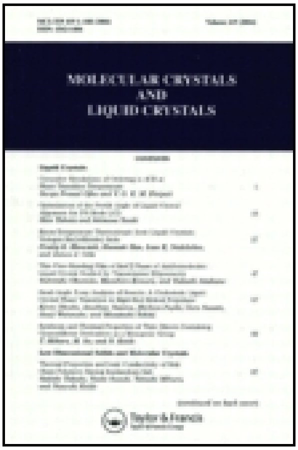

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# Nematic-Isotropic Transition Temperature and Dipole-Dipole Interaction. 4-X-Substituted Phenyl 4-(4-Y-Substituted Benzylideneamino)-benzoates

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

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The nematic-isotropic transition temperature of 4-X-phenyl 4-(4-Y-benzylideneamino)benzoates, where the terminal groups X and Y are CN, $CH_3O$, $NO_2$, Cl, Br, N $(CH_3)_2$, $CH_3$, F, or $CF_3$, was examined. The transition temperature difference between the two series, in which X or Y=$CH_3O$ and F, respectively, decreases in this order: $CF_3 > NO_2 > Cl \fallingdotseq Br \fallingdotseq F > CN > CH_3 > CH_3O > N(CH_3)_2$. Thus, the groups are almost in the order of substituent constants except for the CN group, suggesting that the dipole-dipole interaction contributes significantly to the nematic thermal stability and also that the effective dipole moment of the molecule bearing CN and $CH_3O$ groups is markedly reduced in the mesophase from that of the free molecule because of the anti-parallel molecular association.

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

## INTRODUCTION

Our previous study on the nematic-isotropic (N-I) transition temperature of 4-(4-X-benzylideneamino)phenyl 4-Y-benzoates (1) bearing $CH_3O$, $NO_2$, Cl, Br, N $(CH_3)_2$, $CH_3$, F, or $CF_3$ groups as X and Y, revealed that the order of group efficiency in promoting the nematic thermal stability is markedly affected by the

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nature of the group fixed at the other end of the molecule [1]. While the $CH_3O$ and $CH_3$ series, in which X or Y=$CH_3O$ and $CH_3$, respectively, yield

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

the F series gives

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

and the $CF_3$ series gives

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

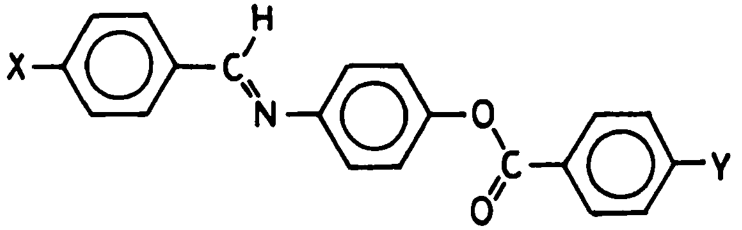
The groups in the last-mentioned order are clearly divided into electron-donating and -withdrawing groups. Apparently, a strong longitudinal dipole arising from the two terminal groups of different polarities leads to comparatively high N-I transition temperatures, indicating that the contribution of dipole-dipole interaction to the nematic thermal stability is not marginal. Such effects are more evidently manifested when the transition temperature of the $CH_3O$ derivative is compared with that of the F or $CF_3$ derivative because the temperature of the former derivative is promoted when the second group is electron-withdrawing and the latter is promoted when the second group is electron-donating. Indeed, the difference in N-I transition temperature between the $CH_3O$ and F series is found in the following order:

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

The difference decreases from 75°C between the $CH_3O$-$CF_3$ and F-$CF_3$ derivatives to 40°C between the $CH_3O$-$N(CH_3)_2$ and F-$N(CH_3)_2$ derivatives. Here, the groups are almost in the order of increasing substituent constants, confirming that the contribution of dipole-dipole interaction to the stabilization of the nematic phase is substantial. In order to demonstrate the generality of our observations, we examined a series of the isomeric compound, 4-X-phenyl 4-(4-Y-benzylideneamino) benzoate (2), in which the carbonyloxy group in compound 1 is inverted.

## EXPERIMENTAL

All the 4-X-substituted phenols and 4-Y-substituted benzaldehydes employed in this work were commercial products. Preparation of the compounds, transition temperature measurement, and mesophase identification were carried out as described in our previous paper [1].



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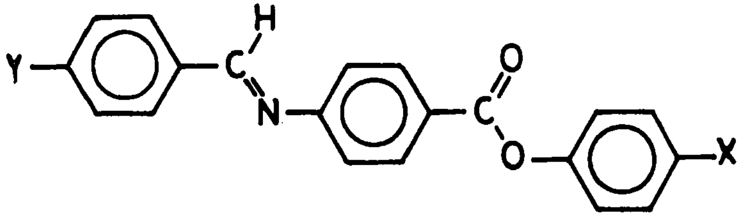

2

## RESULTS AND DISCUSSION

The liquid crystalline transition temperatures and the associated enthalpies of compound 2 are listed in Table I. Here, K, N, $S_A$, and I stand for the crystalline, nematic, smectic A, and isotropic phases, respectively.

TABLE I Transition temperatures (°C) and associated enthalpies (kJ $mol^{-1}$) of compound 2

| *X* | *Y* | *K* | $S_A$ | *N* | *I* |
|---|---|---|---|---|---|
| CN | $CH_3O$ | . 169 (38) | | . 321 (1.6) | . |
| | $NO_2$ | . 199 (40) | | . 318 (1.3) | . |
| | Cl | . 179 (41) | | . 299 (2.1) | . |
| | Br | . 182 (36) | | . 303 (1.7) | . |
| | $N(CH_3)_2$ | . 170 (34) | | . 312 (1.9) | . |
| | $CH_3$ | . 180 (37) | | . 295 (1.7) | . |
| | F | . 153 (39) | | . 263 (1.0) | . |
| | $CF_3$ | . 163 (36) | | . 225 (1.1) | . |
| $CH_3O$ | CN | . 172 (43) | | . 330 (1.8) | . |
| | $CH_3O$. | . 162 (42) | | . 303 (2.0)[a] | . |
| | $NO_2$ | . 163 (36) | | . 307 (1.1)[a] | . |
| | Cl | . 180 (41) | | . 281 (0.8)[b] | . |
| | Br | . 188 (34) | | . 280 (1.3) | . |
| | $N(CH_3)_2$ | . 179 (39) | | . 287 (0.8) | . |

| $X$ | $Y$ | $K$ | $S_A$ | $N$ | $I$ |
|---|---|---|---|---|---|
| | $CH_3$ | . 155 (34) | | . 267 (1.3) | . |
| | F | . 174 (42) | | . 249 (1.0) | . |
| | $CF_3$ | . 199 (28) | . 222 (5.1) | . 241 (0.8) | . |
| $NO_2$ | $CH_3O$ | . 212 (51) | | . 302 (0.8)[a] | . |
| | $NO_2$ | . 226 (48) | | . 270 (0.5) | . |
| | Cl | . 175 (41) | | . 264 (0.5) | . |
| | Br | . 186 (40) | | . 272 (0.6) | . |
| | $CH_3$ | . 195 (45) | | . 270 (0.5) | . |
| | F | . 196 (43) | | . 220 (0.4) | . |
| | $CF_3$ | . 154 (36) | | . 176 (0.3) | . |
| Cl | CN | . 181 (39) | | . 311 (2.5) | . |
| | $CH_3O$ | . 194 (43) | | . 283 (0.8)[b] | . |
| | $NO_2$ | . 167 (34) | | . 275 (0.7) | . |
| | Cl | . 156 (32) | | . 255 (1.0)[a] | . |
| | Br | . 154 (29) | | . 255 (0.9) | . |
| | $N(CH_3)_2$ | . 216 (37) | | . 265 (1.0) | . |
| | $CH_3$ | . 186 (34) | | . 248 (0.7) | . |
| | F | . 180 (46) | | . 218 (0.5) | . |
| | $CF_3$ | . 157 (31) | | . 198 (0.4) | . |
| Br | CN | . 193 (42) | | . 313 (2.0) | . |
| | $CH_3O$ | . 210 (49) | | . 281 (0.9) | . |
| | $NO_2$ | . 181 (27) | | . 282 (0.9) | . |
| | Cl | . 177 (35) | | . 255 (0.7) | . |
| | Br | . 181 (35) | | . 258 (0.9) | . |
| | $N(CH_3)_2$ | . 224 (35) | | . 262 (0.8) | . |
| | $CH_3$ | . 205 (37) | | . 246 (0.5) | . |
| | F | . 181 (38) | | . 216 (0.5) | . |
| | $CF_3$ | . 173 (36) | | . 201 (0.4) | . |
| $CH_3$ | CN | . 200 (42) | | . 307 (2.1) | . |
| | $CH_3O$ | . 141 (33) | | . 271 (1.4) | . |
| | $NO_2$ | . 166 (33) | | . 280 (1.2)[a] | . |
| | Cl | . 184 (35) | | . 249 (0.9) | . |
| | Br | . 189 (34) | | . 248 (0.9) | . |
| | $N(CH_3)_2$ | . 192 (39) | | . 254 (1.0) | . |
| | $CH_3$ | . 156 (34) | | . 234 (1.1) | . |
| | F | . 185 (41) | | . 217 (0.7) | . |
| | $CF_3$ | . 202 (30) | . 231 (10) | | . |
| F | CN | . 166 (34) | | . 274 (1.3) | . |

| *X* | *Y* | *K* | $S_A$ | *N* | *I* |
|---|---|---|---|---|---|
|  | $CH_3O$ | .158 (39) |  | .254 (1.0) | . |
|  | $NO_2$ | .154 (39) |  | .227 (0.6) | . |
|  | Cl | .191 (47) |  | .218 (0.5) | . |
|  | Br | .185 (45) |  | .218 (0.7) | . |
|  | $N(CH_3)_2$ | .184 (38) |  | .243 (1.0) | . |
|  | $CH_3$ | .157 (36) |  | .216 (0.9) | . |
|  | F | .186 (42) |  | .188 (0.5) | . |
|  | $CF_3$ | .136 (35) |  | .158 (0.4) | . |
| $CF_3$ | CN | .171 (29) |  | .233 (1.2) | . |
|  | $CH_3O$ | .205 (35) | .214 (1.7) | .241 (0.5) | . |
|  | $NO_2$ | .164 (33) |  | .178 (0.4) | . |
|  | Cl | .159 (29) |  | .191 (0.4) | . |
|  | Br | .163 (29) |  | .195 (0.6) | . |
|  | $N(CH_3)_2$ | .235 (39) |  | .249 (1.2) | . |
|  | $CH_3$ | .212 (22) | .225 (13) |  | . |
|  | F | .147 (33) |  | .150 (0.4) | . |

a. Taken from Ref. 1.
b. Taken from Ref. 2.

The $CH_3O$ series and the $CH_3$ series yield the same order of group efficiency in promoting N-I transition temperatures; that is,

$$\mathrm{CN} > \mathrm{NO_2} > \mathrm{CH_3O} > \mathrm{N(CH_3)_2} > \mathrm{Cl} > \mathrm{Br} > \mathrm{CH_3} > \mathrm{F} > \mathrm{CF_3}$$

and the F series gives

$$\mathrm{CN} > \mathrm{CH_3O} > \mathrm{N(CH_3)_2} > \mathrm{NO_2} > \mathrm{Cl} \fallingdotseq \mathrm{Br} > \mathrm{CH_3} > \mathrm{F} > \mathrm{CF_3}.$$

The arrangement of the terminal groups within these two orders is essentially the same except for the $NO_2$ group. The shift of the $NO_2$ group toward the end of the order in the F series is undoubtedly related to the nature of the fixed substituents, $CH_3O$ and F. While the combination of the electron-donating $CH_3O$ and electron-withdrawing $NO_2$ groups gives rise to an enhancement in the dipole moment, resulting in the shift of the $NO_2$ group toward the head of the order, the combination of the electron-withdrawing F and $NO_2$ groups gives rise to the cancellation of the moment. Thus, the order of group efficiency of promoting the N-I transition temperature is determined not only by the anisotropy of molecular polarizability but also by the dipole moment. It may be interesting to note that the N-I transition temperatures of the $NO_2$-$CF_3$ derivatives are lower than those of the $NO_2$-H derivatives; 176 vs. 210°C and 178 vs. 192°C respectively [3]. The destabilization of the nematic phase by the introduction of the $CF_3$ group to the molecules of the $NO_2$-H derivatives can be ascribed to the cancellation of the dipole moments arising from the two strongly electron-withdrawing terminal groups.

Naturally, the order given by the $NO_2$ series is different from those given by the $CH_3O$, $CH_3$, and F series; namely,

$$CH_3O > Br > CH_3 > NO_2 \doteq Cl > F > CF_3.$$

The $CF_3$ series, in which the derivatives available are not the same as those in the $NO_2$ series, yields the following order:

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

The latter closely resembles the one found for the same series of compound 1.

The difference in the N-I transition temperature between the two series, in which the fixed groups are electron-donating and -withdrawing respectively, provides an excellent means testing the contribution of dipole-dipole interaction to the nematic thermal stability [1]. In Figure 1, the N-I transition temperatures of the $CH_3O$ and F series are plotted in the order of decreasing the group efficiency of nematic phase generation observed for the $CH_3O$ series. The lines are drawn connecting the average values for the isomeric compounds, in which the positions of X and Y are interchanged if available, as a guide for the eyes. The separation decreases from 87°C between the $CH_3O$-$CF_3$ and F-$CF_3$ derivatives to 44°C between the $CH_3O$-N $(CH_3)_2$ and F-N $(CH_3)_2$ derivatives. The resulting order is as follows:

$$CF_3 > NO_2 > Cl \doteq Br \doteq F > CN > CH_3 > CH_3O > N(CH_3)_2,$$

which is very different from the orders given by the $CH_3O$ and F series themselves. The order of magnitude in the contribution of dipole-dipole interaction to the nematic thermal stability may be roughly estimated based on the following assumptions. The large separation between the $CH_3O$-$CF_3$ and F-$CF_3$ derivatives and also the $CH_3O$-$NO_2$ and F-$NO_2$ derivatives arises mostly from the promotion of N-I transition in the derivatives in the $CH_3O$ series and the small separation between the $CH_3O$-$N(CH_3)_2$ and F-$N(CH_3)_2$ derivatives from the promotion of N-I transition in the derivative in the F series. If so, the separation arising from the anisotropy of molecular polarizability may be about 60°C leaving roughly 20°C for the dipole-dipole interaction. The separation between the $CH_3O$-$CH_3O$ and F-$CH_3O$ derivatives and also the $CH_3O$-$CH_3$ and F-$CH_3$ derivatives are definitely smaller than 60°C; therefore, the stabilization of the nematic phase by dipole-dipole interaction in the F-$CH_3O$ and F-$CH_3$ derivatives is likely. Note that, compared with the estimated stabilization by dipole-dipole interaction, the variation in the N-I transition temperature in the $CH_3O$ series by the second substituent is as large as 90°C.

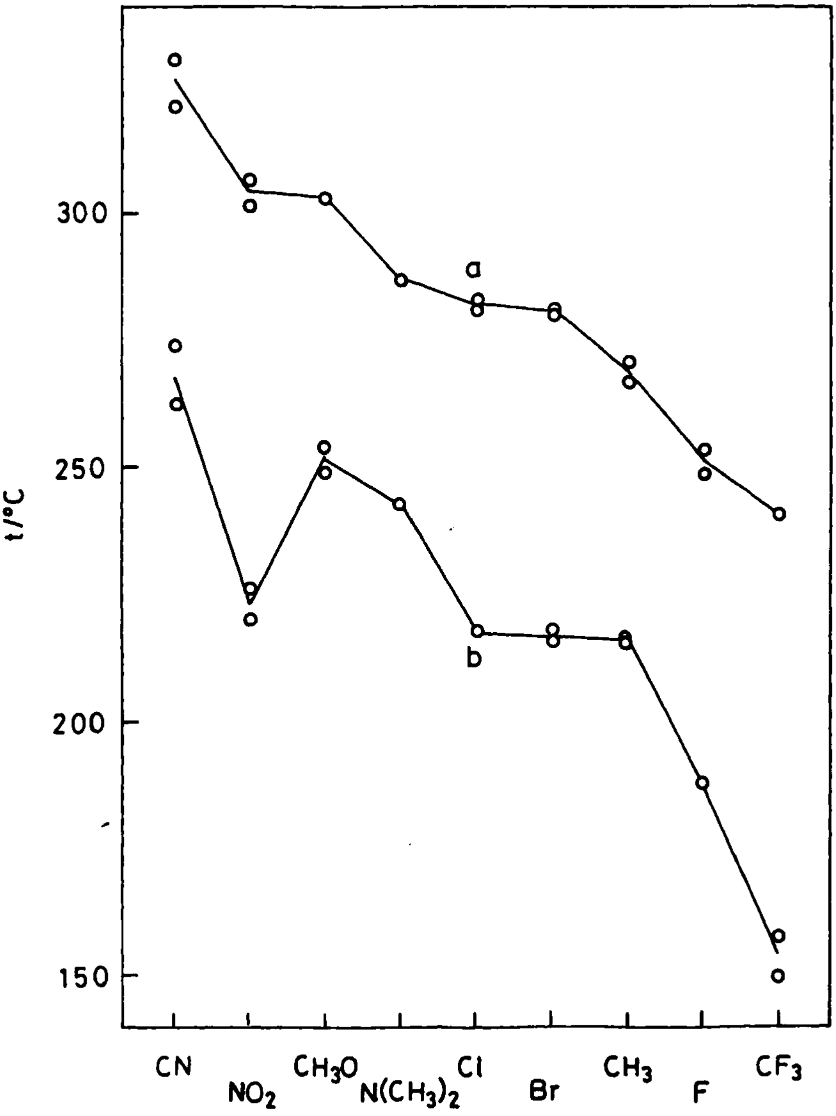

FIGURE 1 Plots of N-I transition temperatures in the order of terminal group efficiency of the nematic phase given by (a) $CH_3O$ series (X or Y=$CH_3O$) and (b) F series (X or Y=F)

The location of the CN group, which was not included in our earlier work, in the order given by the N-I transition temperature difference is anomalous in the sense that the group is strongly electron-withdrawing but it is found in the border between electron-withdrawing and -donating groups. This anomaly can be ensured by comparison of the nematic behavior between the CN and $CH_3$ series. The N-I transition temperatures of the CN and $CH_3$ series are compared in Figure 2. As the N-I transition temperatures of the $CH_3$ series are much lower than those of the CN series, the N-I transition temperature difference increases, in contrast to the afore-mentioned one, from 43°C between the CN-$NO_2$ and $CH_3$-$NO_2$ derivatives to 67°C between the CN-$CH_3$ and $CH_3$-$CH_3$ derivatives in the following order, when started from electron-withdrawing groups:

$$NO_2 < F < Cl < CH_3O < N(CH_3)_2 < Br < CH_3.$$

Contrary to the order obtained by the transition temperature difference between the $CH_3O$ and F series, the electron-donating $CH_3O$ and $N(CH_3)_2$ groups are shifted toward the head of the order, implying that the effective dipole moment of the molecules of the $CH_3O$-CN and N $(CH_3)_2$-CN derivatives in the nematic phase is considerably reduced compared with that of the free molecules.

The thermodynamic data of newly-determined fourteen CN derivatives of compounds 1 are presented in Table II and plotted in Figure 2 with shaded circles. The difference in the N-I transition temperature between the CN and $CH_3$ series changes dramatically, from 24°C between the CN-$CF_3$ and $CH_3$-$CF_3$ derivatives to 76°C between the CN-$CH_3$ and $CH_3$-$CH_3$ derivatives, and is found in the following order:

$$CF_3 < F < CH_3O < Cl < Br \doteqdot N(CH_3)_2 < CH_3.$$

TABLE II Transition temperatures (°C) and associated enthalpies (kJ $mol^{-1}$) of compound 1

| *X* | *Y* | *K* | *N* | *I* |
|---|---|---|---|---|
| CN | $CH_3O$ | . 161 (23) | . 335 (2.0) | . |
| CN | Cl | . 192 (31) | . 318 (2.6) | . |
| CN | Br | . 210 (30) | . 321 (2.3) | . |
| CN | $N(CH_3)_2$ | . 213 (33) | . 335 (2.3) | . |
| CN | $CH_3$ | . 166 (35) | . 317 (1.4) | . |
| CN | F | . 157 (30) | . 287 (1.4) | . |
| CN | $CF_3$ | . 187 (29) | . 248 (1.5) | . |
| $CH_3O$ | CN | . 183 (36) | . 332 (1.7) | . |
| Cl | CN | . 190 (27) | . 314 (2.2) | . |
| Br | CN | . 206 (26) | . 313 (2.4) | . |
| $N(CH_3)_2$ | CN | . 170 (34) | . 312 (1.9) | . |
| $CH_3$ | CN | . 184 (38) | . 318 (1.7) | . |
| F | CN | . 200 (45) | . 271 (1.1) | . |
| $CF_3$ | CN | . 203 (28) | . 245 (1.5) | . |

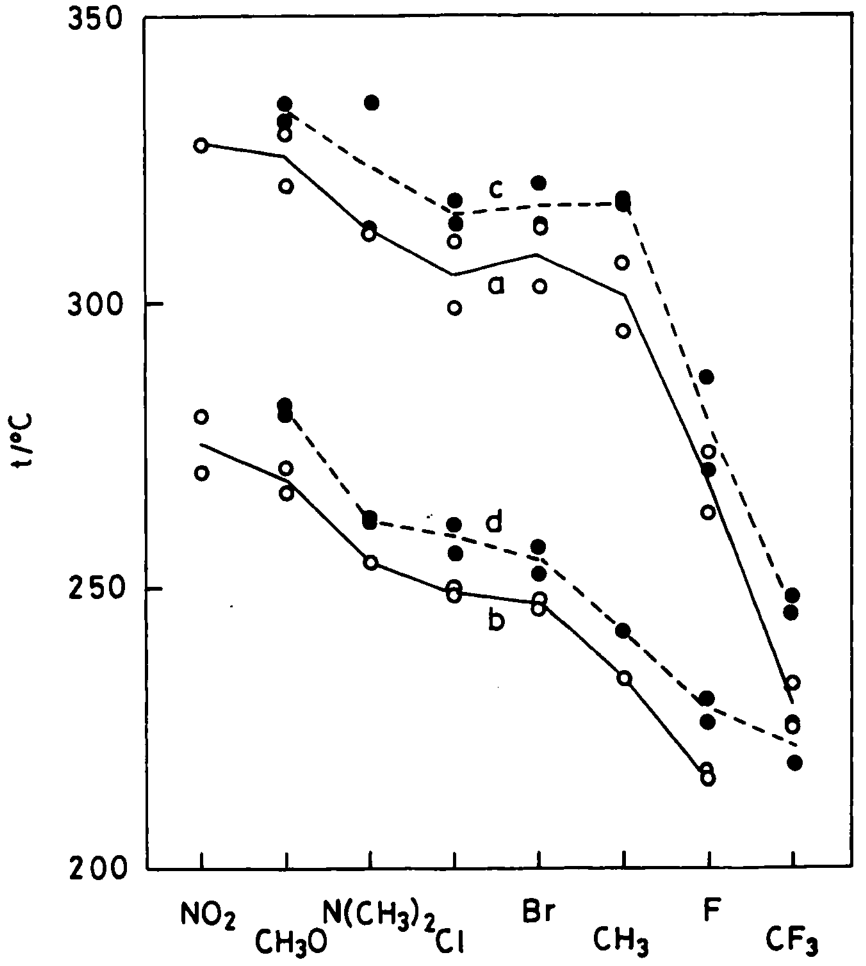

FIGURE 2 Plots of N-I transition temperatures in the order of temrinal group efficiency of the nematic phase given by (a) CN series (X or Y=CN) and (b) $CH_3$ series (X or Y=$CH_3$) of compound 2 (open circles) and (c) CN series and (d) $CH_3$ series of compound 1 (shaded circles)

The $NO_2$ group is absent in this order because of the thermal decomposition of the CN-$NO_2$ derivatives below the clearing temperature. The electron-donating groups tend to be shifted more to the head of the order with respect to those found for compound 2. Besides, the temperature differences are larger by about 10°C compared with those given by compound 2, reflecting the modification of the molecular core. It must be added that the N-I transition temperature of the CN-$N(CH_3)_2$ derivative is sensitive to the position of the $N(CH_3)_2$ group and changes as much as 23°C by the exchange of positions. The bulky off-axial polar N $(CH_3)_2$ group may not always be favorable to the molecular association.

The reduction of the effective dipole moment in the nematic phase noted above may be ascribed to the anti-parallel correlation of these highly polar molecules in the mesophase. Davies et al. and also Dunmur et al. carried out electro-optical studies on some 4-alkyl-4′-cyanobiphenyls and estimated the effective dipole moments in the nematic phase [4,5]. These authors found that the values in the mesophase are about 65 to 80% of the moment evaluated from benzene solution measurements and concluded the presence of a distinct anti-parallel orientation of the molecular dipoles in the line of the nematic director. Moreover, Leadbetter et al. carried out X-ray diffraction studies on the structures of 4-alkyl-4′-cyanobiphenyls in the nematic phase and found a repeat distance along the texture axis of about 1.4 molecular lengths, which is interpreted as arising from an overlapping head to tail arrangement of molecules [6]. On the other hand, the repeat distance close to the molecular length was recorded by the same authors for 4-methoxybenzylidene-4′-cyanoaniline in its nematic phase. Neither dielectric nor X-ray work is available for the present three-ring systems. However, the development of a short-range anti-parallel dipole order for 4-cyanophenyl 4-butylbenzoate in anisotropic solutions was reported by Dunmur and Toriyama [7], supporting our proposition.

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