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Effects of Terminal Substituents on Mesomorphic Properties. 4-(4-*X*-Substituted Benzylideneamino)phenyl 4-*Y*-Substituted Benzoates

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Nematic–isotropic transition temperature was determined for 4-(4-*X*-benzylideneamino)phenyl 4-*Y*-benzoates, where *X* and *Y* were chosen from methoxy, nitro, chloro, bromo, dimethylamino, methyl, fluoro, trifluoromethyl groups. The order of group (*X* or *Y*) efficiency in promoting the nematic–isotropic transition temperature is markedly affected by the nature of the group (*Y* or *X*) located at the other end. For example, the methoxy and methyl series give $NO_2 > CH_3O > N(CH_3)_2 > Cl \fallingdotseq Br > CH_3 > F > CF_3$, whereas the trifluoromethyl series gives $N(CH_3)_2 > CH_3O > CH_3 > Cl \fallingdotseq Br > NO_2 > F$, suggesting that the dipole–dipole interaction contributes significantly to the stabilization of the nematic phase.

Keywords: Nematic; terminal substituent; dipole–dipole interaction

INTRODUCTION

Terminal substituents are known to be one of the most significant molecular features affecting mesomorphic properties. More than thirty years ago, Gray compiled the nematic–isotropic (N–I) transition temperatures of four series of compounds and constructed the following order of efficiency in promoting nematic–isotropic transition temperatures by

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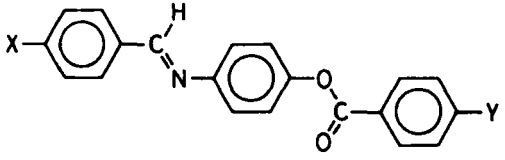
terminal substituents [1].

$$\text{Ph} > \text{NHCOCH}_3 > \text{CN} > \text{CH}_3\text{O} > \text{NO}_2 > \text{Cl} > \text{Br} > \text{N(CH}_3)_2 > \text{CH}_3 > \text{F} > \text{H}$$

Later, Coates and Gray examined two nonmesogenic trifluoromethyl compounds and located the CF_3 group in the order between F and H based on the virtual N–I transition temperatures [2]. This order is purely empirical. Employing the molecular statistical theory of Maier and Saupe, Van der Veen demonstrated a linear relationship between the N–I transition temperature and the anisotropy in the polarizability for C—*X* bonds within two series of compounds, where X = F, CH_3 and Cl [3]. He suggested that the relationship cannot be applied to larger substituents because of their excluded volume effects. The X-ray diffraction work by Leadbetter *et al.*, showed the head-to-tail association of 4-alkyl-4′-cyanobiphenyl molecules in the nematic phase [4]. Dipole–dipole interaction in the mesophase is supposed be more important than that in an isotropic phase because of the orientational ordering of the former phase.

A study on 4-*X*-substituted phenyl 4-(trans-4-pentylcyclohexyl) benzoates by Dabrowski *et al.*, revealed that the N–I transition temperature of the $N(CH_3)_2$ derivative is as high as the CH_3O derivative [5]. Further disagreement with the afore-mentioned order was noted by Takeda *et al.*, for 4′-octyloxybiphenyl-4-yl 4-*X*-benzoates, when $X = CH_3O$, NO_2, Cl and Br [6]. Finally, our previous work on phenyl 4-(4-benzylideneamino) benzoate and its isomeric compounds bearing only one terminal substituent showed that the NO_2 derivatives exhibit higher N–I transition temperatures compared to the CH_3O derivatives, the difference being as large as 23 to 44°C [7]. These inconsistencies may imply that the so-called group efficiency in promoting the N–I transition temperature is not separable from other features of the molecule. Therefore, we proceeded to a systematic study on the N–I transition temperature of compounds bearing two terminal groups. An exploratory work on 4-(4-*X*-substituted benzylideneamino)phenyl 4-*Y*-substituted benzoates (1), where *X* and *Y* are CH_3O, NO_2, Cl, Br, $N(CH_3)_2$, CH_3, F and CF_3, is now described. The present molecular core is one of those examined by Funakoshi *et al.*, and is known to produce a compound



(1)

with the highest N – I transition temperature among the isomeric ones when X is an electron-withdrawing group and Y = H.

EXPERIMENTAL

All the 4-X-substituted benzoic acids and 4-Y-substituted benzaldehydes were commercially available. The desired compound was prepared by condensing a benzaldehyde with 4-aminophenol in refluxing ethanol and then the resulting Schiff's base with a benzoic acid in chloroform at room temperature by the carbodiimide method [8]. The products were purified by recrystallizations from appropriate solvents until sharp constant transition temperatures were recorded. If the compound is insoluble making separation from bis(cyclohexyl) urea difficult, the reaction mixture is dried, and then washed or boiled with a large amount of acetone in order to extract the latter compound, thus aiding purification. Mesophase identification and transition temperature measurements were carried out using a Yanaco melting point apparatus, model PV-500V, with the aid of a polarizing microscope (magnification 60 X) and also a Rigaku differential scanning calorimeter, model TAS-300 DSC8240D.

RESULTS AND DISCUSSION

The transition temperatures and associated enthalpies of sixty-four compounds are summarized in Table I. Here, K, S_A, N and I stand for the crystalline, smectic A, nematic, and isotropic phases, respectively. Hereafter, each compound will be abbreviated as [X, Y]. Almost all the present derivatives possess an enantiotropic N – I transition. Exceptions are [$N(CH_3)_2$, $N(CH_3)_2$] and [CF_3, CF_3]. The former derivative shows only an S phase and the latter shows none. The assignment of the N phase was made on the basis of a schlieren texture. The S phase was readily characterized to be of the A type by the coexistence of fan-shaped and homeotropic textures.

In Figure 1, the N – I transition temperatures of the CH_3O series, [CH_3O, Y] and [X, CH_3O], and CH_3 the series, [CH_3, Y] and [X, CH_3], (shown by open circles) are arranged in the order of decreasing the group (Y or X) efficiency of N phase generation of substituents cited above. These transition temperatures are supplemented with the data for some isomeric compounds given in Table II (shown by shaded circles). The latter values are mostly below the former ones, reflecting the effects of the position and direction of

TABLE I Transition temperatures (°C) and enthalpy changes ($kJ\,mol^{-1}$) of 4-(4-*X*-benzylideneamino)phenyl 4-*Y*-benzoates

X	*Y*	*K*	S_A	*N*	*I*
CH_3O	CH_3O	.150(41)		.307(2.3)	.
	NO_2	.167(34)		decomp.	
	Cl	.158(40)		.290(2.2)	.
	Br	.183(46)		.290(1.5)	.
	$N(CH_3)_2$	.196(34)		.294(2.6)	.
	CH_3	.125(31)		.282(2.4)	.
	F	.153(30)		.264(1.4)	.
	CF_3	.156(33)		.245(1.0)	.
NO_2	CH_3O	.176(45)		.315(0.9)	.
	NO_2	.243(29)		.287(1.2)	.
	Cl	.194(29)		.290(1.0)	.
	Br	.216(33)		.296(1.6)	.
	$N(CH_3)_2$	.249(46)		decomp.	
	CH_3	.166(36)		.295(0.8)	.
	F	.170(33)		.248(1.0)	.
	CF_3	.188(36)		.206(0.6)	.
Cl	CH_3O	.142(30)		.292(1.4)	.
	NO_2	.180(31)		.284(1.7)	.
	Cl	.170(37)		.266(1.0)	.
	Br	.180(40)		.265(1.1)	.
	$N(CH_3)_2$	.194(27)		.274(1.7)	.
	CH_3	.153(25)		.261(1.5)	.
	F	.150(35)		.233(1.0)	.
	CF_3	.161(38)		.211(0.9)	.
Br	CH_3O	.148(38)		.289(1.8)	.
	NO_2	.204(33)		.293(1.6)	.
	Cl	.180(38)		.265(1.0)	.
	Br	.190(43)		.262(1.1)	.
	$N(CH_3)_2$	.194(25)		.268(1.5)	.
	CH_3	.179(39)		.257(1.0)	.
	F	.161(36)		.233(0.9)	.
	CF_3	.177(40)		.213(0.9)	.
$N(CH_3)_2$	CH_3O	.194(42)		.292(2.4)	.
	NO_2	.198(33)		decomp.	
	Cl	.184(36)		.273(1.6)	.
	Br	.188(38)		.264(1.4)	.
	$N(CH_3)_2$	.252(29)	.283(3.6)		.
	CH_3	.290(40)		.261(1.6)	.
	F	.180(34)		.253(0.8)	.
	CF_3	.191(34)		.241(1.7)	.
CH_3	CH_3O	.142(38)		.280(1.9)	.
	NO_2	.160(37)		.284(1.1)	.
	Cl	.153(34)		.256(1.3)	.
	Br	.166(35)		.252(1.0)	.
	$N(CH_3)_2$	.232(43)		.262(1.9)	.
	CH_3	.172(27)		.242(1.7)	.
	F	.132(33)		.226(1.3)	.
	CF_3	.178(21)	.202(2.7)	.219(1.1)	.
F	CH_3O	.118(35)		.257(1.5)	.
	NO_2	.159(35)		.238(0.9)	
	Cl	.157(35)		.226(1.0)	.

TABLE I (Continued)

X	Y	K	S_A	N	I
	Br	.165(31)		.225(0.5)	.
	$N(CH_3)_2$	.223(41)		.253(1.5)	.
	CH_3	.133(33)		.230(1.2)	.
	F	.151(38)		.200(0.9)	.
	CF_3	.138(33)		.169(0.5)	.
CF_3	CH_3O	.157(26)	.179(0.4)	.246(1.1)	.
	NO_2	.186(34)		.197(0.6)	.
	Cl	.164(29)		.208(0.8)	.
	Br	.178(31)		.208(0.7)	.
	$N(CH_3)_2$	.202(32)		.249(1.2)	.
	CH_3	.183(21)	.215(3.4)	.226(0.9)	.
	F	.137(31)	.157(0.2)	.173(0.8)	.
	CH_3	.186(35)			

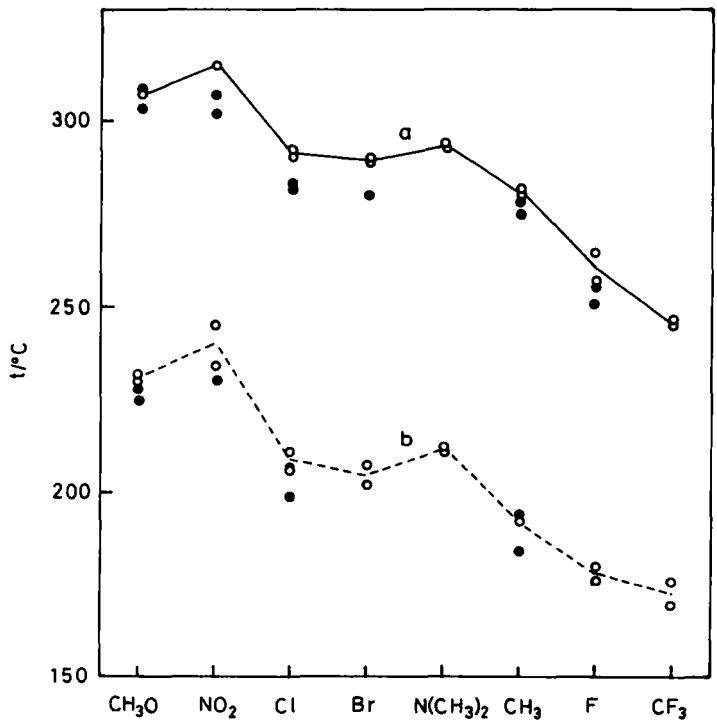


FIGURE 1 Plots of N–I transition temperatures in the order of terminal group (Y or X) efficiency of N phase generation proposed by Gray, (a) CH_3O series, [CH_3O, Y] and [X, CH_3O], and (b) CH_3 series, [CH_3, Y] and [X, CH_3]. The temperatures in the latter series are shifted downward by 50°C. The data given in Table I are shown by open circles and those given in Table II are shown by shaded circles.

TABLE II Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of supplemental compounds

Compound	*K*	*N*	*I*
CH_3O —Φ— CH = N —Φ— COO —Φ— OCH_3	·162(42)	·303(2.0)	·
CH_3O —Φ— CH = N —Φ— COO —Φ— NO_2	·212(51)	·302(0.8)	·
CH_3O —Φ— CH = N —Φ— COO —Φ— Cl	·194(43)	·283(0.8)[a]	·
NO_2 —Φ— CH = N —Φ— COO —Φ— OCH_3	·163(36)	·307(1.1)	·
NO_2 —Φ— CH = N —Φ— COO —Φ— CH_3	·166(33)	·280(1.2)	·
Cl —Φ— CH = N —Φ— COO —Φ— OCH_3	·180(41)	·281(0.8)[a]	·
Cl —Φ— CH = N —Φ— COO —Φ— Cl	·156(32)	·255(1.0)	·
Cl —Φ— CH = N —Φ— COO —Φ— CH_3	·184(35)	·249(0.8)	·
Br —Φ— CH = N —Φ— COO —Φ— Br	·181(35)	·257(0.8)	·
CH_3 —Φ— CH = N —Φ— COO —Φ— CH_3	·156(34)	·234(1.1)	·
CH_3O —Φ— N = CH —Φ— COO —Φ— Cl	·170(39)	·290(0.8)[a]	·
Cl —Φ— N = CH —Φ— COO —Φ— OCH_3	·168(39)	·284(0.8)[a]	·
Br —Φ— N = CH —Φ— COO —Φ— OCH_3	·169(42)	·280(0.7)[b]	·
CH_3 —Φ— N = CH —Φ— COO —Φ— OCH_3	·149(36)	·275(0.9)[b]	·
F —Φ— N = CH —Φ— COO —Φ— OCH_3	·146(36)	·251(0.8)[b]	·
CH_3O —Φ— N = CH —Φ— OOC —Φ— OCH_3	·153(39)	·308(2.2)	·
CH_3O —Φ— N = CH —Φ— OOC —Φ— Cl	·179(41)	·290(1.2)[a]	·
CH_3O —Φ— N = CH —Φ— OOC —Φ— CH_3	·138(38)	·281(1.5)	·
NO_2 —Φ— N = CH —Φ— OOC —Φ— NO_2	·235(47)	·280(1.1)	·
NO_2 —Φ— N = CH —Φ— OOC —Φ— Cl	·184(35)	·281(1.5)	·
Cl —Φ— N = CH —Φ— OOC —Φ— OCH_3	·172(27)	·285(1.6)[c]	·
Cl —Φ— N = CH —Φ— OOC —Φ— Cl	·146(28)	·256(1.0)[c]	·
Cl —Φ— N = CH —Φ— OOC —Φ— CH_3	·169(29)	·257(0.6)[c]	·
Br —Φ— N = CH —Φ— OOC —Φ— OCH_3	·187(38)	·280(0.9)[c]	·
CH_3 —Φ— N = CH —Φ— OOC —Φ— OCH_3	·129(28)	·278(1.1)[c]	·
CH_3 —Φ— N = CH —Φ— OOC —Φ— Cl	·167(32)	·256(1.0)	·
CH_3 —Φ— N = CH —Φ— OOC —Φ— CH_3	·169(35)	·244(1.0)	·
F —Φ— N = CH —Φ— OOC —Φ— OCH_3	·131(32)	·255(0.8)[c]	·

[a] Taken from Ref. [9].
[b] Taken from Ref. [10].
[c] Taken from Ref. [11].

the linkage groups in the molecule but follow the tendencies shown by compounds 1. The lines are drawn only as a guide for the eyes ignoring the shaded circles. Note that, for convenience, the temperatures of the second series not only in this figure but also in the following ones are shifted downward by 50°C. The two plots are alike and are supposed to follow well the order given by Gray [1]. Nevertheless, the N – I transition temperature of the CH_3O derivatives is lower than those of the NO_2 derivatives; compare [CH_3O, CH_3O] with [NO_2, CH_3O] and [CH_3, CH_3O] and [CH_3O, CH_3] with [CH_3, NO_2] and [NO_2, CH_3], in qualitative agreement with the results reported by Funakoshi *et al.* [7]. Furthermore, the transition temperatures of the $N(CH_3)_2$ derivatives are clearly higher than those of the Cl and Br derivatives but lower than those of the CH_3O derivatives.

The behavior of the F and CF_3 series shown in Figure 2 differs markedly from that of the afore-mentioned series. In the F series, the NO_2 derivative

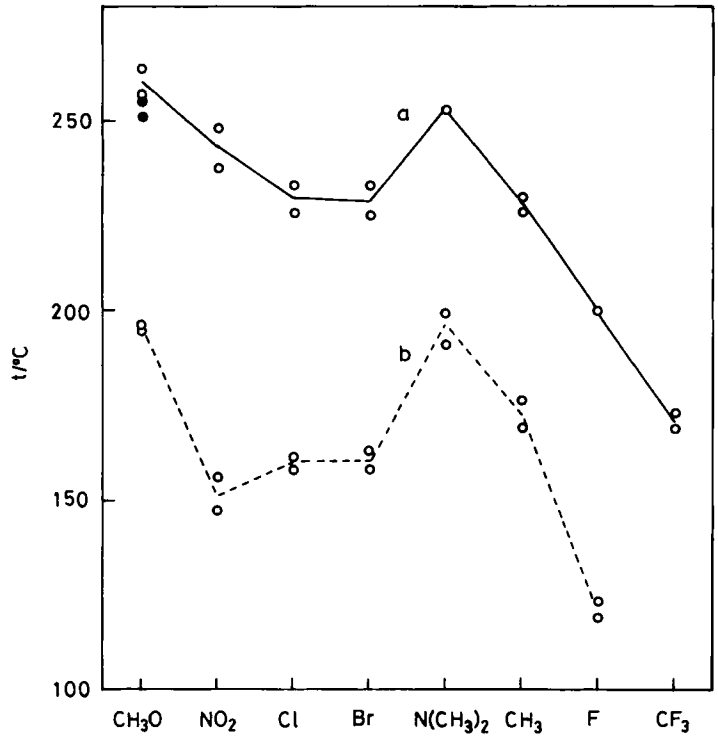


FIGURE 2 Plots of N–I transition temperatures in the order of terminal group (Y or X) efficiency of N phase generation proposed by Gray, (a) F series, [F, Y] and [X, F], and (b) CF_3 series, [CF_3, Y] and [X, CF_3]. The temperatures in the latter series are shifted downward by 50°C. As to open and shaded circles, see the caption of Figure 1.

follows the order proposed by Gray, that is, it clears at a temperature lower by 18°C on average than the CH_3O derivative but higher than the Cl and Br derivatives. On the other hand, the N–I transition of the NO_2 derivatives in the CF_3 series is located lower than those of the Cl and Br derivatives. The $N(CH_3)_2$ derivatives in these two series exhibit N–I transition temperatures higher by about 25 to 35°C than the Cl and Br derivatives. They are followed by the very steep fall of the N–I transition. For example, the temperature difference between the $N(CH_3)_2$ and CF_3 derivatives in the F series is about 80°C compared with about 40 to 50°C for the CH_3O and CH_3 series. The slope is even steeper in the CF_3 series.

The N–I transition temperatures for the Cl and Br series are plotted in Figure 3. It may be noted that the plot for the Br series bears fairly close similarity to that for the CH_3O series. On the other hand, the transitions given by the CH_3O and NO_2 derivatives of the Cl series are located at nearly

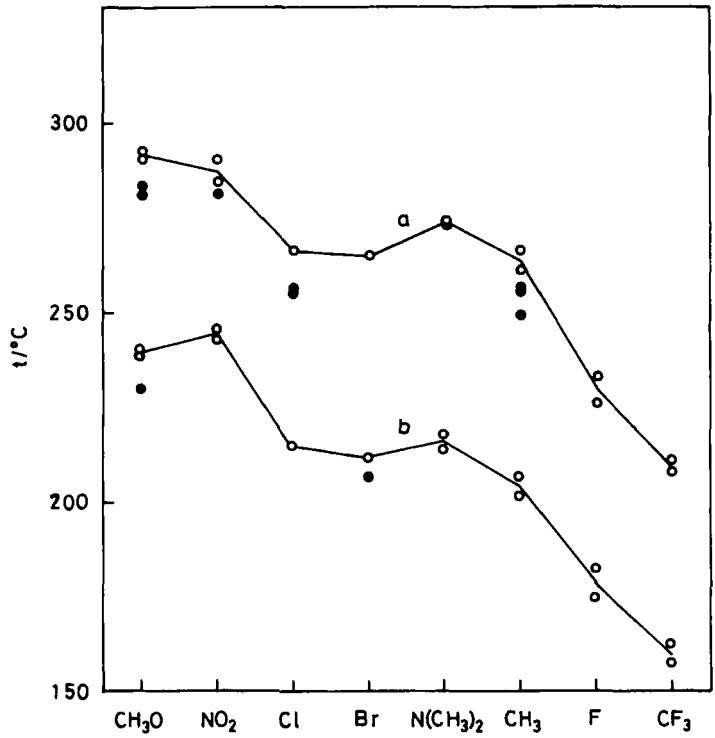


FIGURE 3 Plots of N–I transition temperatures in the order of terminal group (*Y* or *X*) efficiency of N phase generation proposed by Gray, (a) Cl series, [Cl, *Y*] and [*X*, Cl], and (b) Br series, [Br, *Y*] and [*X*, Br]. The temperatures in the latter series are shifted downward by 50°C. As to open and shaded circles, see the caption of Figure 1.

the same temperature. The $N(CH_3)_2$ derivatives give higher temperatures than the Cl and Br derivatives and the differences among these three derivatives are less significant in the Br series. The transition temperature in the Cl series between the $N(CH_3)_2$ and CF_3 derivatives falls more steeply than that in the Br series.

The behavior of the NO_2 series could not be fully studied (see Fig. 4). Due to decomposition occurring in the nematic phase, it was not possible to observe the transition into an isotropic liquid for both dark violet colored [$N(CH_3)_2$, NO_2] and orange colored [NO_2, $N(CH_3)_2$], but the plot of the rest appears to bear some resemblance to that of the CF_3 series. The temperature difference between the NO_2 and CH_3 derivatives is small and that between the CH_3 and F derivatives is as large as those in the F and CF_3 series. It is interesting to see that the N–I transition temperature of [NO_2, CF_3] is much lower than that of the parent compound, 223°C of [NO_2, H], reported by

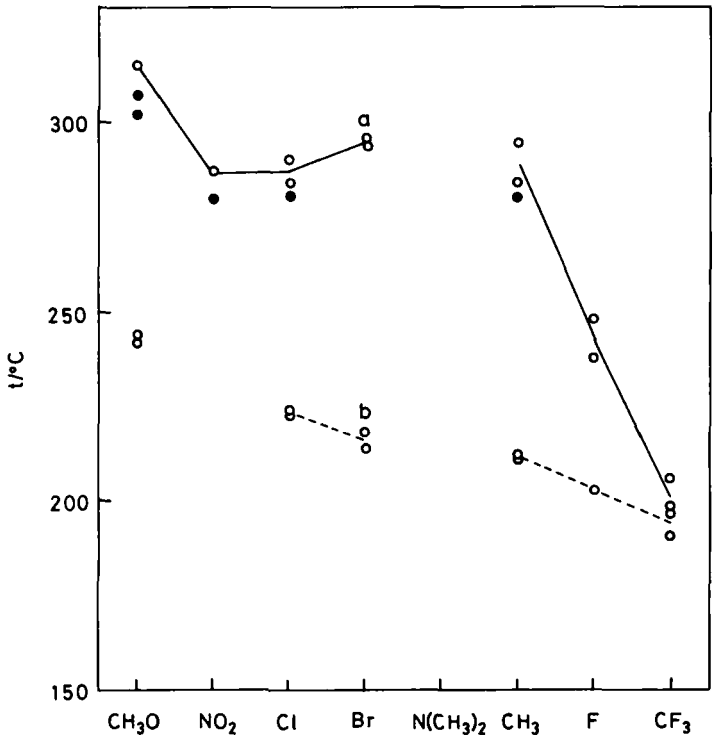


FIGURE 4 Plots of N–I transition temperature in the order of terminal group (Y or X) efficiency of N phase generation proposed by Gray, (a) NO_2 series, [NO_2, Y] and [X, NO_2], and (b) $N(CH_3)_2$ series, [$N(CH_3)_2$, Y] and [X, $N(CH_3)_2$]. The temperatures in the latter series are shifted downward by 50°C. As to open and shaded circles, see the caption of Figure 1.

Funakoshi *et al.* [7]. Thus, the substitution at terminal positions does not necessarily give rise to a promotion of the N–I transition temperature. This finding is in sharp conflict to the remark made by Gray that all the terminal substituents enhance the nematic thermal stabilities [1].

As is shown in Figure 4, the data for the $N(CH_3)_2$ series are rather fragmental; nevertheless, the transition temperature difference between the CH_3O and CF_3 derivatives is definitely less than those for the CH_3O and F series. The Cl derivatives give markedly higher transition temperatures than the Br derivatives in contrast to the NO_2 series.

Summarizing the above results, we obtain a remarkably different order of group efficiency in promoting N–I transition temperatures for each series carrying a fixed substituent; namely, for the CH_3O and CH_3 series

$$NO_2 > CH_3O > N(CH_3)_2 > Cl \fallingdotseq Br > CH_3 > F > CF_3$$

for the $N(CH_3)_2$ series

$$CH_3O > Br > Cl > Br > CU_3 > F > CF_3.$$

These two seem to be in agreement with each other. However, we obtains for the NO_2 series

$$CH_3O > Br > NO_2 \fallingdotseq Cl \fallingdotseq CH_3 > F > CF_3$$

for the Cl series

$$CH_3O \fallingdotseq NO_2 > N(CH_3)_2 > Cl \fallingdotseq Br \fallingdotseq CH_3 > F > CF_3$$

for the F series

$$CH_3O > N(CH_3)_2 > NO_2 > Cl \fallingdotseq Br \fallingdotseq CH_3 > F > CF_3$$

and for the CF_3 series

$$N(CH_3)_2 > CH_3O > CH_3 > Cl \fallingdotseq Br > NO_2 > F.$$

It must be emphasized that the substituents in the last-mentioned order are sharply divided into electron-donating and -withdrawing ones. Apparently, a strong longitudal dipole arising from the two substituents of different polarities leads to comparatively high N–I transition temperatures and a weak dipole arising from the two substituents of the similar polarities leads to low N–I transition temperatures, suggesting that the contribution of dipole–dipole interaction to the thermal stability is particularly important in the anisotropic liquid phase given by the CF_3 series. The CF_3 series may be the most suitable choice to demonstrate the significance of dipole–dipole interaction as its contribution is expected to be more influential when the N–I transition temperature is low.

Taking the efficiency order for the CH_3O and CH_3 series as the reference, the shift of the NO_2 group in the orders displayed by the F, Cl, and NO_2 series may be attributed to a weak dipole moment resulting from the substituents of similar polarities but the effects are not so evident as those in the CF_3 series. These observations are not unexpected because the change of the terminal substituent influences not only the dipole moment of the molecule but also the molecular volume, configuration, polarizability, rigidity *etc.* They are all well-known factors governing the thermal stability of the mesophase.

The variation in the transition temperature difference between the CH_3O and CF_3 (or F) series can be correlated to the nature of the substituents. If X

is an electron-donating substituent, [X, CH_3O] gives a relatively low transition temperature and [X, CF_3] and [X, F] give relatively high temperatures. The reverse is true if X is an electron-withdawing substituent. Indeed, the following order of the temperature difference between the CH_3O and F series is obtained: $NO_2 \fallingdotseq CF_3 > Cl \fallingdotseq Br \fallingdotseq F > CH_3 > CH_3O > N(CH_3)_2$. Here again, the electron-withdrawing groups and the electron-donating groups are well separated. A further work on this subject is now in progress.

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