reliable values.

The electrostatic effect of the substituents extends only to the carbonyl group at position Y, and the charges at the other atoms incorporated in the ester group at position X and the ether oxygen at the terminal position are almost irrespective of the electrostatic nature of the substituents. The effect is more apparent in compound **2** than in compound **1**. Furthermore, we have to note that the charges of the substituents are also reduced by the electron-withdrawing nature of the carbonyl group at position Y in compound **2**.

TABLE V

MNDO calculations of substituted derivatives

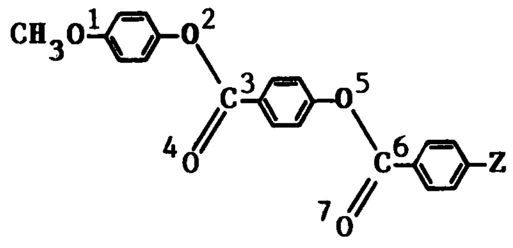
a) compound 1



atoms	Z = —OCH_3	—H	—Cl	—NO_2
1(O)	−0.295	−0.295	−0.295	−0.295
2(C)	0.401	0.401	0.401	0.401
3(O)	−0.228	−0.228	−0.228	−0.228
4(O)	−0.385	−0.385	−0.385	−0.384
5(C)	0.395	0.396	0.397	0.399
6(O)	−0.230	−0.231	−0.231	−0.231
7(O)	−0.383	−0.382	−0.380	−0.377
atoms in substituents	−0.296(O)	0.066(H)	−0.096(C1)	0.497(N) −0.324(O) −0.346(O)
Total dipole moment (D)	4.28	3.80	5.43	8.81

TABLE V Cont.

b) compound 2



atoms	Z = —OCH_3	—H	—Cl	—NO_2
1(O)	−0.296	−0.297	−0.297	−0.297
2(O)	−0.230	−0.228	−0.228	−0.228
3(C)	0.395	0.397	0.396	0.395
4(O)	−0.383	−0.382	−0.381	−0.397
5(O)	−0.228	−0.228	−0.228	−0.227
6(C)	0.401	0.394	0.392	0.385
7(O)	−0.385	−0.374	−0.368	−0.359
atoms in substituents	−0.295(O)	0.066(H)	−0.091(Cl)	0.491(N) −0.317(O) −0.342(O)
Total dipole moment (D)	4.28	4.38	3.61	4.58

DISCUSSION

In this paper, we examined the substituent effect on the smectic A thermal stability. Apparently, the smectic A-nematic (isotropic) transition temperature is strongly dependent not only on the orientation of the ester linkage but also on the electrostatic nature of the substituents. The effect of the ester linkage arose from the change in the electrostatic nature at position Y. The relative efficiency order for the substituents in promoting the S_A–N(I) transition temperature is given by:

For compound **1**

$NO_2 > COCH_3 > Br > Cl > F > CH_3 > OCH_3 > H > CN$

For compound **2**

$COCH_3 > CF_3 > Br > Cl > CN > F > NO_2 > H > CH_3, OCH_3$

For compound **3**

$NO_2 > CN$

For compound **4**

$COCH_3 > Br > Cl > F > CN > CH_3 > H > OCH_3 > NO_2$

A similar order has been known in several liquid crystalline systems.[13] It is apparent that the orders are not worthy of notice since the orders do not have any correlation with the electrostatic nature of the substituents. However, we have to notice the fact that the smectic A thermal stability is apparently dependent on the electrostatic nature of the substituents. In fact, the MNDO calculation suggests that the charges at the ester group at position Y and the substituents are affected by the electrostatic nature of the substituents and the ester group. That is, the electron-donating substituent such as the methoxy group in compound **2** increases the charge of the carbonyl group of the ester at position Y, and the electron-withdrawing substituents such as chlorine and the nitro group decreases it. The electronic correlation reminds us of Hammett's equation in chemical reactions.

Hammett and Taft have demonstrated that rate constants for some chemical reactions involving para-substituted benzoates have a linear correlation with the electrostatic nature of the substituents, and introduced new parameters such as σ_p and σ_p^+.[2] These parameters are the function of the inductive and resonance nature of the substituents. For example, the substituent parameters have a very good correlation with the stretching vibrations of the carbonyl group in some para-substituted benzoates and acetophenones.[14] These correlations are interpreted in terms of the change in the polarity of the carbonyl group due to the electrostatic interactions between the carbonyl groups and substituents.

In order to correlate the smectic properties of the present molecules with the substituent parameters, the ratios (R) of T_{S_A-N}/T_{N-I}[15] were plotted against Hammett's substituent parameters (σ_p), and the results are shown in Figure 3.

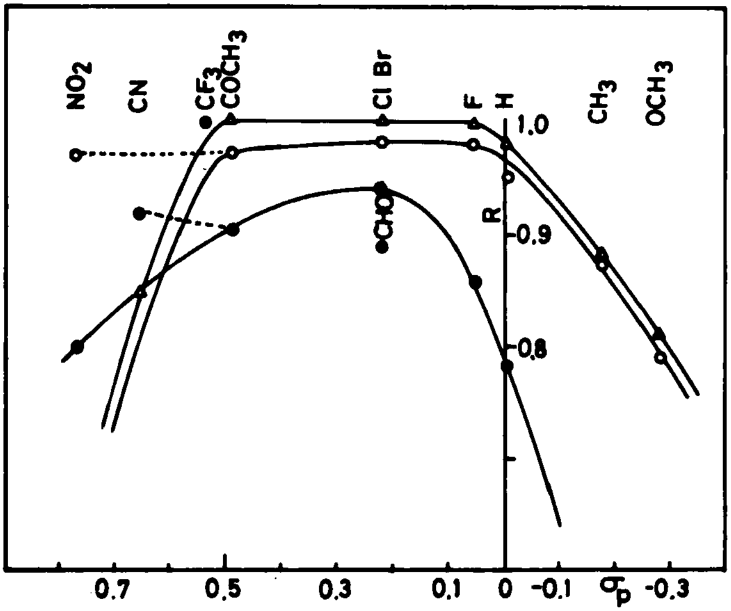


FIGURE 3. Plots of $R(T_{S_A-N}/T_{N-I})$ against σ_p for substituents. ○; compound **1**, ●; compound **2**, and △; compound **4**.

In the figure, the plots for the nitro and cyano derivatives of compounds **1** and **2** are connected by the dashed lines since the S_A phases apparently have a partially bilayer arrangement.[5,8] The S_A (monolayer)–N transition temperatures should be considerably low as shown in Figure 3, similar to the cyano derivative of compound **4**.

Although the ratios and σ_p values lack a linear correlation, the plots show a somewhat interesting correlation. In the plots for compounds **1** and **4**, the substituents having an electron-withdrawing nature such as the nitro and cyano groups steeply decrease the S_A thermal stability, while these substituents for compounds **2** and **3** moderately decrease it. As we can see from Table V, these substituents for compound **2** decrease the charge on the carbonyl group at position Y, and the carbonyl group at position Y decreases the charge on the substituents, due to the inductive and resonance interactions between these groups. On the other hand, these substituents for compound **1** also decrease the charge on the carbonyl group at position Y, and the ether oxygen at position Y increases the charge on the substituents. Therefore, the steep reduction of the S_A–N transition temperatures for compounds **1** and **4** should be concerned with the increase in the charge on the substituents. Oppositely, the electron-donating substituents such as the methyl and methoxy groups for compounds **2** and **3** steeply decrease the S_A thermal stability, while the reduction is moderate for compounds **1** and **4**. As shown in Table V, the methoxy group for compound 2 considerably increases the charge on the carbonyl group at position Y, while the increase for compound **1** is small. Therefore, the increase in the charge on the ester group at position Y should be responsible for the steep reduction of the S_A–N transition temperatures for compounds **2** and **3**. The halogenated and acetyl compounds have the largest R values. Certainly, the charge on the carbonyl group for the chloro derivative is the lowest of all, and the charge on chlorine is also low.

In the current concept, polar interactions involving dipole-dipole and dipole-induced dipole ones are supposed to facilitate the layer arrangement of molecules, probably due to the attractive interactions inthe antiparallel arrangement. However, the present results apparently indicate that the increase in the polarity around the ester group and substituents is unfavorable for the formation of the layer arrangement. These facts suggest that the repulsive interactions due to parallel arrangement of the charges and/or dipoles in the parallel arrangement play a more important role than the attractive ones in the antiparallel arrangement. In connection with the electrostatic interactions, the following facts are noteworthy.

The first is that R for the trifluoromethyl derivative of compound **2** (1.0) is larger than those (0.90 and 0.88) for the acetyl and formyl ones, while the σ_p value (0.54) for trifluoromethyl benzene is larger than those (0.50 and 0.22) for acetophenone and benzaldehyde, respectively. In these derivatives, the dipole moment for trifluoromethylbenzene (2.56 D) is smaller than acetophenone (2.95 D) and benzaldehyde (3.02 D).[16]

The second is that the S_A–N transition temperatures for compounds **1** and **4** gradually rise and become almost constant on elongating the alkoxy chain, while the electrostatic nature around the core changes a little. On the other hand, the smectic A properties for compounds **2** and **3** are very poor even if the alkoxy chain is considerably long. For compound **2** the smectic A phase rather suddenly commences from the hexyloxy derivative. Incidentally, the only difference between compounds **1** and **2** is that both terminal alkoxy groups are opposite with respect to the orientation of the ester groups, so that the octyloxy derivatives are identical. These facts suggest that the geometry of the entirety of the molecules is important in determining the smectic properties in connection with the electrostatic interactions.

Some comments on the thermal properties of the S_C phase: The S_C phase is formed only by those derivatives having long alkoxy and alkyl chains at the terminal position. As we can see from the tables and Figure 1, many derivatives having small substituents at the terminal position are very poor in their tilt nature, while some of them have a very rich smectic A nature. The thermal stability of the S_C phase is also dependent on the orientation of the ester linkages, especially in the ester group at position Y. However, the S_C phase is formed throughout four compounds. These facts suggest that the tilt nature in the layer arrangement is strongly dependent on the geometrical factor of the substituents.[17]

Some interesting behaviors are recognized in binary phase diagrams. In Figures 1a and 1d, the S_C–S_A transition temperatures steeply decrease with an increase in the concentration of the fluoro derivatives, and the mixtures show a reentrant phenomenon of the S_A–S_C–S_A–*N*–I type. A similar trend has been observed in the binary mixture of bisphenyl-1,3,4-thiadiazole compounds.[18] The steep change of the S_C phase may be interpreted in terms of the decrease in the tilt angle with an increase in the concentration of the fluoro derivatives. The S_C–S_A(N) transition temperature for the binary mixtures of compounds **2** and **3** (Figures 1b and 1c) also shows a non-ideal solution behavior. In Figure 1b, a non-ideal solution behavior is also recognized in the S_A–N transition temperature. As a complicating feature, the polar interactions may play some role.

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