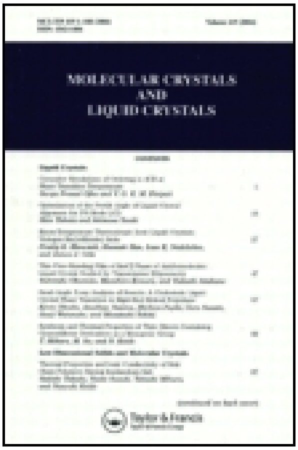

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Effects of Lateral Substituents on Mesomorphic Behavior. III. N-4-(4-Alkoxybenzoyloxy)benzylidene]-anilines

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Effects of Lateral Substituents on Mesomorphic Behavior. III. *N*-[4-(4-Alkoxybenzoyloxy)benzylidene]-anilines

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The mesomorphic properties of *N*-[4-(4-alkoxybenzoyloxy)benzylidene]-2- and -3-*X*-anilines, where X = Me, F, Cl, Br or I, were examined. The 2-Me derivatives give higher nematic-isotropic transition temperatures than the 3-Me derivatives, whereas the reverse is true for the F compounds. The intersection between the plots of the transition temperatures of the 2-*X* and 3-*X* derivatives against the alkyl chain length is found for the Cl, Br, and I compounds, respectively. The smectic A-nematic transition temperature recorded for the heptyloxy member is promoted by the 3-*X* substitution as much as 32°C (X = F) and 16° (X = Cl).

Keywords: Nematic; smectic; lateral substituent

INTRODUCTION

We earlier reported on the mesomorphic properties of 4-(2-*X*- and 3-*X*-benzylideneamino)phenyl 4-alkoxybenzoates (1) carrying Me or Cl as *X* [1]. These two lateral substituents have nearly the same size; nevertheless, the nematic-isotropic (N–I) transition temperature is differently depressed by the kind and the position of the substituent. While the nematic phase given by the 2-Me derivative is thermally more stable by 10 to 15°C than that of the 2-Cl derivative, the opposite is true for the 3-*X* derivatives, the difference

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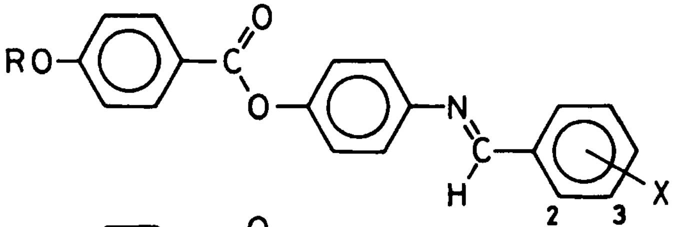
being 14 to 21°C . The parent compounds (*X* = H) are purely nematogenic but the higher homologous members become smectogenic by the incorporation of F, Cl, or Br into the 3-position. In sharp contrast to the depressions of the smectic-nematic (S – N) transition temperature of 4'-alkoxybiphenyl-4-carboxylic acid by lateral substitution recorded by Gray and Worrall [2], the S – N transition temperatures of the octyloxy members in this series are higher than the temperature where the nematic melt of the parent compound solidifies. This paper presents the properties of *N*-[4-(4-alkoxybenzoyloxy) benzylidene)-2- and 3-*X*-anilines (2), where the azomethine group in compound 1 is inverted.



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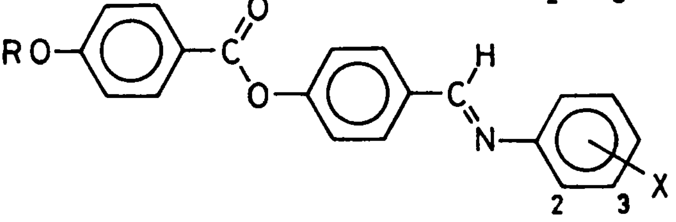

2

EXPERIMENTAL

All the anilines and 4-alkoxybenzoic acids were commercially available. The desired compound was obtained by the condensation of a 2-*X*- or 3-*X*-substituted aniline with 4-hydroxybenzaldehyde in refluxing ethanol and then by the esterification of the resulting Schiff's base with a 4-alkoxybenzoic acid in chloroform at room temperature by the procedure of Hassner and Alexanian [3]. The products were recrystallized from appropriate solvents till sharp constant transition temperatures were achieved. Transition temperature measurements and mesophase identification were carried out using a Yanaco melting point apparatus and a Rigaku differential scanning calorimeter as described in our previous paper [1].

RESULTS AND DISCUSSION

The transition temperatures and associated enthalpies of seventy-eight compounds of series 2 are presented in Table I. Here, the crystalline, smectic A, nematic, and isotropic liquid phases are denoted by K, S_A, N, and I, respectively. In contrast to compound 1, a smectic A phase could be detected for the heptyloxy and octyloxy members of the parent compounds (X = H). The methoxy member of the 3-Cl derivatives and the methoxy, ethoxy, and propoxy members of the 3-Br derivatives are not listed in Table I as we failed to observe any mesophase. It must be noted that the octyloxy members of the 3-Cl and 3-Br derivatives are purely smectogenic, whereas those of the 3-F and 3-I derivatives can exhibit both nematic and smectic phases.

The unsubstituted compounds have higher N – I transition temperatures compared to those in compound 1 as is indicated by Δt_{NI} in Table I. The work by Funakoshi *et al.* revealed that the nematic phase of 4-(benzylideneamino) phenyl 4-X-benzoate is thermally less stable than that of the isomeric N-(4-X-benzoyloxy)benzylideneaniline, where $X = CH_3O$ and C_2H_5O [7]. Our Δt_{NI} values are nearly independent of the alkyl chain length and the mean value 8°C is larger than theirs; 7°C for n = 1 and 2°C for n = 2. The rigid molecular core in compound 2 is supposed to be more extended than that in compound 1 by the inversion of azomethine linkage because of an increased pi-electron interaction between the linkage and the middle ring and gives rise to the enhanced thermal stability of the mesophase.

As is shown in Figure 1, the odd-even alternation of N – I transition temperature is enhanced by the incorporation of a lateral substituent as found for compound 1. On the other hand, the associated enthalpy changes are diminished by the substitution (see Tab. I). The N – I transition temperatures of the 2-Me derivatives are higher than those of the 3-Me derivatives. The difference found here is much larger than that for compound 1 and decreases as the alkyl chain length increases; that is 33°C when n = 1 and 5°C when n = [8]. Similarly, the lower homologous members of the 2-Cl derivative give higher transition temperatures than those of the 3-Cl derivative but the difference at n = 1 is smaller and this relation is reversed above n = 5. Such an intersection between the plots of N – I transition temperatures of the 2- and 3-X derivatives against the number of carbon atoms in the alkyl chain is not new. We observed one for 4-(4-alkoxybenzylideneamino)phenyl 2- and 3-methylbenzoates and noted

TABLE I Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of *N*-[4-(alkoxybenzoyloxy) benzylidene]-2- and 3-*X*-anilines[a]

n[b]	X	K	S_A	N	I	Δt_{NI}
1	H	· 129 (31)		· 177 (0.4)[d]	·	7
2	H	· 147 (36)		· 186 (0.7)	·	5
3	H	· 129 (44)		· 163 (0.5)	·	7
4	H	· 123 (38)		· 168 (0.7)	·	10
5	H	· 125 (48)		· 158 (0.6)	·	8
6	H	· 113 (30)		· 159 (0.8)	·	9
7	H	· 108 (33)	[· 102 (0.4)][c]	· 153 (0.7)	·	10
8	H	· 104 (47)	· 115 (0. 5)	· 152 (0.8)	·	8
1	2-Me	· 150 (41)		[· 121 (0.2)][c,d]	·	39
2	2-Me	· 147 (41)		[· 139 (0.4)][c]	·	28
3	2-Me	· 112 (31)		· 121 (0.3)	·	33
4	2-Me	· 97 (29)		· 130 (0.5)	·	26
5	2-Me	· 84 (35)		· 120 (0.4)	·	27
6	2-Me	· 96 (39)		· 122 (0.4)	·	24
7	2-Me	· 89 (43)		· 116 (0.5)[e]	·	24
8	2-Me	· 82 (46)		· 116 (0.5)[f]	·	20
1	3-Me	· 111 (34)		[· 88 (0.1)][c,d]	·	16
2	3-Me	· 114 (42)		· 116 (0.3)	·	12
3	3-Me	· 98 (36)		[· 92 (0.2)][c]	·	17
4	3-Me	· 113 (38)		[· 110 (0.4)][c]	·	15
5	3-Me	· 102 (36)		· 104 (0.3)	·	19
6	3-Me	· 105 (40)		· 111 (0.5)	·	17
7	3-Me	· 92 (38)	[· 88 (1.2)][c]	· 107 (0.5)	·	19
8	3-Me	· 86 (30)	· 99 (1.7)	· 111 (0.7)	·	15
1	2-Cl	· 129 (34)		[· 118 (0.3)][c,d,g]	·	48
2	2-Cl	· 150 (39)		[· 133 (0.4)][c,h]	·	34
3	2-Cl	· 121 (31)		[· 112 (0.4)][c,i]	·	38
4	2-Cl	· 116 (37)		· 122 (0.4)[j]	·	31
5	2-Cl	· 98 (31)		· 114 (0.4)[k]	·	26
6	2-Cl	· 111 (43)		· 116 (0.4)[l]	·	28
7	2-Cl	· 104 (47)		· 111 (0.4)[m]	·	31
8	2-Cl	· 97 (44)		· 112 (0.4)[n]	·	27
2	3-Cl	· 123 (43)		· 124 (0.2)	·	3
3	3-Cl	· 111 (41)		[· 105 (0.3)][c]	·	6
4	3-Cl	· 109 (32)	[· 103 (1.2)][c]	· 116 (0.4)	·	4
5	3-Cl	· 101 (36)	· 103 (1.2)	· 116 (0.4)	·	10
6	3-Cl	· 108 (41)	· 114 (1.7)	· 121 (0.5)	·	7
7	3-Cl	· 85 (36)	· 118[o]	· 120[o]	·	11
8	3-Cl	· 82 (44)	· 123 (4.3)		·	
1	2-F	· 135 (39)		· 145 (0.3)[d]	·	
2	2-F	· 139 (32)		· 157 (0.4)	·	
3	2-F	· 118 (43)		· 135 (0.3)	·	
4	2-F	· 114 (32)		· 144 (0.5)	·	
5	2-F	· 129 (46)		· 134 (0.4)	·	
6	2-F	· 111 (44)		· 136 (0.5)	·	22
7	2-F	· 106 (44)		· 129 (0.5)	·	
8	2-F	· 101 (42)		· 132 (0.6)	·	
1	3-F	· 135 (39)		· 150 (0.4)[d]	·	
2	3-F	· 123 (38)		· 162 (0.4)	·	
3	3-F	· 123 (45)		· 143 (0.3)	·	
4	3-F	· 108 (23)		· 151 (0.3)	·	
5	3-F	· 108 (39)	· 118 (0.7)	· 144 (0.6)	·	
6	3-F	· 107 (32)	· 128 (1.4)	· 147 (0.8)	·	8

TABLE I (Continued)

n[b]	X	K	S_A	N	I	Δt_{NI}
7	3-F	· 102 (38)	· 134 (1.9)	· 143 (0.8)	·	9
8	3-F	· 90 (38)	· 139 (3.1)	· 144 (1.3)	·	9
1	2-Br	· 140 (34)		[· 105 (0.2)][d]	·	
2	2-Br	· 141 (35)		[· 120 (0.3)]	·	
3	2-Br	· 114 (31)		[· 101 (0.2)]	·	
4	2-Br	· 110 (43)		[· 113 (0.3)]	·	
5	2-Br	· 92 (32)		[· 104 (0.3)]	·	
6	2-Br	· 107 (38)		[· 107 (0.3)][c]	·	31
7	2-Br	· 105 (40)		[· 101 (0.3)][c]	·	
8	2-Br	· 90 (40)		· 105 (0.4)	·	
4	3-Br	· 106 (49)	[· 85 (0.5)][c]	[· 106 (0.3)][c]	·	
5	3-Br	· 109 (36)	[· 92 (1.0)][c]	[· 104 (0.3)][c]	·	
6	3-Br	· 108 (46)	[· 102 (1.5)][c]	· 110 (0.5)	·	7
7	3-Br	· 81 (43)	· 106 (2.2)	· 108 (0.8)	·	9
8	3-Br	· 86 (35)	· 112 (3.7)		·	
4	2-I	· 105 (44)		[· 97 (0.3)][c]	·	
5	2-I	· 103 (41)		[· 89 (0.2)][c]	·	
6	2-I	· 111 (45)		[· 93 (0.3)][c]	·	
7	2-I	· 101 (39)		[· 90 (0.3)][c]	·	
8	2-I	· 92 (36)		· 93 (0.5)	·	
4	3-I	· 107 (33)		[· 90 (0.2)][c]	·	
5	3-I	· 109 (38)		[· 87 (0.3)][c]	·	
6	3-I	· 109 (45)	[· 88 (1.6)][c]	[· 95 (0.5)][c]	·	
7	3-I	· 98 (44)	[· 91 (2.0)][c]	[· 94 (0.5)][c]	·	
8	3-I	· 94 (37)	· 97[p]	· 98[p]	·	

[a] The enthalpy changes are in parentheses.

[b] The number of carbon atoms in the alkyl group.

[c] Monotropic transition.

[d] Takem from Ref. [4].

[e] 110. 2°C (0.6035 kJ mol^{-1}), [f] 111. 2°C (0.5536 kJ mol^{-1}) by Alapati, Saran, and Raman (Ref. [5]).

[g] 133 and 120°C, [h] 148 and 137°C, [i] 119 and 117°C, [j] 107 and 122°C, [k] 90 and 115°C, [l] 109 and 117°C, [m] 102 and 114°C, and [n] 96 and 114°C by Vora and Patel (Ref. [6]). [o]The combined enthalpy value is 4.1 kJ mol^{-1}, [p]The comined enthalpy value is 3.5 kJ mol^{-1}.

that the presence of the flexible alkyl chain cannot be ignored in the consideration of the molecular breadth [8].

In order to find out how the N – I transition temperature for the 2- and 3-*X* derivatives is affected by the size of the substituent and the alkyl chain length, the work was extended to the F, Br, and I (only in part) compounds. The N – I transition temperature of the 3-F derivatives is higher than that of the 2-F derivatives throughout the series, the difference being 5 to 14°C (see Fig. 2). The difference in the thermal stability of the nematic phase between the 2-*X* and 3-*X* derivatives becomes smaller by the increase in the size of halogen and the two plots intersect at the pentyloxy members when X = Br and between the pentyloxy and hexyloxy members when X = I. Thus, the relation between the transition temperature and the size of the lateral substituents is not simple but varies remarkably with the alkyl chain length.

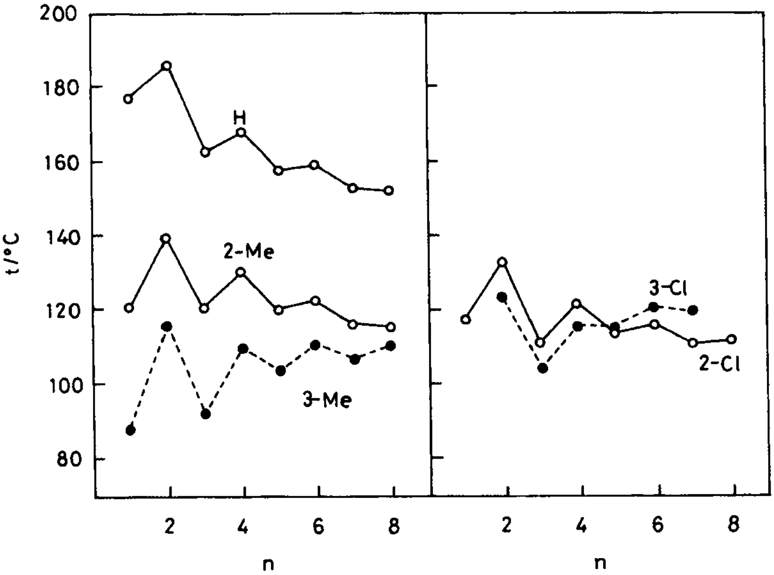

FIGURE 1 Dependence of the N–I transition temperature of the parent compounds and the Me and Cl derivatives on the number of carbon atoms in the alkyl group (*n*).

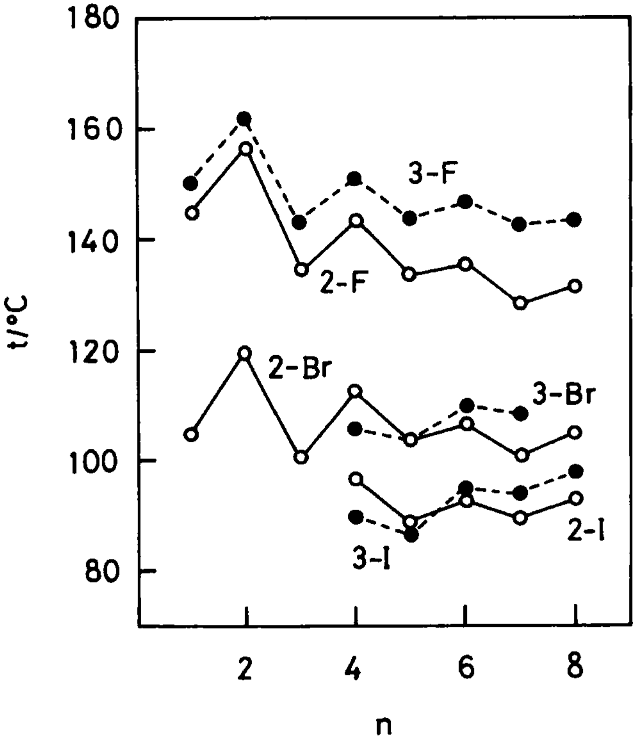

FIGURE 2 Dependence of the N–I transition temperature of the F, Br, and I derivatives on the number of carbon atoms in the alkyl group (*n*).

The N–I transition temperatures of the butoxy members are plotted against van der Waals volume of the lateral substituents proposed by Bondi [9] in Figure 3. The curve connecting the points for X = H and halogens of the 2-X derivatives are on a smooth curve which is slightly concave upwards and crosses the curve for the 3-X derivatives between the points for F and Cl. There must be a point of inflection on the latter curve. Although the hexyloxy members of 3-X derivatives give consistently higher temperatures than the 2-X derivatives, the general features of two curves of the butoxy members are maintained.

The depressions in the N–I transition temperature due to the 2-X substituent in the present series are much less than those in compounds 1, resulting in a small separation between the two curves. For example, the temperature drop between X = H and 2-Cl for the hexyloxy member is reduced to 43°C from 62°C but that between X = H and 3-Cl is hardly

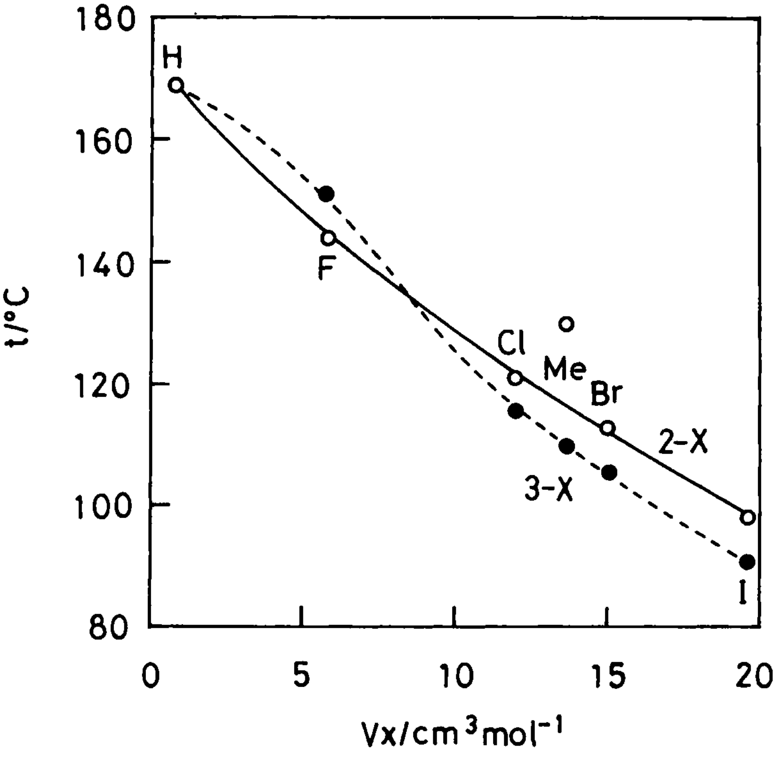

FIGURE 3 Plots of the N–I transition temperature of the butoxy members against van der Waals volume of substituent.

affected by the change of the molecular core. The separation between the N – I transition temperatures of the 2-Cl and 3-Cl derivatives is 20°C in compounds 1, whereas it is merely 5°C in compounds 2.

The points for X = 2-Me and 3-Me of compounds 1 do not fit in the curves given by the points for X = H and halogens, indicating that the change of the N – I transition temperature by the incorporation of a lateral substituent cannot be explained by its geometrical factor only. As a matter of fact, the point for X = 2-Me of the hexyloxy member is well above the curve for 2-X substituents and the point for X = 3-Me is below not only the curve for 3-X substituents but also the point for X = 2-Me. In the present compounds, the situation is quite different; that is, the point for 3-Me of the butoxy member fits in the curve for 3-X substituents but that of the hexyloxy member is found a little below the curve. On the other hand, the points for X = 2-Me of both the butoxy and hexyloxy members are located above the curve for 2-X substituents.

The Δt_{NI} values of the 2-X derivatives are generally large, particularly so for the lower homologous members; for example, the value is 48°C when X = Cl and $n = 1$ and then decreases gradually as the alkyl chain length is increased. The values for the hexyloxy members are as follows: 22°C for 2-F, 27°C for 2-Cl, 30°C for 2-Br, 8°C for 3-F, 6°C for 3-Cl, and 7°C for 3-Br. The N-phenyl moiety bearing a lateral substituent in the present compound is conformationally more mobile than the CH-phenyl moiety in compound 1. According to Bernstein *et al.*, the minimum energy conformation of *N*-benzylideneaniline corresponds to a rotation about the N-phenyl bond of about 45° and a rotation about the CH-phenyl bond of 0° [10]. The rotation of the end phenyl group about the azomethine linkage may diminish the disruption of molecular packing in a nematic phase imposed particularly by the 2-X-substituent and may yield a large Δt_{NI} value.

The parent compounds in series 1 and also 4-(4-alkoxybenzylideneamino) phenyl benzoate are purely nematogenic but the higher homologous members of their 3-halogeno derivatives exhibit a smectic A phase [1, 8]. In contrast to the depression of the N – I transition temperature, the S – N transition temperature of these compounds is promoted by the 3-halogeno substituent though the extent could not be determined. As not only the higher homologous members of the 3-Cl derivatives but also the parent compounds in the present series are smectogenic, the promotion of the transition temperature by 3-X-substitution could be quantitatively evaluated for the first time; that is, 32°C (X = F) , 16°C (X = Cl, 0°C (X = Br), and –11°C (X = I) for the heptyloxy member. The promotion of the smectic phase is not independent of the alkyl chain length. For the octyloxy member, we found 24°C (X = F), 8°C (X = Cl), −3°C (X = Br), and −18°C (X = I). The decrease in the extent in the higher members may be ascribed to the levelling out of the transition temperature in the halogeno derivatives. Figure 4 demonstrates that the S−N/I transition temperatures of the octyloxy members of the F, Cl, Br, and I derivatives plotted against van der Waals volume of the substituents are on a smooth curve. It must be noted that the S−N/I transition temperatures themselves given by the present 3-halogeno derivatives shown by open circles are higher than those of the corresponding derivatives in series 1 shown by shaded circles. However, the afore-mentioned extents of the promotion are less than the estimations made for compounds 1; namely, 24°C *versus* > 26°C (X = F) , 8°C *versus* > 13°C (X = Cl), and −3°C *versus* > 3°C (X=Br)in the case of the

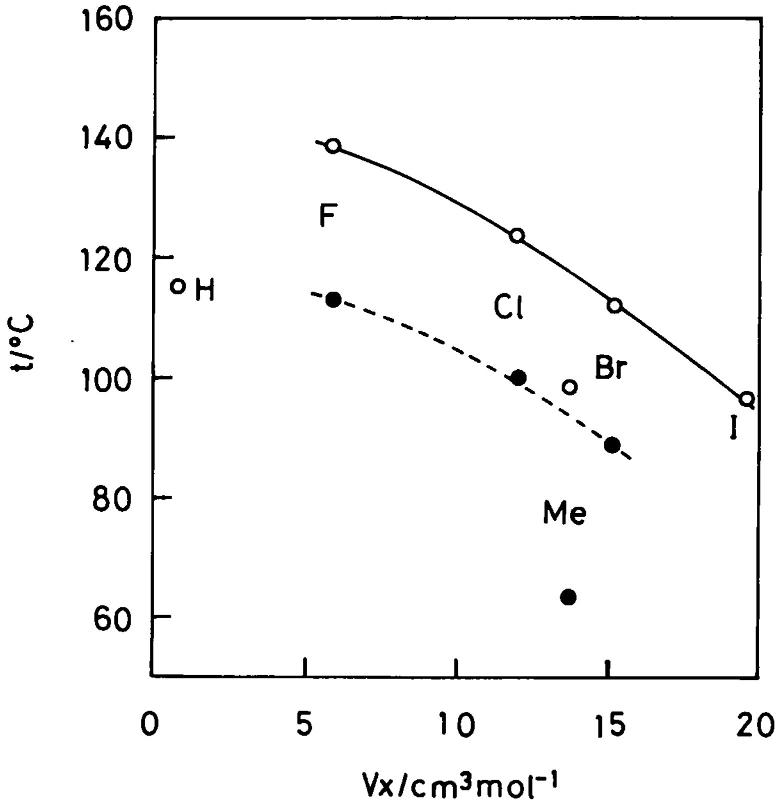

FIGURE 4 Plots of the S−N/I transition temperature of the octyloxy members against van der Waals volume of substituent. Compounds 1 are represented by shaded circles and compounds 2 by open circles.

octyloxy members. These observations clearly indicate that the promotion of a smectic A phase is sensitive to the inversion of the azomethine linkage located close to the lateral substituent. By contrast, the 3-Me substitution results in a large depression; −14°C for the heptyloxy member and −16°C for the octyloxy member. In Figure 4, the points for X = H and Me are far below a curve drawn through the points for halogens in accordance with the view that the dipole moment of C−X bonds is crucial in enhancing the lateral attractions which retain the smectic order [11].

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