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Effects of Polysubstitution on Mesomorphic Properties: Chloro and Methyl Derivatives of *N*-[4-(4-Substituted benzoyloxy)benzylidene]anilines

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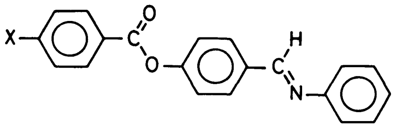
The effects of mono-, di-, and trichloro substitution of the aniline moiety on the nematic-isotropic transition temperature of *N*-[4-(4-X-substituted benzoyloxy)benzylidene]anilines, where X=CH_3O, CH_3, or Cl, have been studied, while paying particular attention to the vicinal chlorines. While the substituent on the 2 or 3 position of the aniline moiety lowers the transition temperature of the parent compound and the 4-chloro derivative, the 2,3-dichloro derivative shows a temperature higher than that of either the 2- or 3-chloro derivative. Moreover, the transition temperature of the 2,3,4-trichloro derivative exceeds that of the 3,4-dichloro derivative and is a little below that of the 2,4-dichloro isomer. In contrast, the introduction of 4-substituent increases the temperature, regardless of the position(s) of the other substituent(s). Methyl substitution exerts effects closely similar to those described above.

The effects of polysubstitution on mesomorphic thermal stabilities have been the subjects of many studies.[1] These studies have demonstrated that lateral substitution of a mesomorphic compound causes a pronounced lowering of the mesomorphic transition temperature. Therefore, the increased intermolecular separation seems to decrease the intermolecular cohesion to an extent outweighing any enhancement in these cohesive forces arising from increased polarity and polarizability. It has been concluded that the effects of two substituents are approximately additive.[2] However, Young et al. have noted that the transition temperature drops more slowly with each additional substituent when the molecule contains three or four substituents.[3] A survey of the literatures revealed that the substituents in almost all cases are located on different aromatic rings or are not bonded to the neighboring carbon atoms if they are located on the same ring. The work by Panse et al. on 4-(4-alkoxybenzoyloxy)-4′-alkylazobenzenes includes some exceptional cases.[4] For instance, the nematic–isotropic (N-I) transition temperature of the 2,3-dimethyl derivative was recorded to be 215 °C when the terminal substituents were butoxyl and butyl groups, respectively. This value is appreciably higher than that of the corresponding 3-methyl derivative, 183 °C. Moreover, the effects of two lateral cyano groups introduced into the neighboring positions on the mesomorphic behavior of four esters were described by Osman.[5] He concluded that the second substituent has little effect on the clearing point since it fills the space produced by the introduction of the first one and does not increase the intermolecular separation.

We have undertaken systematic examinations of the effects of substituents attached to the neighboring carbon atoms in the same benzene ring on the thermal stability of mesophases. As the decreases in thermal stability of the mesophase by the introduction of lateral substituent(s) are often large, the thermal stabilities of mesophases and the temperature ranges over which the mesophases exist must be considerable, if one is to study the effects of di- and polysubstitution upon the mesomorphic transition temperatures. For this purpose, we have chosen *N*-[4-(4-substituted benzoyloxy)benzylidene]anilines (**1**) as the parent compounds and methyl and/or chloro substituent(s) to be introduced to the aniline moieties. The van der Waals radii of these two substituents are about 0.23 and 0.18 nm respectively; however, the difference in the radius is almost cancelled by the difference in the ring-X bond length; these two are expected to affect the thermal stability of mesophase nearly to the same extent when they are employed as lateral substituents.[1] The stable or metastable nematic phase may hopefully be detected with the selected compounds, since *N*-[4-(4-methoxybenzoyloxy)benzylidene]-4-methylaniline has been reported to exhibit a nematic phase over the temperature range from 129 to 274.5 °C and the 4-chloro analog from 165 to 274 °C.[6,7]



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Experimental

Materials. 4-(4-X-substituted benzoyloxy)benzaldehydes were prepared by reacting 4-X-substituted benzoyl chlorides and 4-hydroxybenzaldehyde in the presence of pyridine. The Schiff's bases were synthesized by condensing the abovementioned benzaldehydes with appropriate anilines in ethanol. The products were recrystallized from ethanol, benzene, or the mixtures until constant transition temperatures were obtained.

Measurements. Transition temperatures were determined by calorimetric curves recorded with a Rigaku Thermoflex differential scanning calorimeter at a heating or cooling rate of 5 °C min^{-1}. Enthalpy changes were estimated by comparing the peak areas with that due to the melting of indium, 3.26 kJ mol^{-1}. When no mesophase was detectable, the virtual transition temperature was estimated by the extrapolation of the clearing point curve in the binary system with 4,4′-azoxydianisole.

Results and Discussion

The transition temperatures and the associated enthalpy changes of the monofluoro, monochloro, monobromo, monoiodo, and monomethyl derivatives of *N*-[4-(4-methoxybenzoyloxy)benzylidene]aniline (X=CH_3O) are summarized in Table 1. Here, crystalline, nematic, and isotropic phases are denoted by K, N, and I respectively. Gray and Worrall have shown that the clearing point (N-I transition temperature) of 3′-substituted 4′-octyloxybiphenyl-4-carboxylic acids decreases smoothly with increasing the molecular breadth.[8] Gray and his coworkers have also studied the mesomorphic properties of 2′- and 3′-X-substituted 4-[(4-alkoxybenzylidene)amino]biphenyls.[9] The 2′-isomers give much larger depressions of the clearing point because of a twisting effect superimposed on a broadening effect. In our case, a twisting effect is essentially absent and the substituent on the 2 position of the aniline moiety may be less exposed than that on the 3 position, because the lines defining the molecular breadth have their positions determined by the stereochemistry of the -COO- and -CH=N- units. The substituent on the 3 position is so effective in reducing the temperature that the mesophase is eliminated when chlorine, bromine, and iodine atoms are employed. In these cases, the virtual transition temperature estimated by the extrapolation of the clearing point curve in the binary system with 4,4′-azoxydianisole is listed in Table 1. As a result, the depression of the clearing point by the 2-chloro substituent was found to be 59 °C and that by the 3-substitution 82 °C. The methyl substitution results in similar differences.

Table 1. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of 2-, 3-, and 4-Substituted *N*-[4-(4-Methoxybenzoyloxy)benzylidene]anilines[a]

Substituent	K		N		I
None	.	129 (31)	.	177 (0.4)	.
2-F	.	135 (39)	.	145 (0.3)	.
2-CH_3	.	150 (41)	[.	121 (0.2)]	.
2-Cl[b]	.	129 (34)	[.	118 (0.3)]	.
2-Br	.	140 (34)	[.	105 (0.2)]	.
2-I	.	133 (36)	[.	81 (0.2)]	.
3-F	.	135 (39)	.	150 (0.4)	.
3-CH_3	.	111 (34)	[.	88 (0.1)]	.
3-Cl	.	160 (47)	[.	95[c]]	.
3-Br	.	159 (36)	[.	60[c]]	.
3-I	.	132 (33)	[.	57[c]]	.
4-F	.	131 (32)	.	255 (0.8)	.
4-CH_3[d]	.	129 (28)	.	278 (1.1)	.
4-Cl[e]	.	172 (27)	.	285 (1.6)	.
4-Br	.	187 (38)	.	280 (0.9)	.
4-I	.	202 (21)	.	274 (0.4)	.

a) The latter quantities are in parentheses. b) 133 and 120 °C by Vora and Patel (Ref. 7). c) The virtual transition temperature estimated by the extrapolation of the clearing point curve in the binary system with 4,4′-azoxydianisole. d) 129 and 274.5 °C by Dave and Kurian (Ref. 6). e) 165 and 274 °C by Vora and Patel (Ref. 7).

Table 2 presents the transition temperatures and the associated enthalpy changes of the dichloro and trichloro derivatives of *N*-[4-(4-methoxybenzoyloxy)-benzylidene]aniline. The change in the clearing point by the chloro substituents is well demonstrated by the diagram shown in Fig. 1a. The 4-substitution promotes the thermal stability of the mesophase in the 2-chloro, 3-chloro, and 2,3-dichloro derivatives. The extents are not much different from that found with the parent compound. Furthermore, the depression of the transition temperature of the 4-chloro derivative by the 2- or 3-substitution appears to be similar to those arising from the substitution on the parent compound. Thus, the effects are approximately additive in these cases. Serious deviations from the additivity rule are clearly seen when the thermal stability of mesophase is compared between the 2,3-dichloro derivative and the 2- or 3-chloro derivative, and also between the 2,3,4-trichloro derivative and the 2,4- or 3,4-dichloro derivative. Namely, the 2,3-dichloro derivative exhibits a temperature higher than either the 2-chloro or the 3-chloro derivative. Stabilization by the second substituent is about twice as large when the first one is located on the 3 position. A similar, but less pronounced, tendency is found among the trichloro and dichloro derivatives mentioned above.

While the clearing point of the monomethyl derivative is close to that of the corresponding monochloro derivative, the difference is somewhat larger among the disubstituted compounds (see Table 2). The changes in the transition temperature by methyl substitution are summarized in Fig. 1b. It may be noted that all of the compounds employed in this

Table 2. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Di- and Trisubstituted *N*-[4-(4-Methoxybenzoyloxy)benzylidene]anilines[a]

Substituents	K		N		I
2,3-Cl_2	.	147 (29)	[.	139 (0.3)]	.
2,4-Cl_2	.	143 (43)	.	231 (2.1)	.
3,4-Cl_2	.	201 (22)	[.	192 (0.5)]	.
2,3,4-Cl_3	.	183 (42)	.	222 (0.4)	.
2,3-$(CH_3)_2$	.	126 (31)	.	158 (0.4)	.
2,4-$(CH_3)_2$	.	142 (36)	.	222 (0.8)	.
3,4-$(CH_3)_2$	.	118 (26)	.	182 (0.5)	.
2-CH_3-3-Cl	.	139 (31)	.	149 (0.4)	.
3-Cl-4-CH_3	.	159 (44)	.	191 (0.4)	.

a) The latter quantities are in parentheses.

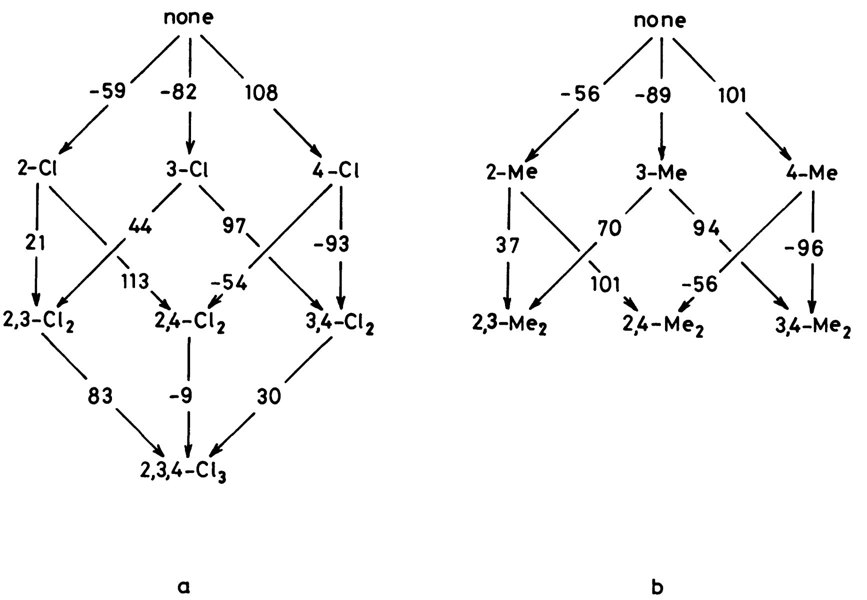

Fig. 1. The change in the clearing point (°C) of *N*-[4-(4-methoxybenzoyloxy)benzylidene]aniline by (a) chloro and (b) methyl substitution.

figure exhibit a stable or metastable mesophase; in other words, all of the transition temperatures are measurable. The mesophase is promoted by 4-methyl substitution as much as by the 4-chloro substitution presented in Fig. 1a. Moreover, the phase of the 4-methyl derivative is destabilized by 2- or 3-methyl substitution to an extent which is well compared with that given by the corresponding chloro derivative. Since the 2,3-dimethyl derivative exhibits an N-I transition temperature higher by 19 °C than the 2,3-dichloro derivative, the deviation from the additivity rule observed in Fig. 1b is more striking than that given in Fig. 1a.

The resemblance in the mesomorphic behavior between the chloro and methyl derivatives indicates that dispersive forces play a major role compared with dipole attractive forces, as pointed out by Osman.[5] This conclusion is supported by our additional data on the 2-methyl-3-chloro and 3-chloro-4-methyl derivatives. Their clearing points are in the order; 2,3-dichloro<2-methyl-3-chloro<2,3-dimethyl and 3,4-dimethyl<3-chloro-4-methyl<3,4-dichloro, respectively.

Table 3. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Mono-, Di-, and Trisubstituted *N*-[4-(4-Methylbenzoyloxy)benzylidene]anilines[a]

Substituent(s)	K		N		I
None	.	142 (35)	[.	124 (0.3)]	.
2-Cl	.	165 (37)	[.	76[b]]	.
3-Cl	.	138 (38)	[.	63[b]]	.
4-Cl	.	169 (29)	.	257 (0.6)	.
2,3-Cl$_2$	.	152 (37)	[.	85[b]]	.
2,4-Cl$_2$	.	166 (37)	.	197 (0.6)	.
3,4-Cl$_2$	.	152 (41)	.	155 (0.3)	.
2,3,4-Cl$_3$	.	176 (33)	.	190 (0.5)	.
2-CH$_3$-3-Cl	.	153 (44)	[.	102[b]]	.
3-Cl-4-CH$_3$	.	133 (28)	.	149 (0.3)	.

a) The latter quantities are in parentheses. b) The virtual transition temperature estimated by the extrapolation of the clearing point curve in the binary system with 4,4′-azoxyldianisole.

The thermodynamic data for compounds with $X=CH_3$ are presented in Table 3 and the changes in the clearing point are given in Fig. 2a. As the 2-chloro, 3-chloro, and 2,3-dichloro derivatives are not mesogenic, the changes involving these derivatives may not be very accurate. Nevertheless, the general feature in Fig. 2a is in good agreement with those found in Figs. 1a and b. The enhancement in the thermal stability of mesophase by the 4-chloro substituent seems to be more pronounced than that in the previously-described series. As demonstrated by the clearing points of the 4-chloro, 2,4-dichloro, and 3,4-dichloro derivatives, the 3-chloro substituent is more efficient to reduce the clearing point than the 2-chloro substituent. The difference in the clearing point between the 2,3,4-trichloro derivative and the 2,4-dichloro or 3,4-dichloro derivative contrasts markedly with the above-mentioned and definitely indicates that the anomaly is caused by the substituents located at the 2 and 3 positions. It must be added that the 2-methyl-3-chloro derivative is not mesogenic in conformity with the behavior of the 2,3-dichloro derivative. The clearing

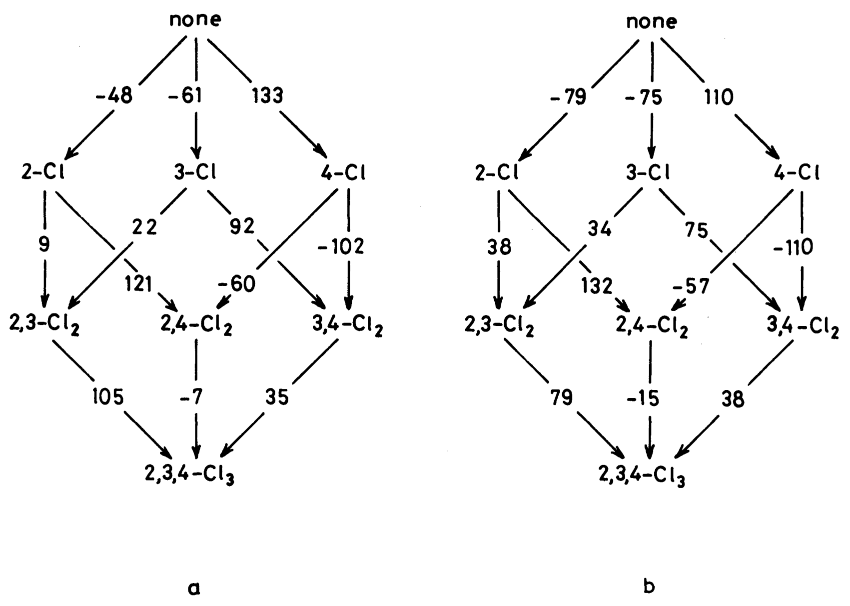

Fig. 2. The change in the clearing point (°C) by chloro substitution of *N*-[4-(4-X-substituted benzoyloxy)benzylidene]aniline; (a) X=CH_3 and (b) X=Cl.

Table 4. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Mono-, Di-, and Trisubstituted *N*-[4-(4-Chlorobenzoyloxy)benzylidene]anilines$^{a)}$

Substituent(s)	K		N		I
None	.	158 (39)	[.	146 (0.4)]	.
2-Cl	.	137 (35)	[.	67$^{b)}$]	.
3-Cl	.	146 (28)	[.	71$^{b)}$]	.
4-Cl	.	146 (28)	.	256 (1.0)	.
2,3-Cl_2	.	170 (43)	[.	105$^{b)}$]	.
2,4-Cl_2	.	147 (33)	.	199 (0.6)	.
3,4-Cl_2	.	135 (36)	.	146 (0.3)	.
2,3,4-Cl_3	.	155 (34)	.	184 (0.5)	.
2-CH_3-3-Cl	.	155 (37)	[.	86 (0.4)]	.
3-Cl-4-CH_3	.	145 (38)	.	161 (0.3)	.

a) The latter quantities are in parentheses. b) The virtual transition temperature estimated by the extrapolation of the clearing point curve in the binary system with 4,4′-azoxyldianisole.

point given by the 3-chloro-4-methyl derivative is lower than that of the 3,4-dichloro derivative.

Table 4 summarizes the effect of chloro substitution on the mesomorphic behavior of compounds with X=Cl. These compounds are unique in the sense that all the substituents are chlorine atoms. This situation is reflected by some irregularities in the thermal behavior. Compared with the compound listed in Table 3, the clearing point of the parent compound is higher by 22 °C. In contrast, the mesophase of the 3,4-dichloro derivative in the present series is transformed into an isotropic liquid at a temperature lower by 9 °C and that of the 2,3,4-trichloro derivative by 6 °C. The clearing point exhibited by the remaining two, the 4-chloro and 2,4-dichloro derivatives, is almost the same as that of the corresponding methyl compound. Thus, the compounds carrying only chloro substituents do not seem follow the well-known order of nematic group efficiency for terminal substituents.

The thermal stability of mesophase varies by the substitution as shown in Fig. 2b. In this series too, no mesophase is detectable for the 2-chloro, 3-chloro, and 2,3-dichloro derivatives. It seems to be reasonable to see that the clearing point of the 2,4-dichloro derivative is much higher than that of the 3,4-dichloro derivative. Therefore, the observation that the 2-chloro and 3-chloro substituents contribute nearly equally in reducing the clearing point of the parent compound looks very strange and might be ascribed to the uncertainties in the virtual clearing points of these chloro derivatives. Even so, the anomalously high thermal stabilities in the 2,3-dichloro and 2,3,4-trichloro derivatives are firmly demonstrated by this diagram.

The following general comments may be made about the results presented in this work. The terminal substituent (the substituent on the 4 position) promotes the thermal stability of mesophase irrespective of the presence of a lateral substituent, even when the latter is bonded to the neighboring carbon atom. In these cases, the effects of the terminal and lateral substituents are roughly additive. When two lateral substituents are bonded to the neighboring carbon atoms (the 2 and 3 positions), the effects deviate greatly from the additivity rule. The second substituent is accommodated, more or less, in the space produced by the introduction of the first one; therefore, it may be possible that the enhancement of the intermolecular cohesion arising from the increased polarizability outweighs the decrease in the cohesion due to the increased intermolecular separation. If the nature of substituents is markedly different from that in the compounds studied here, the outcome may become less significant, as reported by Osman.5)

The presence of a short-range order of the molecular positions in the nematic phase, such as the smectic C-type and one-dimensional correlation along the nematic director, has been pointed out in addition to the long-range orientational order along the director.10,11) Furthermore, a molecule with a polar terminal substituent is known to exhibit a strong tendency to molecular association.12) The terminal substituents employed in the present work are so different in polarity from each other that the favorable relative arrangement of the molecules in the nematic phase may not be identical. Consequently, it seems reasonable that compounds carrying X=Cl exhibit a thermal behavior somewhat anomalous compared with those carrying the other substituents.

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