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Effects of Polysubstitution on Mesomorphic Properties: Chloro Derivatives of 4-Methoxyphenyl 4-(Phenyliminomethyl)-benzoate and Related Compounds

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The effects of mono-, di-, and trichloro substitution of one of the end phenyl rings upon the nematic-isotropic transition temperature have been studied employing seven three-ring systems with a terminal methoxyl group, in which the linkage groups are —CO—O— and —CH=N—. The transition temperatures in these compounds were mostly in this order; 4-Cl > 2,4-Cl_2 > 2,3,4-Cl_3 > 3,4-Cl_2 > unsubstituted > 2,3-Cl_2 > 2-Cl or 3-Cl. Both the substituents on the 2- and 3-positions drastically lowered the transition temperature of the parent compound and the extent of depression by the former substituent varied by a factor of more than two when the —CH=N— group nearby was inverted. The condition that the thermal stabilities of mesophases and the temperature ranges over which the mesophases exist must be considerable in a parent compound was not necessarily required for the appearance of an enantiotropic nematic-isotropic transition in laterally substituted derivatives.

Keywords: Liquid crystals; nematic; smectic; lateral substituent

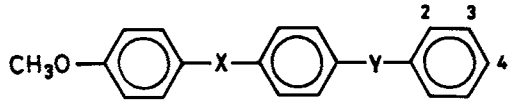
INTRODUCTION

The effects of polysubstitution on the mesomorphic behavior have been the subjects of many studies.[1] These works have established 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 the increased polarity and polarizability. However, very little work has been published on compounds with lateral substituents attached to the neighboring carbon atoms in the same phenyl or phenylene ring in regard to the thermal stability of mesophases.[2–5]

We studied earlier 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.[6] While

the substituent on the 2- or 3-position of the aniline moiety was found to greatly lower the transition temperature of the parent compound and also the 4-chloro derivative in accordance with what has been known, the 2,3-dichloro derivative showed a temperature higher than that of either the 2- or 3-chloro derivative. Moreover, the transition temperature of the 2,3,4-trichloro derivative exceeded that of the 3,4-dichloro derivative and was located a little below that of the 2,4-dichloro isomer. Methyl substitution was shown to exert effects closely similar to those described above.

In order to find out how the above-mentioned effects on the thermal stability of mesophases of substituents attached to the neighboring carbon atoms in the same ring are influenced by the arrangement of the linkage groups, we attempted a systematic structural modification study employing seven compounds closely-related to N-[4-(4-methoxybenzoyloxy)benzylidene]aniline (1a) examined previously; that is, those with three rings connected by —CO—O— and —CH=N— groups in various ways (1b, 2a, 2b, 3a, 3b, 4a, and 4b).



1a X = —CO—O—, Y = —CH=N—. 1b X = —O—CO—, Y = —CH=N—.
2a X = —CO—O—, Y = —N=CH—. 2b X = —O—CO—, Y = —N=CH—.
3a X = —CH=N—, Y = —CO—O—. 3b X = —N=CH—, Y = —CO—O—.
4a X = —CH=N—, Y = —O—CO—. 4b X = —N=CH—, Y = —O—CO—.

EXPERIMENTAL

All the anilines, benzaldehydes, phenols, and benzoic acids except for 2,3-dichlorobenzoic acid were commercial products. 2,3-Dichlorobenzaldehyde was oxidized to the corresponding acid by boiling a solution in propionic acid in the presence of cobalt and manganese bromides as catalysts while passing in oxygen.[7] Every desired compound was obtained by condensing an aniline with a benzaldehyde and then the resulting Schiff's base with a phenol or a benzoic acid. Esterification was carried out in chloroform, following the procedure of Hassner and Alexanian.[8] The products were recrystallized from ethanol, benzene, or mixtures thereof till constant transition temperatures were obtained.

Calorimetric measurements were carried out as described in a previous paper.[6] The virtual nematic-isotropic transition temperature of the 3-chloro derivative of compound 2b 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 eight parent compounds (1a to 4b) are compared with each other in Table I. Here, K, N, and I stand for the crystalline, nematic, and isotropic phases respectively. The effects

TABLE I

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of parent compounds.[a]

Compound	K	N	I
1a	. 129 (31)	. 177 (0.4)	.
1b	. 151 (40)	. 173 (0.3)	.
2a	. 139 (33)	. 170 (0.6)	.
2b	. 153 (33)	. 158 (0.5)	.
3a	. 139 (32)	. 174 (0.4)	.
3b	. 145 (34)	. 187 (0.3)	.
4a	. 118 (33)	. 179 (0.5)	.
4b	. 144 (38)	. 184 (0.4)	.

a) The latter quantities are in parentheses.

of structural variations on the crystal and mesophase stabilities are so significant that the melting point (K-N transition temperature) is scattered in the range from 118 to 153°C and the clearing point (N-I transition temperature) in the range from 158 to 187°C. Both the highest melting point and the lowest clearing point are given by compound 2b and the lowest melting point and the third highest clearing point are exhibited by compound 4a. Consequently, the temperature range of stable existence of a nematic phase varies greatly by how the three rings are connected (the position and the sense of the linkage groups relative to the terminal substituent) and increases in this order: 2b < 1b < 2a < 3a < 4b < 3b < 1a < 4a. The range in compound 2b is as narrow as 5°C and that in compound 4a is as wide as 61°C. Dewar and Goldberg compared the N-I transition temperatures of 1,4-phenylene bis(4-alkoxybenzoates) and the isomeric bis(4-alkoxyphenyl) terephthalates and found the value for the former ester to be invariably higher.[9] They proposed that the enhancement of polarity of the carbonyl group in conjugation with the electron-releasing terminal group stabilizes the mesophase, whereas there is little effect on the latter. Our results (1b < 1a and 2b < 2a) lend support to their argument.

Previously, we assumed that the thermal stabilities of mesophases and the temperature ranges over which the mesophases exist must be considerable in a parent compound, if one has to study the effects of lateral substitution upon the mesomorphic transition temperatures. A study of the effects of chloro substitution on the mesomorphic behavior of these eight compounds may provide an excellent means of testing the validity of the above assumption. As will be described in the following paragraphs, the order of the temperature range of stable existence of the

nematic phase found for the parent compounds is not always maintained when terminal and/or lateral chloro substituents are introduced.

The thermodynamic data of the chloro derivatives of compound 1b are presented in Table II. The clearing points of the 4-chloro, 2,4- and 3,4-dichloro, and 2,3,4-trichloro derivatives are located closely to those reported for the corresponding derivatives of compound 1a respectively. On the other hand, the transition temperatures in the 2-chloro and 2,3-dichloro derivatives are increased by 13 to 14°C and that in the 3-chloro derivative by 22°C when the —CO—O— group is inverted. The last figure is only approximate because the transitions in these two 3-chloro derivatives are virtual. Contrary to the 3,4-dichloro derivative of compound 1a where the nematic phase is metastable, the mesophase in the corresponding derivative of compound 1b is stable over 49°C. It must be added that a metastable smectic phase appears in the 2,3-dichloro derivative of series 1b.

The change in the clearing point of compound 1b by chloro substituents is summarized in Figure 1. For the sake of convenience, a similar diagram for compound 1a is reproduced in the same figure. The 4-chloro substituent promotes the thermal stability of mesophase irrespective of the presence of lateral substituent(s), but the increment is less when the latter is bonded to the 3-position. The clearing point

TABLE II

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of the mono-, di-, and trichloro derivatives of compound 1b.[a]

Substituent (s)	K	S_A	N	I
2-Cl	. 129 (35)		. 132 (0.3)	.
3-Cl	. 151 (38)		[. 117[b]]	.
4-Cl	. 168 (39)		. 284 (0.8)	.
2,3-Cl_2	. 159 (37)	. 112 (3.5)[c]	. 152 (0.4)[c]	.
2,4-Cl_2	. 170 (37)		. 230 (0.7)	.
3,4-Cl_2	. 140 (32)		. 189 (0.3)	.
2,3,4-Cl_3	. 177 (40)		. 222 (0.5)	.

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'-azoxydianisole.

c) The transition is monotropic.

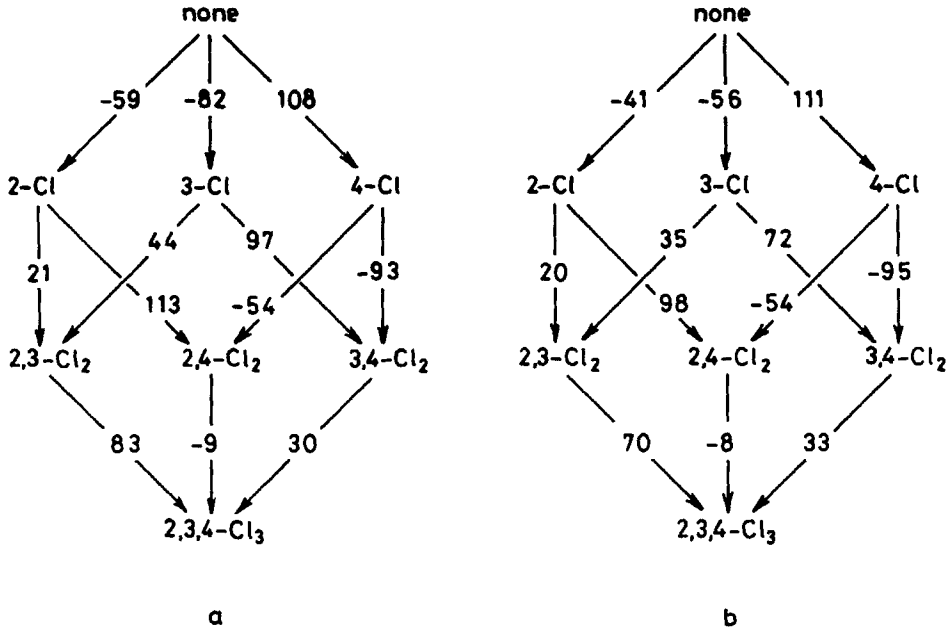


FIGURE 1 The change in the clearing point (°C) of (a) compound 1a and (b) compound 1b by chloro substitution.

depression by the 2-chloro substituent is less than that by the 3-chloro substituent, suggesting that a twisting is essentially absent and also that the 2-chloro substituent is less exposed compared to the 3-chloro substituent. While the N-I transition temperature of the 2-chloro derivative is raised by 20°C by the addition of a 3-chloro substituent and that of the 3,4-dichloro derivative by 33°C by a 2-chloro substituent, the N-I transition temperature of the 2,4-dichloro derivative is lowered by 8°C by the introduction of a 3-chloro substituent. Our earlier conclusion that the second lateral substituent is accommodated, more or less, in the space produced by the introduction of the first one and enhances the intermolecular cohesion because of the increased polarizability is confirmed by these observations. Thus, all of the changes presented in Figure 1b closely resemble those in 1a. However, the depressions of the clearing point of the parent compound 1b resulting from the introduction of 2-chloro and 3-chloro substituents are diminished by 18°C and 26°C respectively compared with the corresponding values for compound 1a. As a result, the nematic phase given by the 2-chloro derivative of compound 1b becomes stable, whereas the transition in the 3-chloro derivative remains virtual.

Table III presents the thermodynamic data of compounds 2a and 2b and their chloro derivatives. The effects of inverting the —CH=N— group on the K-N and N-I transition temperatures are significant. Compared with the N-I transition temperatures in series 1a and 1b, those given in Table III are mostly lower. Nevertheless, it is noted that all the N-I transitions are measurable even though the parent compound 2b exhibits the narrowest temperature range (5°C) of stable existence of the nematic phase.

TABLE III

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of mono-, di-, and trichloro derivatives of compounds 2a and 2b.[a]

Substituent(s)	K	S_A	N	I
		Compound 2a		
2-Cl	. 116 (31)		. 67 (0.2)[b]	.
3-Cl	. 130 (32)		. 104 (0.2)[b]	.
4-Cl	. 141 (33)		. 293 (1.2)	.
2,3-Cl_2	. 136 (35)		. 125 (0.3)[b]	.
2,4-Cl_2	. 140 (37)		. 216 (0.8)	.
3,4-Cl_2	. 149 (40)		. 203 (0.3)	.
		Compound 2b		
2-Cl	. 122 (37)	. 18 (1.8)[b]	. 81 (0.3)[b]	.
3-Cl	. 140 (41)		. 105 (0.3)[b]	.
4-Cl	. 180 (41)		. 281 (0.8)	.
2,3-Cl_2	. 169 (44)	. 115 (5.2)[b]	. 137 (0.7)[b]	.
2,4-Cl_2	. 151 (41)		. 204 (0.7)	.
3,4-Cl_2	. 164 (44)	. 130 (3.5)[b]	. 190 (0.4)	.

a) The latter quantities are in parentheses.

b) The transition is monotropic.

The following features may be worthwhile mentioning in regard to the data in Table III. The clearing point of the 4-chloro derivative of compound 2a is located at the highest temperature among those of 4-chloro derivatives examined in this work, and its K-N transition is at the lowest temperature; therefore, the widest temperature range of stable existence of the nematic phase (152°C) for the 4-chloro derivative is achieved with this compound. The 2-chloro derivative of compound 2a exhibits the lowest N-I transition temperature and the difference between melting point and monotropic N-I transition temperature is the largest among the corresponding derivatives.

The 4-chloro and 2,4-dichloro derivatives of compound 2b exhibit nematic phases of the lowest thermal stability among the respective derivatives. The latter compound shows the narrowest temperature range of stable existence of the mesophase

among the 2,4-dichloro derivatives, whereas the 2-chloro derivative shows the widest temperature range, despite its second lowest clearing point. The N-I transition temperature of the 2,3-dichloro derivative is the second lowest among the corresponding derivatives and is as much as 32°C below the melting point. Thus, the lowest clearing point and the narrowest range of stable existence of the nematic phase in the parent compound 2b are not necessarily reflected by the thermal properties of these chloro derivatives.

The 2-chloro, 2,3-dichloro, and 3,4-dichloro derivatives of compound 2b exhibit a metastable smectic phase. While the observation of the smectic phase for the 2-chloro derivative may be attributed to the extensive supercooling of the nematic phase, the detection for the other two dichloro derivatives may be correlated with the stabilization of the smectic phase by the introduction of chloro substitution at the 3-position.

The clearing point of compounds 2a and 2b changes by chlorination as depicted in Figure 2. In contrast to the changes shown in Figure 1, the depression by the 2-chloro substituent introduced to the parent compound is larger than that by the 3-chloro substituent. A twisting, possibly caused by the hydrogen atom in the azomethine group, contributes to the destabilization of the mesophase, superimposing a broadening effect due to the 2-chloro substituent.[10] In consequence, the stabilization of the nematic phase of the 2-chloro derivative by the 3-chlorination (58°C and 56°C) is more pronounced than that of the 3-chloro derivative by the 2-chlorination (21°C and 32°C).

Thermodynamic data of the chloro derivatives of compounds 3a and 3b are summarized in Table IV. The N-I transitions in the 2,3-dichloro and 2,3,4-trichloro derivatives of the former parent compound are the lowest among the corresponding derivatives. The narrowest temperature range of stable existence of the nematic phase in the 4-chloro and 2,3,4-trichloro derivatives is given by this series (89°C and 34°C).

In accordance with the fact that the clearing point of compound 3b is the highest

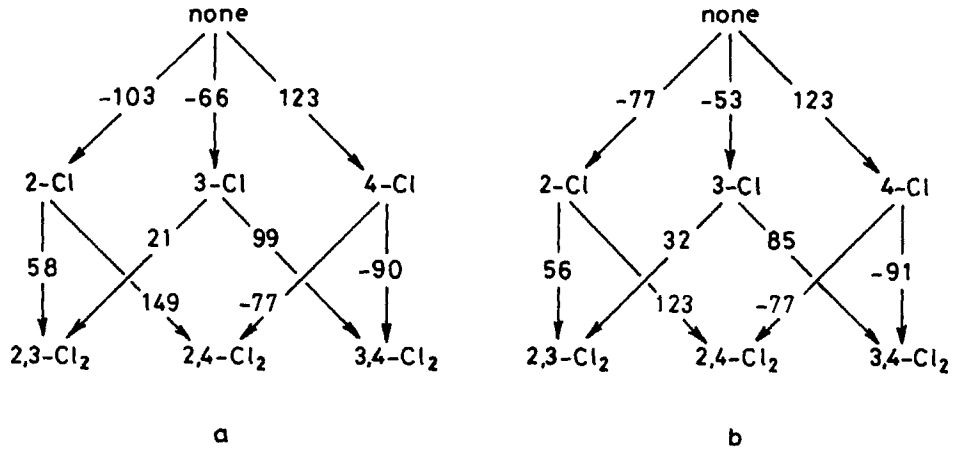


FIGURE 2 The change in the clearing point (°C) of (a) compound 2a and (b) compound 2b by chloro substitution.

TABLE IV

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of mono-, di-, and trichloro derivatives of compounds 3a and 3b.[a]

Substituent (s)	K	N	I
	Compound 3a		
2-Cl	. 138 (32) .	131 (0.4)[b]	.
3-Cl	. 144 (43) .	113 (0.2)[b]	.
4-Cl	. 194 (43) .	283 (0.8)	.
2,3-Cl_2	. 149 (36) .	124 (0.3)[b]	.
2,4-Cl_2	. 136 (34) .	233 (0.8)	.
3,4-Cl_2	. 194 (52) .	198 (0.3)	.
2,3,4-Cl_3	. 186 (42) .	220 (0.4)	.
	Compounds 3b		
2-Cl	. 134 (32) .	146 (0.4)	.
3-Cl	. 134 (30) .	127 (0.1)[b]	.
4-Cl	. 170 (39) .	290 (0.8)	.
2,3-Cl_2	. 142 (39) .	145 (0.3)	.
2,4-Cl_2	. 166 (44) .	242 (0.8)	.
3,4-Cl_2	. 170 (47) .	203 (0.3)	.
2,3,4-Cl_3	. 171 (34) .	232 (0.6)	.

a) The latter quantities are in parentheses.

b) The transition is monotropic.

among the parent compounds examined, the nematic phase in all the derivatives of this series is comparatively stable. The highest clearing point is recorded for the following three derivatives: the 2-chloro, 2,4-dichloro, and 2,3,4-trichloro derivatives. The mesophase of the last derivative is stable over 61°C, the broadest among the ranges given by the trichloro derivatives. It may be noted that the N-I transition exhibited by the 3-chloro derivative is monotropic but is located at only 7°C below the melting point.

As is shown in Figure 3, the clearing point depression by the 2-chloro substituent is less than that by the 3-chloro substituent in these two series because of the

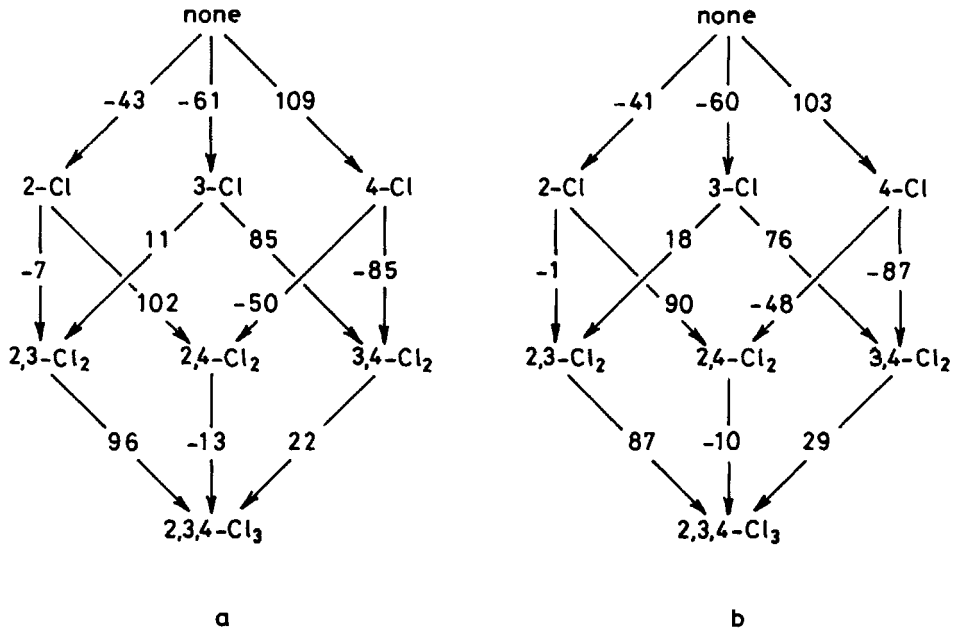


FIGURE 3 The change in the clearing point (°C) of (a) compound 3a and (b) compound 3b by chloro substitution.

location of the oxygen atom in the carbonyl group far from the chloro-substituted phenyl ring. The specific features to be mentioned here are as follows; the clearing point of the 2-chloro derivative is not promoted but depressed by the introduction of the 3-chloro substituent (-1°C and -7°C). Accordingly, the promotion of the nematic phase in the 3-chloro derivatives by the 2-chlorination is as little as 11°C (3a) and 18°C (3b).

The transition temperatures and the enthalpy changes presented in Table V are concerned with the chloro derivatives of compounds 4a and 4b. The clearing points of the 3-chloro derivative and also of the 2,3- and 3,4-dichloro derivatives in the former series are the second highest among the respective derivatives. The range of stable existence of the nematic phase of the 2,3-dichloro derivative is the widest along with the similar derivative of compound 4b and that of the 3,4-dichloro derivative is solely the widest among the corresponding derivatives.

The 3-chloro, 2,3-dichloro, and 3,4-dichloro derivatives of compound 4b have nematic phases of the highest thermal stability among the respective derivatives. Therefore, all the chloro derivatives with the highest clearing point except the 4-chloro derivative belong to series 3b and 4b in conformity with the fact that their parent compounds have the highest or the second highest clearing points. As to the 2,4-dichloro derivatives, the broadest range of stable existence of the nematic phase is attained by series 4b. According to the argument by Dewar and Goldberg, the 4-chloro substituent (electron-releasing but also electron-withdrawing inductively) is also expected to stabilize the mesophase of 4a and 4b relative to that of 3a and 3b respectively.[9] As a matter of fact, the nematic-isotropic transition tem-

TABLE V

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of the mono-, di-, and trichloro derivatives of compounds 4a and 4b.[a]

Substituent (s)	K	S_A	N	I
		Compound 4a		
2-Cl	. 113 (37)		. 122 (0.2)	.
3-Cl	. 147 (41)		. 133 (0.2)[b]	.
4-Cl	. 158 (38)		. 288 (1.1)	.
2,3-Cl_2	. 124 (33)		. 166 (0.4)	.
2,4-Cl_2	. 140 (36)		. 230 (0.7)	.
3,4-Cl_2	. 137 (39)		. 209 (0.5)	.
		Compound 4b		
2-Cl	. 116 (32)		. 124 (0.1)	.
3-Cl	. 165 (45)		. 135 (0.2)[b]	.
4-Cl	. 179 (41)		. 290 (1.2)	.
2,3-Cl_2	. 130 (37)	. 51 (1.1)[b]	. 172 (0.3)	.
2,4-Cl_2	. 123 (32)		. 233 (0.7)	.
3,4-Cl_2	. 165 (42)	. 122 (2.6)[b]	. 210 (0.4)	.

a) The latter quantities are in parentheses.

b) The transition is monotropic.

peratures are in this order: 3a < 4a < 3b = 4b, supporting only partially their proposition.

The nematic-smectic A transition located far below the clearing point was recorded for the 2,3- and 3,4-dichloro derivatives. It is interesting to note that all the derivatives for which a smectic A phase could be observed are laterally substituted (2-chloro, 2,3-dichloro, and/or 3,4-dichloro derivative) and also have an —O—CO— group as X or Y (1b, 2b, and 4b).

Figure 4 indicates that the depression of the clearing point of the parent compound by 2-chloro substitution is larger than that by 3-chloro substitution, demonstrating the presence of a marked twisting caused by the steric hindrance between the former substituent and the carbonyl group. However, it is pertinent to note that the difference in the clearing point depression between the 2-chloro and 3-chloro derivatives is smaller compared with similar difference found for the 2a and

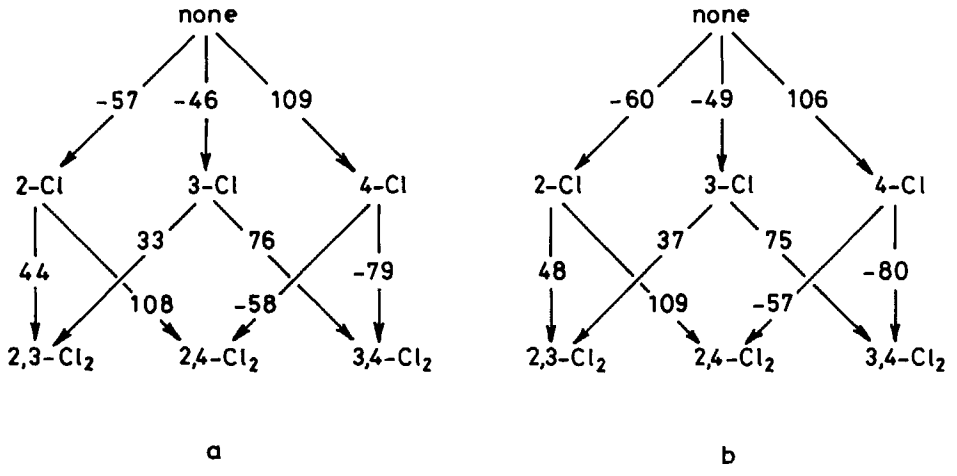


FIGURE 4 The change in the clearing point (°C) of (a) compound 4a and (b) compound 4b by chloro substitution.

2b series (see Figure 2). The stabilization of the mesophase to some degree by the conjugation between the 2-chloro substituent and the carbonyl group may account for this finding. There is no other outstanding feature to be mentioned about these diagrams.

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