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### Nematic-Isotropic Transition Temperature and Dipole-Dipole Interaction. 4-(4-X-Substituted Phenyliminomethyl)phenyl 4-Y-Substituted Benzoates and 4-X-Substituted Phenyl 4-(4-Y-Substituted Phenyliminomethyl) benzoates

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# Nematic-Isotropic Transition Temperature and Dipole-Dipole Interaction. 4-(4-X-Substituted Phenyliminomethyl)phenyl 4-Y-Substituted Benzoates and 4-X-Substituted Phenyl 4-(4-Y-Substituted Phenyliminomethyl)benzoates

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Nematic-isotropic transition temperature was determined for 4-(4-X-phenyliminomethyl)phenyl 4-Y-benzoates and 4-X-phenyl 4-(4-Y-phenyliminomethyl)benzoates, where X and Y are CN, CH<sub>3</sub>O, NO<sub>2</sub>, Cl, Br, N(CH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>, F, or CF<sub>3</sub> groups. The transition temperature in the absence of the dipole-dipole interaction was estimated by extending Van der Veen's approximation. While a large positive deviation is found for the CH<sub>3</sub>O-NO<sub>2</sub> and CH<sub>3</sub>-NO<sub>2</sub> derivatives, indicating the significant contribution of dipole-dipole interaction to the nematic thermal stability, no deviation in the CH<sub>3</sub>O-CN derivatives suggests the anti-parallel molecular association in the mesophase.

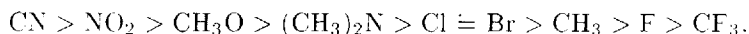
**Keywords:** nematic; terminal groups; dipole-dipole interaction; anti-parallel dimerization

## INTRODUCTION

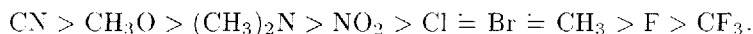
Our studies on 4-(4-X-benzylideneamino)phenyl 4-Y-benzoates and 4-X-phenyl 4-(4-Y-benzylideneamino)benzoates, where X and Y are CN, CH<sub>3</sub>O, NO<sub>2</sub>, Cl,

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Br,  $\text{N}(\text{CH}_3)_2$ ,  $\text{CH}_3$ , F, or  $\text{CF}_3$  groups have revealed that the order of efficiency of terminal substituents in promoting nematic-isotropic (N-I) transition temperature varies considerably by the kind of substituent fixed at the other end of the molecule [1,2]. For example, the following order was obtained based on the  $\text{CH}_3\text{O}$  and  $\text{CH}_3$  series, X or  $\text{Y}=\text{CH}_3\text{O}$  and  $\text{CH}_3$ , respectively:



which is fairly close to the one compiled by Gray many years ago [3]. On the other hand, the F series yields this order:

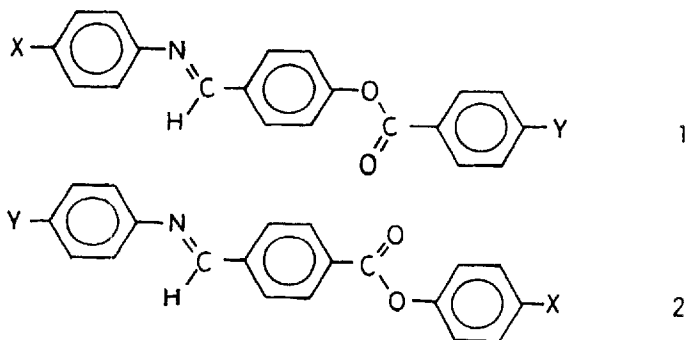


Thus, the electron-withdrawing  $\text{NO}_2$  group is shifted toward the end of the efficiency order by the change of the fixed group from the electron-donating  $\text{CH}_3\text{O}$  or  $\text{CH}_3$  group to the electron-withdrawing F group. When the fixed group is  $\text{CF}_3$ , the electron-donating and -withdrawing groups are entirely separated in the efficiency order; that is,



Such changes in the efficiency order indicate undoubtedly that the contribution of dipole-dipole interaction to the stabilization of the nematic phase cannot be ignored.

Here, our examination was extended to two isomeric compounds, 4- (4-X-phenyliminomethyl)phenyl 4-Y-benzoates (1) and 4-X-phenyl 4-(4-Y-phenyliminomethyl)benzoates (2), in which the azomethine group in the previously-studied two compounds is inverted. As the N-I transition temperature of related mono-substituted derivatives has been shown to be affected as much as  $30^\circ\text{C}$  by the arrangement of the linking groups [4], works on isomeric compounds seemed desirable to confirm the generality of our observations.



## EXPERIMENTAL

The 4-X or Y-substituted anilines, 4-X-substituted phenols, and 4-Y-substituted benzoic acids were commercially available. Preparation of the compounds, transition temperature measurements and mesophase identification were carried out as described in our previous paper [1].

## RESULTS AND DISCUSSION

Transition temperatures and associated enthalpies of compound 1 are listed in Table I. Here, the crystalline, smectic A, nematic, and isotropic phases are denoted by K,  $S_A$ , N, and I, respectively. Note that the  $\text{CH}_3\text{-CF}_3$  derivatives are purely smectogenic.

TABLE I Transition temperatures ( $^{\circ}\text{C}$ ) and associated enthalpies ( $\text{kJ mol}^{-1}$ ) of 4-(4-X-phenyliminomethyl)phenyl 4-Y-benzoates (1)

X	Y	K	$S_A$	N	I	$t_{calc}$
CN	CN	.245(25)		.345(3.7)	.	
	$\text{CH}_3\text{O}$	.180(38)		.324(0.8)	.	327
	Cl	.185(30)		.311(2.7)	.	305
	Br	.193(27)		.314(2.8)	.	305
	$(\text{CH}_3)_2\text{N}$	.243(33)		.321(0.5)	.	
	$\text{CH}_3$	.156(30)		.308(2.0)	.	295
	F	.171(40)		.280(1.3)	.	273
	$\text{CF}_3$	.155(31)		.239(1.3)	.	
	$\text{CH}_3\text{O}$	.176(37)		.322(1.9)	.	327
	$\text{CH}_3\text{O}$	.153(39)		.308(2.2) <sup>a</sup>	.	
$\text{CH}_3\text{O}$	Cl	.179(41)		.290(1.2) <sup>b</sup>	.	286
	Br	.200(46)		.285(1.1)	.	287
	$(\text{CH}_3)_2\text{N}$	.167(31)		.286(2.2)	.	
	$\text{CH}_3$	.138(38)		.281(1.5) <sup>a</sup>	.	276
	F	.151(36)		.260(1.4)	.	254
	$\text{CF}_3$	.165(31)	.220(4.0)	.247(1.1)	.	
	$\text{CH}_3\text{O}$	.227(47)		.315(0.8)	.	294
	$\text{NO}_2$	.235(47)		.280(1.1) <sup>a</sup>	.	
	Cl	.184(35)		.281(1.5) <sup>a</sup>	.	272

<i>X</i>	<i>Y</i>	<i>K</i>	<i>S<sub>A</sub></i>	<i>N</i>	<i>I</i>	<i>t<sub>calc</sub></i>
Cl	Br	. 206(34)		. 286(1.1)	.	273
	CH <sub>3</sub>	. 169(37)		. 287(0.8)	.	262
	F	. 159(37)		. 241(0.8)	.	240
	CF <sub>3</sub>	. 165(26)		. 197(0.4)	.	
	CN	. 162(36)		. 311(3.3)	.	305
	CH <sub>3</sub> O	. 172(27)		. 285(1.6) <sup>c</sup>	.	286
	NO <sub>2</sub>	. 164(24)		. 281(0.9)	.	272
	Cl	. 149(32)		. 264(1.1)	.	
	Br	. 155(33)		. 260(0.9)	.	265
	(CH <sub>3</sub> ) <sub>2</sub> N	. 198(38)		. 267(1.4)	.	
Br	CH <sub>3</sub>	. 172 (32)		. 259(1.0)	.	254
	F	. 145(38)		. 233(0.6)	.	232
	CF <sub>3</sub>	. 155(31)		. 208(0.8)	.	
	CN	. 185(23)		. 309(2.1)	.	305
	CH <sub>3</sub> O	. 187(38)		. 280(0.9) <sup>c</sup>	.	287
	NO <sub>2</sub>	. 196(29)		. 290(1.2)	.	273
	Cl	. 159(32)		. 265(1.1)	.	265
	Br	. 173(33)		. 265(0.7)	.	
	(CH <sub>3</sub> ) <sub>2</sub> N	. 207(36)		. 263(1.1)	.	
	CH <sub>3</sub>	. 192(35)		. 258(0.6)	.	255
(CH <sub>3</sub> ) <sub>2</sub> N	F	. 158(32)		. 232(0.5)	.	233
	CF <sub>3</sub>	. 140(24)		. 211(0.8)	.	
	CH <sub>3</sub> O	. 193(40)		. 286(1.5)	.	
	Cl	. 203(32)		. 260(1.1)	.	
	Br	. 213(39)		. 255(0.8)	.	
	CH <sub>3</sub>	. 205(30)		. 253(1.4)	.	
	F	. 181(38)		. 241(1.4)	.	
	CF <sub>3</sub>	. 218(19)	. 231(1.2)	. 239(1.0)	.	
	CN	. 178(33)		. 303(17)	.	295
	CH <sub>3</sub> O	. 129(28)		. 278(1.1) <sup>c</sup>	.	276
CH <sub>3</sub>	NO <sub>2</sub>	. 165(35)		. 279(0.6)	.	262
	Cl	. 167(32)		. 256(1.0) <sup>a</sup>	.	254
	Br	. 179(31)		. 254(0.7)	.	255
	(CH <sub>3</sub> ) <sub>2</sub> N	. 213(32)		. 258(0.9)	.	
	CH <sub>3</sub>	. 169(35)		. 244(1.0) <sup>a</sup>	.	

<i>X</i>	<i>Y</i>	<i>K</i>	<i>S<sub>A</sub></i>	<i>N</i>	<i>I</i>	<i>t<sub>calc</sub></i>
F	F	. 144(31)		. 228(1.1)	.	222
	CF <sub>3</sub>	. 181(24)	. 235 (9.8)		.	
	CN	. 141(32)		. 273(1.4)	.	273
	CH <sub>3</sub> O	. 134(36)		. 258(1.4)	.	254
	NO <sub>2</sub>	. 158(35)		. 232(1.0)	.	240
	Cl	. 174(40)		. 226(0.6)	.	232
	Br	. 166(40)		. 224(0.7)	.	233
	(CH <sub>3</sub> ) <sub>2</sub> N	. 208(28)		. 249(1.1)	.	
	CH <sub>3</sub>	. 149(35)		. 226(0.9)	.	222
	F	. 185(48)		. 200(0.6)	.	
CF <sub>3</sub>	CF <sub>3</sub>	. 129(36)		. 165(0.4)	.	
	CN	. 179(22)		. 237(1.6)	.	
	CH <sub>3</sub> O	. 207(15)	. 216(3.6)	. 242(0.9)	.	
	NO <sub>2</sub>	. 173(32)		. 188(0.7)	.	
	Cl	. 150(29)		. 197(0.7)	.	
	Br	. 168(23)		. 198(0.8)	.	
	(CH <sub>3</sub> ) <sub>2</sub> N	. 241(31)		. 248(0.7)	.	
	CH <sub>3</sub>	. 186(11)	. 236(16) <sup>d</sup>		.	
	F	. 135(30)		. 167(0.4)	.	

a. Taken from Ref 1.

b. Taken from Ref 5.

c. Taken from Ref 6.

d. S<sub>B</sub>-S<sub>A</sub> transition at 232°C (7.4 kJ mol<sup>-1</sup>).

In order to determine the contribution of dipole-dipole interaction to the nematic thermal stability, one has to know the N-I transition temperature without such an interaction. As the moments due to the terminal groups are largely cancelled in the X-X derivatives, the anisotropy of the molecular polarizability is supposed to be the dominating factor in determining the N-I transition temperature of these derivatives. Our results for the X-X derivatives give this efficiency order:



If the dipole-dipole interaction were absent in the mesophase of the X-Y derivatives, the transition temperature could be estimated by the following procedure on the basis of the data for the X-X and Y-Y derivatives. According to the molecular statistical theory of Maier and Saupe, the N-I transition temperature ( $T_{\text{NI}}$ ) is proportional to the square of the anisotropy of the molecular polarizability. Con-

sequently, Van der Veen suggested that the influence of terminal substituents upon the N-I transition temperature within a series can be related to the anisotropy in the polarizability of the  $C_{Ar}$ -X bond [8]. The anisotropy of the polarizability of a molecule M-X,  $\Delta\alpha_{MX}$ , may be approximated by the sum of anisotropies of polarizabilities of the molecular core  $\Delta\alpha_M$  and the substituent  $\Delta\alpha_X$ ; namely,

$$\Delta\alpha_{MX} = \Delta\alpha_M + \Delta\alpha_X$$

where  $\Delta\alpha_M$  may be considered to be constant within a series. Therefore, the relation between  $T_{NI}$  and  $\Delta\alpha_X$  is approximated by

$$T_{NI}(M-X) \propto (\Delta\alpha_{MX})^2 \doteq (\Delta\alpha_M)^2 + 2\Delta\alpha_M(\Delta\alpha_X)$$

since  $\Delta\alpha_M \gg \Delta\alpha_X$ . If we apply this approach to disubstituted molecules, the X-X, Y-Y, and X-Y derivatives, the N-I transition temperature of the X-Y derivative is given by the arithmetic mean of those of the X-X and Y-Y derivatives; namely,

$$T_{NI}(X-Y) \doteq 1/2[T_{NI}(X-X) + T_{NI}(Y-Y)]$$

or

$$t_{NI}(X-Y) \doteq 1/2[t_{NI}(X-X) + t_{NI}(Y-Y)]$$

because

$$(\Delta\alpha_{XMX})^2 \doteq (\Delta\alpha_M)^2 + 4\Delta\alpha_M(\Delta\alpha_X)$$

$$(\Delta\alpha_{YMY})^2 \doteq (\Delta\alpha_M)^2 + 4\Delta\alpha_M(\Delta\alpha_Y)$$

$$(\Delta\alpha_{XMY})^2 \doteq (\Delta\alpha_M)^2 + 2\Delta\alpha_M(\Delta\alpha_X + \Delta\alpha_Y).$$

The observed transition temperature may agree with  $t_{NI}(X-Y)$  provided that the intermolecular interaction is predominantly due to dispersion forces. If the nematic phase is stabilized by the dipole-dipole interaction, the N-I transition temperature must be higher than the estimated one. This condition is not strictly fulfilled by the present compounds as the present molecular core is neither symmetric nor rigid; therefore, the dipole moment is not zero even in the X-X and Y-Y derivatives. Another serious problem is related to the geometrical structure of the conjugated system which may be affected by the terminal groups and may influence the term  $\Delta\alpha_M$ . As a result, our estimated N-I transition temperature, denoted by  $t_{calc}$  instead of  $t_{NI}(X-Y)$  in Table I, is rough. Indeed, some observed transition temperatures are distinctly lower than the calculated ones.

The N-I transition temperatures for the  $CH_3O$  and F series of compound 1 are plotted in Figure 1 in the order of decreasing the group (Y or X) efficiency of the nematic phase generation observed in our previous work [2]. The transition tem-



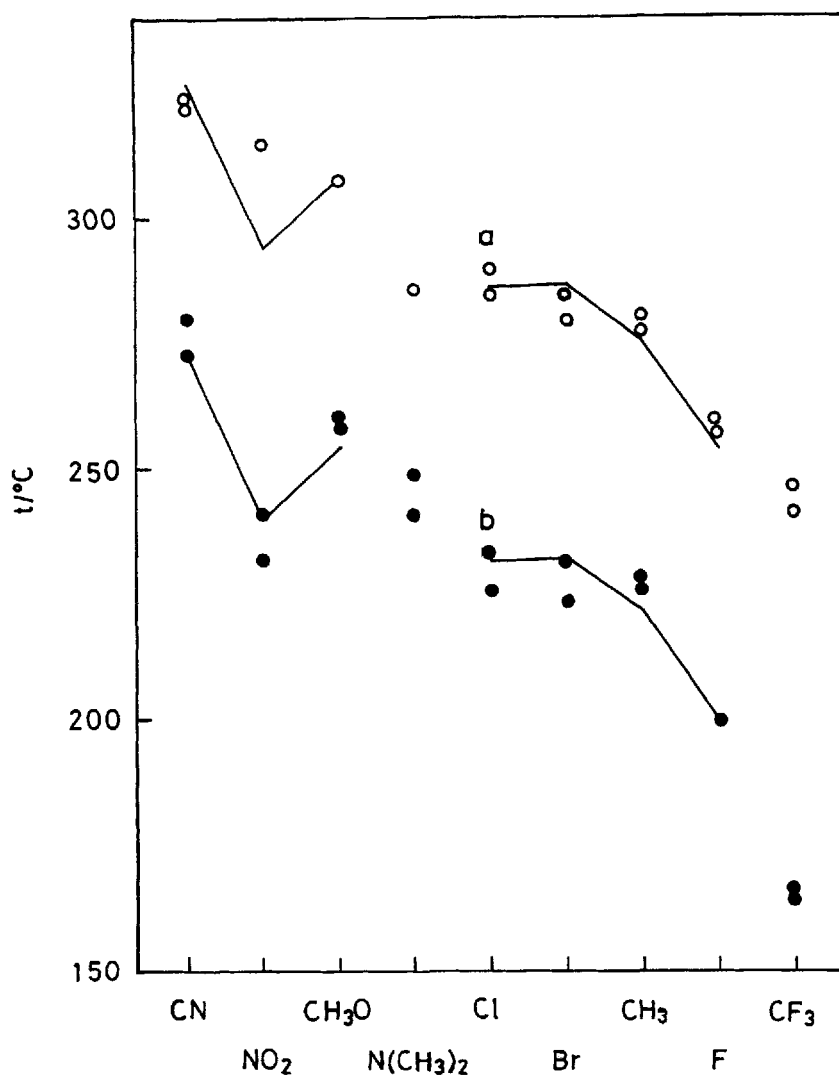


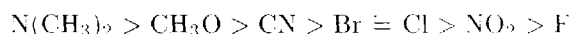
FIGURE 1 Plots of N-I transition temperatures of compound 1 in the order of terminal groups given below. (a)  $\text{CH}_3\text{O}$  series (X or Y =  $\text{CH}_3\text{O}$ ) ○ and (b) F series (X or Y = F) ●

perature tends to be raised by the inversion of the azomethine group. Especially, the mesophase stability of the F- $\text{NO}_2$ , F-Cl, and F-Br derivatives is promoted by  $10^\circ\text{C}$  or more. The lines are drawn by connecting the calculated values. A large positive deviation is found for the  $\text{CH}_3\text{O}-\text{NO}_2$  and smaller ones for the  $\text{CH}_3\text{O}-\text{F}$

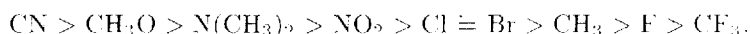
and  $\text{CH}_3\text{-F}$  derivatives in accord with the view that the dipole-dipole interaction stabilizes the nematic phase. The separation between the two series ranges from  $41^\circ\text{C}$  between the  $\text{CH}_3\text{O-N(CH}_3)_2$  and  $\text{F-N(CH}_3)_2$  derivatives to  $80^\circ\text{C}$  between the  $\text{CH}_3\text{O-CF}_3$  and  $\text{F-CF}_3$  derivatives. Therefore, it seems certain that the mesophase of the  $\text{F-N(CH}_3)_2$  and  $\text{CH}_3\text{O-CF}_3$  derivatives is markedly stabilized although no calculated value is available. These findings are consistent with the above-mentioned view. On the other hand, no deviation is found for the  $\text{CH}_3\text{O-CN}$  derivatives, suggesting that the effective dipole moment in the mesophase is drastically reduced by the anti-parallel molecular association in the mesophase [9–11].

Figure 2 presents the plots of the N-I transition temperature of the CN and  $\text{CH}_3$  series. Large positive deviations from the calculated values are noted for the  $\text{CH}_3\text{-NO}_2$  derivatives and a smaller one for the  $\text{CH}_3\text{-CN}$  derivative. The difference in the N-I transition temperature of these two series ranges from  $39^\circ\text{C}$  between the CN-CN and  $\text{CH}_3\text{-CN}$  derivatives to  $65^\circ\text{C}$  between the CN- $\text{N(CH}_3)_2$  and  $\text{CH}_3\text{-N(CH}_3)_2$  derivatives. Moreover, the large separation of transition temperature between the latter derivatives indicates the promotion of the nematic thermal stability in the CN- $\text{N(CH}_3)_2$  derivative. Positive deviations from the calculated values noted in Table I for the CN-Br and  $\text{NO}_2\text{-Br}$  derivatives are rather unexpected. The promotion might be ascribed to the electron-donating resonance effect exerted by the halogeno group bearing unshared-pair electrons, particularly of low electronegativity.

It may be interesting to compare the order of N-I transition temperatures given by the  $\text{CF}_3$  series,



and that given by the F series,



As the  $\text{CF}_3$  group is more strongly electron-withdrawing than the F group, the dipole moment appears to be the predominant factor in determining the order of thermal stability of the mesophase in the  $\text{CF}_3$  series. Our observations that the introduction of a  $\text{CF}_3$  group to the  $\text{NO}_2\text{-H}$  derivatives reduces the nematic thermal stability ( $223$  [4] to  $197^\circ\text{C}$  and  $199$  [4] to  $188^\circ\text{C}$ ) may be ascribed to the cancellation of the dipole moment of the parent compound by the added terminal group.

Transition temperatures and associated enthalpies of compound 2 are presented in Table II and the N-I transition temperatures of the  $\text{CH}_3\text{O}$  and F series and those of the CN and  $\text{CH}_3$  derivatives are plotted in Figures 3 and 4, respectively. While the transition temperature of the  $\text{CH}_3\text{O}$  series changes little by the inver-

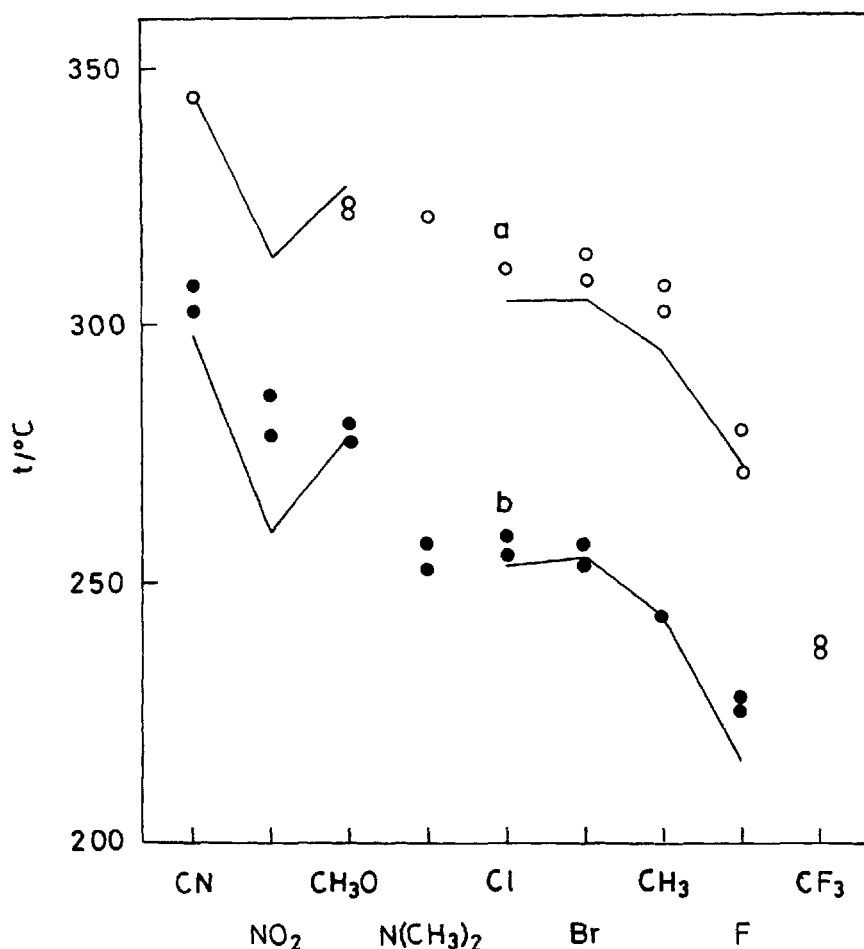


FIGURE 2 Plots of N-I transition temperatures of compound 1 in the order of terminal groups given below, (a) CN series (X or Y=CN) ○ and (b) CH<sub>3</sub> series (X or Y=CH<sub>3</sub>) ●

sion of the carbonyloxy group except for the CH<sub>3</sub>O-NO<sub>2</sub> and CH<sub>3</sub>O-CF<sub>3</sub> derivatives, that of the F and CN series tends to be lower by several to ten degrees. It may be noted that the transition temperature of the CH<sub>3</sub>O-NO<sub>2</sub> and CH<sub>3</sub>O-CF<sub>3</sub> derivatives is also depressed by the structural modification to a similar extent. No positive deviation from the calculated value is found for the CN-Cl and CN-Br derivatives of compound 2. However, the general tendency of the transition temperature remains the same through the structural modification. The stabi-

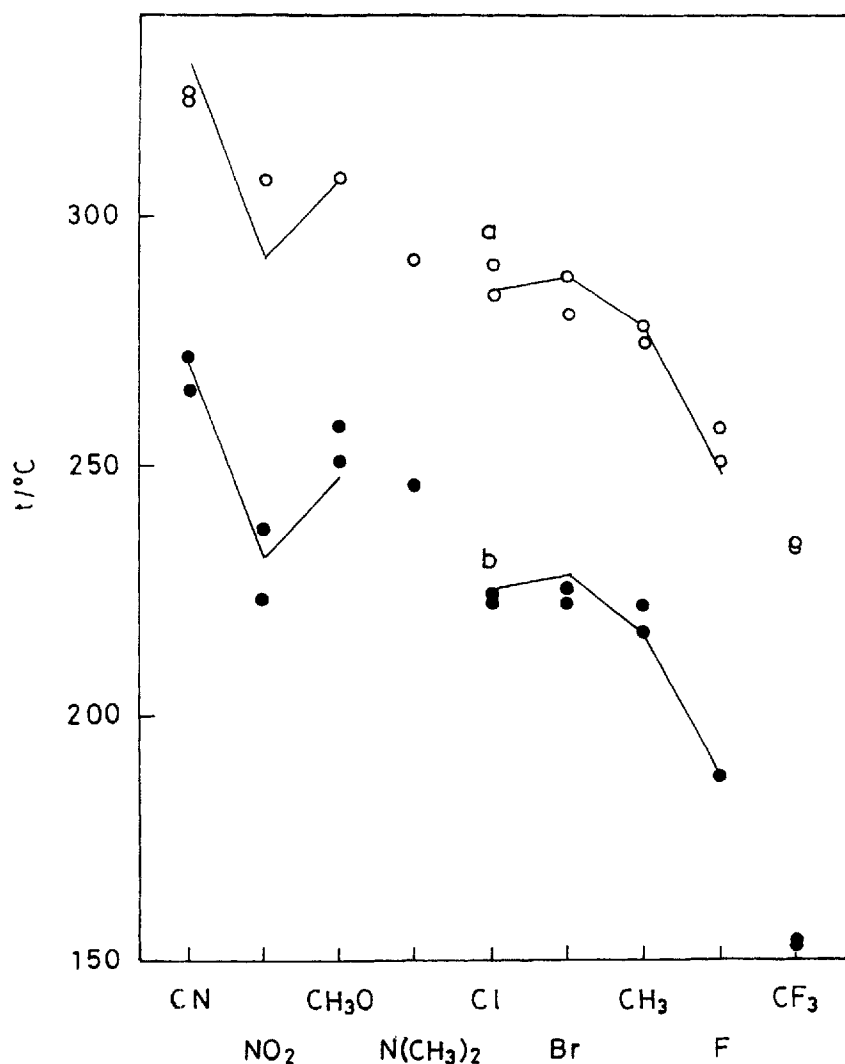
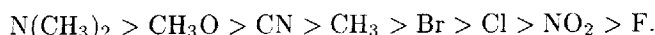


FIGURE 3 Plots of N-I transition temperatures of compound 2 in the order of terminal groups given below, (a) CH<sub>3</sub>O series (X or Y=CH<sub>3</sub>O) ○ and (b) F series (X or Y=F) ●

lization of the nematic phase in the CH<sub>3</sub>O-NO<sub>2</sub>, CH<sub>3</sub>O-F, and CH<sub>3</sub>-NO<sub>2</sub> derivatives of compound 2 by the dipole-dipole interaction is clearly demonstrated by the positive deviation of the N-I transition temperature from the calculated one. The separation in the N-I transition temperature between the

$\text{CH}_3\text{O}-\text{CF}_3$  and  $\text{F}-\text{CF}_3$  derivatives is as large as  $80^\circ\text{C}$  and that between the  $\text{CN}-\text{CF}_3$  and  $\text{CH}_3-\text{CF}_3$  derivatives is as small as  $22^\circ\text{C}$ . The corresponding value for the latter combination is not found for compound 1 in Figure 2 because of the lack of the nematic phase in the  $\text{CH}_3-\text{CF}_3$  derivatives. The  $\text{CF}_3$  series of compound 2 yields the following order of efficiency of terminal groups in promoting the N-I transition temperature:



The transition temperature of the  $\text{NO}_2-\text{CF}_3$  derivatives of compound 2 is also lower than that of the  $\text{NO}_2-\text{H}$  derivatives [4]; that is,  $186$  vs.  $221^\circ\text{C}$  and  $189$  vs.  $210^\circ\text{C}$ .

TABLE II Transition temperatures ( $^\circ\text{C}$ ) and associated enthalpies ( $\text{kJ mol}^{-1}$ ) of 4-X-phenyl 4 (4-Y-phenyliminomethyl) benzoates (2)

X	Y	K	$S_A$	N	I	$t_{c1c}$
CN	CN	.194(26)	.227(1.5)	.353(4.3)	.	
	$\text{CH}_3\text{O}$	.172(34)		.325(2.6)	.	331
	$\text{NO}_2$	.201(38)		.323(2.0)	.	315
	Cl	.158(33)		.305(2.8)	.	308
	Br	.172(37)		.302(2.1)	.	310
	$\text{CH}_3$	.171(35)		.299(1.8)	.	298
	F	.140(38)		.265(1.3)	.	271
	$\text{CF}_3$	.149(28)		.232(1.6)	.	
	$\text{CH}_3\text{O}$	.164(32)		.324(2.5)	.	331
	$\text{CH}_3\text{O}$	.169(47)		.308(1.9)	.	
$\text{CH}_3\text{O}$	$\text{NO}_2$	.186(36)		.307(1.2)	.	292
	Cl	.168(39)		.284(0.8) <sup>a</sup>	.	285
	Br	.169(42)		.280(0.7) <sup>b</sup>	.	288
	$(\text{CH}_3)_2\text{N}$	.182(37)		.291(0.7)	.	
	$\text{CH}_3$	.149(36)		.275(0.9) <sup>b</sup>	.	278
	F	.146(36)		.251(0.8) <sup>b</sup>	.	248
	$\text{CF}_3$	.171(33)		.234(0.9)	.	
	$\text{NO}_2$	.209(42)		.276(1.1)	.	
	Cl	.157(33)		.273(0.8)	.	269
	Br	.182(41)		.283(1.1)	.	272
$\text{NO}_2$	$\text{CH}_3$	.187(30)		.275 (0.4)	.	260
	F	.149(36)		.223(0.6)	.	232
	$\text{CF}_3$	.161(32)		.186(0.8)	.	
	Cl	.141(38)		.309(3.1)	.	308
	$\text{CH}_3\text{O}$	.170(39)		.290(0.8) <sup>a</sup>	.	285

<i>X</i>	<i>Y</i>	<i>K</i>	<i>S<sub>A</sub></i>	<i>N</i>	<i>I</i>	<i>t<sub>calc</sub></i>
Br	NO <sub>2</sub>	.166(34)	.181(2.5)	.279(0.9)	.	269
	Cl	.166(41)		.262(1.4)	.	
	Br	.175(39)		.264(1.0)	.	265
	(CH <sub>3</sub> ) <sub>2</sub> N	.200(32)		.265(1.6)	.	
	CH <sub>3</sub>	.167(38)		.256(0.9)	.	253
	F	.143(30)		.222(0.6)	.	225
	CF <sub>3</sub>	.162(35)		.197(0.6)	.	
	CN	.169(28)		.313(2.5)	.	310
	CH <sub>3</sub> O	.186(44)		.288(1.1)	.	288
	NO <sub>2</sub>	.194(42)		.286(1.0)	.	272
	Cl	.169(42)		.262(0.9)	.	265
	Br	.182(42)		.267(1.0)	.	
	(CH <sub>3</sub> ) <sub>2</sub> N	.204(37)		.264(0.7)	.	
	CH <sub>3</sub>	.178(34)		.255(0.8)	.	255
	F	.159(33)		.222(0.5)	.	228
	CF <sub>3</sub>	.175(36)		.203(0.8)	.	
CH <sub>3</sub>	CN	.159(34)	.181(2.5)	.302(2.1)	.	298
	CH <sub>3</sub> O	.130(28)		.278(1.3)	.	278
	NO <sub>2</sub>	.193(37)		.279(0.6)	.	260
	Cl	.155(32)		.245(0.8)	.	253
	Br	.159(31)		.251(0.7)	.	255
	CH <sub>3</sub>	.166(37)		.243(1.2)	.	
	F	.152(34)		.217(0.9)	.	216
	CF <sub>3</sub>	.172(23)		.212(0.9)	.	
	CN	.194(42)		.272(1.4)	.	271
	CH <sub>3</sub> O	.164(42)		.258(1.0)	.	248
	NO <sub>2</sub>	.162(36)		.237(0.7)	.	232
	Cl	.144(37)		.224(0.6)	.	225
	Br	.145(33)		.225(0.7)	.	228
	(CH <sub>3</sub> ) <sub>2</sub> N	.191(38)		.246(0.8)	.	
	CH <sub>3</sub>	.158(39)		.222(0.8)	.	216
	F	.144(38)		.188(0.5)	.	
CF <sub>3</sub>	CF <sub>3</sub>	.134(34)	.181(2.5)	.154(0.4)	.	
	CN	.150(26)		.240(1.5)	.	
	CH <sub>3</sub> O	.177(39)		.243(0.8)	.	
	NO <sub>2</sub>	.150(28)		.189(0.4)	.	
	Cl	.140(24)		.203(0.6)	.	
	Br	.154(25)		.208(0.9)	.	

<i>X</i>	<i>Y</i>	<i>K</i>	<i>S<sub>A</sub></i>	<i>N</i>	<i>I</i>	<i>t<sub>calc</sub></i>
	(CH <sub>3</sub> ) <sub>2</sub> N	.235(32)	.253 <sup>c</sup>	.256 <sup>c</sup>	.	.
	CH <sub>3</sub>	.172(28)	.194(2.6)	.215(0.9).	.	.
	F	.120(19)	.	.153(0.2).	.	.

a. Taken from Ref. 5.

b. Taken from Ref. 7.

c. The combined enthalpy value is 5.3 kJ mol<sup>-1</sup>.

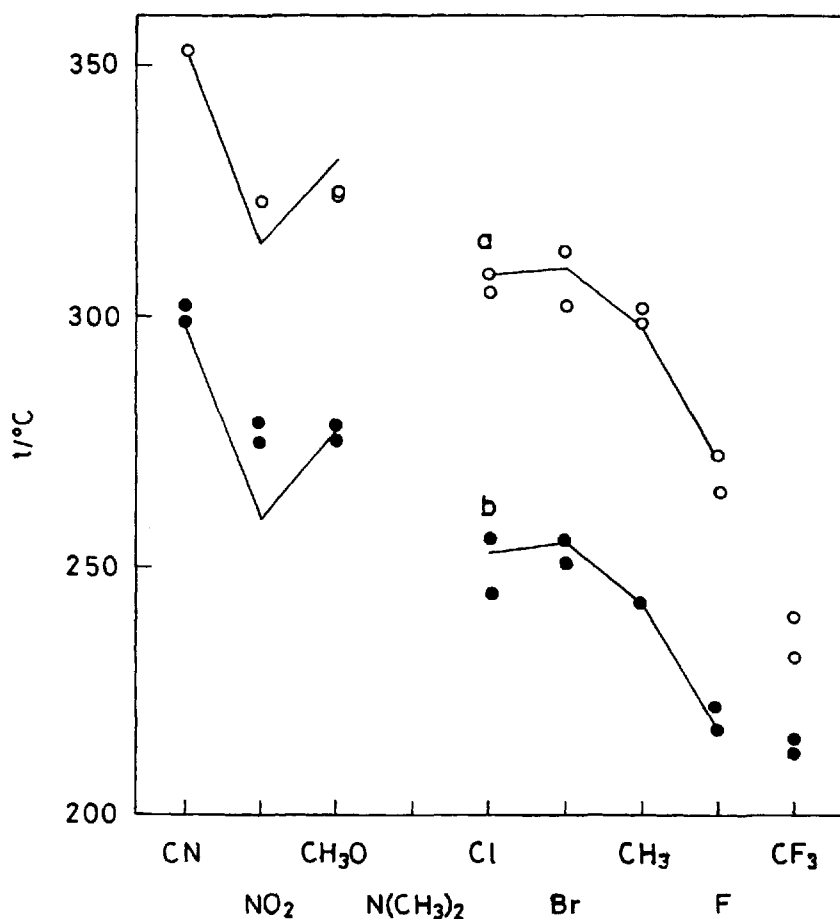


FIGURE 4 Plots of N-I transition temperatures of compound 2 in the order of terminal groups given below. (a) CN series ( $X$  or  $Y=\text{CN}$ ) ○ and (b) CH<sub>3</sub> series ( $X$  or  $Y=\text{CH}_3$ ) ●

Finally, it must be noted that there are a few theoretical studies of model mesogens with multipolar interactions but the conclusions are not in agreement with each other. Williamson and Rio presented the theory for the N-I transition of dipolar hard-spherocylinders which explicitly includes three-body interactions in the orientationally ordered phase and predicted the destabilization with respect to the isotropic phase in sharp contrast to our results [12]. These authors suggested that the reason for the stabilization of the nematic phase predicted by earlier theories lies in the two-body character of their approach.

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