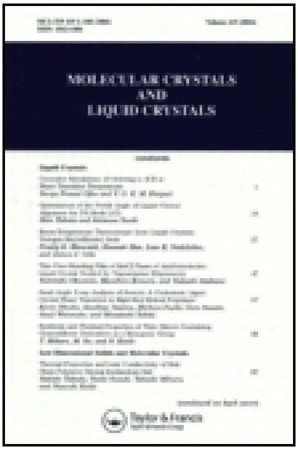

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# Effects of Lateral Substituents on Mesomorphic Behavior. II. 4-(4-Alkoxybenzylideneamino)phenyl Benzoates

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# Effects of Lateral Substituents on Mesomorphic Behavior.
# II. 4-(4-Alkoxybenzylideneamino)phenyl Benzoates

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The mesomorphic properties of 4-(4-alkoxybenzylideneamino)phenyl 2- and 3-$X$-benzoates, where $X =$ Me or Cl, were examined. While the nematic-isotropic transition temperatures of the 2-Me and 2-Cl derivatives are nearly identical, the 3-Cl derivatives give higher transition temperatures than the 3-Me derivatives, the difference being 20°C or more. The nematic phase given by the lower homologous members of the 2-Me derivative is thermally more stable than that of the 3-Me derivative but this relation is reversed for the higher members. In contrast to the purely nematogenic parent compounds, the 3-halogeno derivatives of the higher homologous members exhibit a smectic A phase.

*Keywords:* Nematic; smectic; lateral substituent

## INTRODUCTION

In the first paper of this series, we described the mesomorphic properties of 2- and 3-$X$-phenyl 4-(4-alkoxybenzylideneamino)benzoates (1) bearing Me or Cl as $X$ [1]. Although the two lateral substituents are nearly the same in size, the depressions in nematic-isotropic (N-I) transition temperature by the lateral substitution are markedly different. The N-I transition temperature of the 2-Me derivative is higher by 10 to 15°C than that of the 2-Cl

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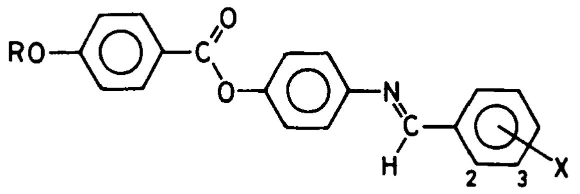
derivative, whereas the opposite is true for the 3-*X* derivatives and the difference is as much as 21°C. The parent compounds (*X* = H) are purely nematogenic but the higher homologous members carrying the 3-halogeno substituent are smectogenic. Besides, the smectic-nematic (S-N) transition temperatures of the octyloxy members, 113°C for 3-F, 100°C for 3-Cl, and 89°C for 3-Br, are higher than 87°C where the nematic melt of the parent compound solidifies. The generation of a smectic A phase by the 3-halogeno substituent is in sharp contrast to the depressions of the S-N transition temperature of 4′-octyloxybiphenyl-4-carboxylic acid by the lateral substituent reported by Gray and Worrall [2]. This paper presents the behavior of 4-(4-alkoxybenzylideneamino)phenyl 2-*X*- and 3-*X*-benzoates (2), where the whole molecular core is kept the same as compound 1 but the end groups carrying substituents are interchanged.



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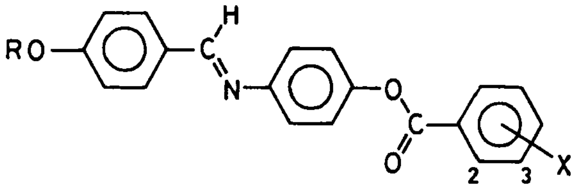

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## EXPERIMENTAL

All the benzaldehydes and benzoic acids were commercial products. The desired compound was obtained by condensing 4-aminophenol with a 4-alkoxybenzaldehyde in refluxing ethanol and then the resulting Schiff's base with a benzoic acid in chloroform at room temperature by the procedure of Hassner and Alexanian [3]. The products were purified by recrystallization from appropriate solvents till sharp constant transition temperatures were achieved. Transition temperature measurements and mesophase identification were performed using a Yanaco melting point apparatus and a Rigaku differential scanning calorimeter as described in details in a previous paper [1].

## RESULTS AND DISCUSSION

The transition temperatures and associated enthalpies of fifty-one compounds in series 2 are summarized in Table I. Here, the crystalline, smectic A, nematic, and isotropic liquid phases are denoted by K, $S_A$, N, and I, respectively. No smectic phase could be detected for the parent compounds ($X$ = H) and the 2-$X$ derivatives. The 3-I derivatives are not mesogenic.

The unsubstituted compounds have higher N-I transition temperatures compared to those in series 1 as is indicated by $\Delta t_{\text{N-I}}$ in Table I. Funakoshi *et al.* examined the N-I transition temperature of 4-(4-$X$-substituted benzylideneamino)phenyl benzoate and its seven isomeric compounds, where $X$ = CN, $NO_2$, $CH_3O$, and $C_2H_5O$ [4]. A comparison between four pairs of the isomeric compounds with the same molecular core revealed that a higher N-I transition temperature is acquired when any terminal substituent, which is the most dominant factor in determining the thermal behavior, is attached to the phenyl group linked through an azomethine group to the rest of molecule. Thus, an azomethine linkage is a more ideal unit for building up a rigid linear conjugated system contributing to mesophase stability than a carbonyloxy linkage. Our $\Delta t_{\text{N-I}}$ values for $n = 1$ and 2 are in good agreement with theirs; namely, 9 and 5°C.

As is shown in Figure 1, the N-I transition temperatures of the 2- and 3-Me derivatives are close to each other and the plots against the number of carbon atoms in the alkyl chain intersect between $n = 3$ and 4, indicating that the alkyl chain length is critical in determining the nematic thermal stability. Gray and Worrall defined the molecular breadth as the diameter of the smallest cylinder through which the dimerized aromatic carboxylic acid would pass, the flexible alkyl chain being assumed not to interfere, and found that the N-I transition temperature of their compounds decreases regularly with increasing molecular breadth [2]. The intersection between the transition temperature plots for the 2-Me and 3-Me derivatives shown in Figure 1 does not support their assumption concerning the alkyl chain.

The enhancement of the odd-even alternation of the N-I transition temperatures by the incorporation of a lateral substituent found for series 1 is also noted for the present one. In opposition to the case of methyl derivatives, the thermal stability of the 3-Cl derivatives is higher by 11 to 15°C than the 2-Cl derivatives when $n = 1$ and 2, and then the difference increases up to 28°C. Moreover, it must be pointed out that, in the present series, the N-I transition temperatures of the 2-Me and 2-Cl derivatives are essentially the same, whereas those of the 3-Cl derivatives are higher by 20°C or more than those of the 3-Me derivatives.

TABLE I Transition temperatures (°C) and enthalpy changes (kJ mol$^{-1}$) of 4-(4-alkoxybenzylideneamino)phenyl 2- or 3-*X*-benzoates [a]

| *n*[b] | *X* | *K* | $S_A$ | *N* | *I* | $\Delta t_{N\text{-}I}$ |
|---|---|---|---|---|---|---|
| 1 | H | .118 (33) | | .179 (0.5) [d] | . | 9 |
| 2 | H | .143 (33) | | .188 (0.8) [d] | . | 7 |
| 3 | H | .122 (39) | | .164 (0.6) | . | 8 |
| 4 | H | .115 (31) | | .169 (0.8) | . | 11 |
| 5 | H | .99 (40) | | .158 (0.7) | . | 8 |
| 6 | H | .110 (34) | | .159 (0.9) | . | 9 |
| 7 | H | .110 (36) | | .152 (0.8) | . | 9 |
| 8 | H | .110 (42) | | .151 (0.8) | . | 7 |
| 1 | 2-Me | .98 (31) | | .115 (0.1) | . | 33 |
| 2 | 2-Me | .100 (34) | | .133 (0.2) | . | 22 |
| 3 | 2-Me | .94 (33) | | .103 (0.1) | . | 15 |
| 4 | 2-Me | .89 (30) | | .117 (0.2) | . | 13 |
| 5 | 2-Me | .77 (35) | | .105 (0.3) | . | 12 |
| 6 | 2-Me | .81 (31) | | .110 (0.3) | . | 12 |
| 7 | 2-Me | .83 (44) | | .104 (0.3) | . | 12 |
| 8 | 2-Me | .83 (45) | | .108 (0.4) | . | 12 |
| 1 | 3-Me | .120 (39) | | [.97 (0.2)] [c] | . | 25 |
| 2 | 3-Me | .128 (45) | | .128 (0.5) | . | 24 |
| 3 | 3-Me | .110 (41) | | [.101 (0.3)] [c] | . | 26 |
| 4 | 3-Me | .88 (34) | | .119 (0.5) | . | 24 |
| 5 | 3-Me | .88 (42) | | .107 (0.4) | . | 22 |
| 6 | 3-Me | .91 (38) | | .114 (0.6) | . | 20 |
| 7 | 3-Me | .89 (48) | | .108 (0.5) | . | 20 |
| 8 | 3-Me | .89 (47) | | .112 (0.7) | . | 16 |
| 1 | 2-Cl | .113 (37) | | .122 (0.2) [e] | . | 52 |
| 2 | 2-Cl | .102 (34) | | .134 (0.3) | . | 35 |
| 3 | 2-Cl | .88 (34) | | .102 (0.2) | . | 27 |
| 4 | 2-Cl | .97 (36) | | .117 (0.3) | . | 26 |
| 5 | 2-Cl | .87 (34) | | .104 (0.2) | . | 26 |
| 6 | 2-Cl | .92 (36) | | .110 (0.3) | . | 22 |
| 7 | 2-Cl | .80 (34) | | .104 (0.4) | . | 24 |
| 8 | 2-Cl | .78 (43) | | .108 (0.4) | . | 23 |
| 1 | 3-Cl | .147 (41) | | [.133 (0.4)] [c, e] | . | 35 |
| 2 | 3-Cl | .142 (43) | | .149 (0.4) | . | 27 |
| 3 | 3-Cl | .134 (42) | | [.127 (0.3)] [c] | . | 28 |
| 4 | 3-Cl | .125 (42) | | .139 (0.5) | . | 27 |
| 5 | 3-Cl | .118 (44) | | .130 (0.4) | . | 26 |
| 6 | 3-Cl | .117 (48) | [.110 (0.3)] [c] | .135 (0.9) | . | 21 |
| 7 | 3-Cl | .119 (54) | [.116 (0.8)] [c] | .130 (0.5) | . | 21 |
| 8 | 3-Cl | .118 (53) | .124 (1.5) | .133 (0.9) | . | 20 |
| 6 | 2-F | .87 (31) | | .138 (0.6) | . | 24 |
| 6 | 2-Br | .100 (40) | | [.98 (0.3)] [c] | . | 22 |
| 6 | 2-I | .111 (30) | | [.78 (0.2)] [c] | . | – |
| 5 | 3-F | .109 (45) | | .150 (0.6) | . | – |
| 6 | 3-F | .104 (41) | .118 (0.7) | .152 (0.9) | . | 13 |
| 7 | 3-F | .111 (48) | .124 (1.0) | .147 (0.8) | . | 13 |
| 8 | 3-F | .107 (47) | .133 (1.5) | .148 (1.0) | . | 13 |
| 5 | 3-Br | .126 (53) | | [.122 (0.4)] [c] | . | – |
| 6 | 3-Br | .126 (50) | | .127 (0.6) | . | 24 |
| 7 | 3-Br | .126 (60) | | [.123 (0.6)] [c] | . | 24 |
| 8 | 3-Br | .125 (60) | [.115 (1.0)] [c] | [.125 (0.9)] [c] | . | 23 |

[a] The enthalpy changes are in parentheses; [b] The number of carbon atoms in the alkyl group; [c] Monotropic transition; [d] Taken from Ref. [4]; [e] Taken from Ref. [5].

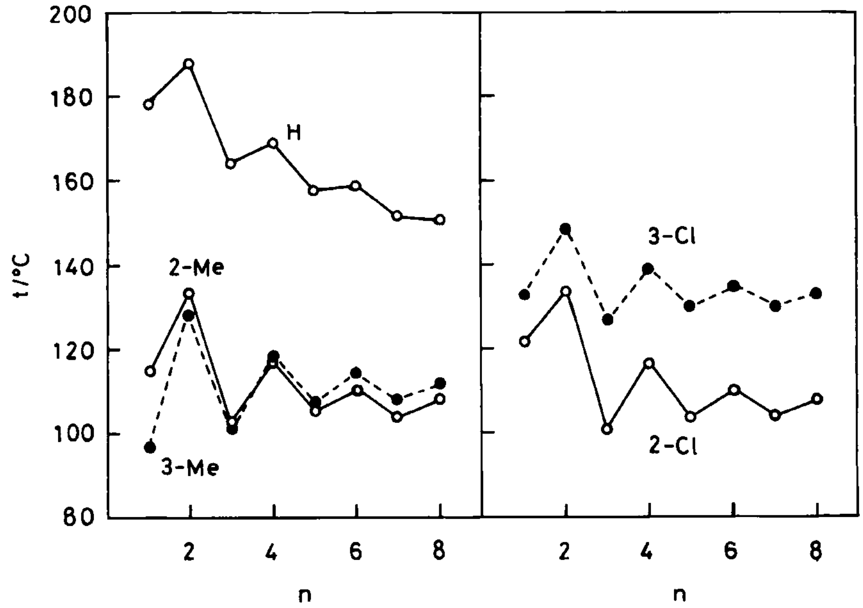

FIGURE 1 Dependence of the N-I transition temperature on the number of carbon atoms ($n$) in the alkyl group.

In Figure 2, the N-I transition temperatures of the hexyloxy members are plotted against van der Waals volume of the lateral substituents proposed by Bondi [6]. The points for $X$ = H and halogens are on a smooth curve for the 2-$X$ and 3-$X$ derivatives respectively. While the former curve is almost straight, the latter is slightly convex upwards. The 2-$X$ substituent produces larger depression than the 3-$X$ substituent. A similar tendency was observed for series 1 but all the depressions in this series are much less than those in the previous one. For example, the difference between $X$ = H and 2-Cl is reduced to 49°C from 62°C and that between $X$ = H and 3-Cl is reduced to 24°C from 36°C. Consequently, the difference in the N-I temperature between series 1 and 2 ($\Delta t_{\text{N-I}}$ in Tab. I) is amplified by the introduction of a lateral substituent. It is exceptionally large when $n$ = 1 and 2, and then decreases gradually as the alkyl chain length increases. The mean values for the higher four homologous members are as follows: 12°C for 2-Me, 16°C for 2-Cl, 20°C for 3-Me, 22°C for 3-Cl. These findings may be ascribed to the conformationally mobile benzoyloxy moiety into which a lateral substituent is incorporated. Rotating the end phenyl group around the linkage diminishes partially the disruption of molecular packing in a nematic phase imposed by the lateral substituent and gives rise to a smaller

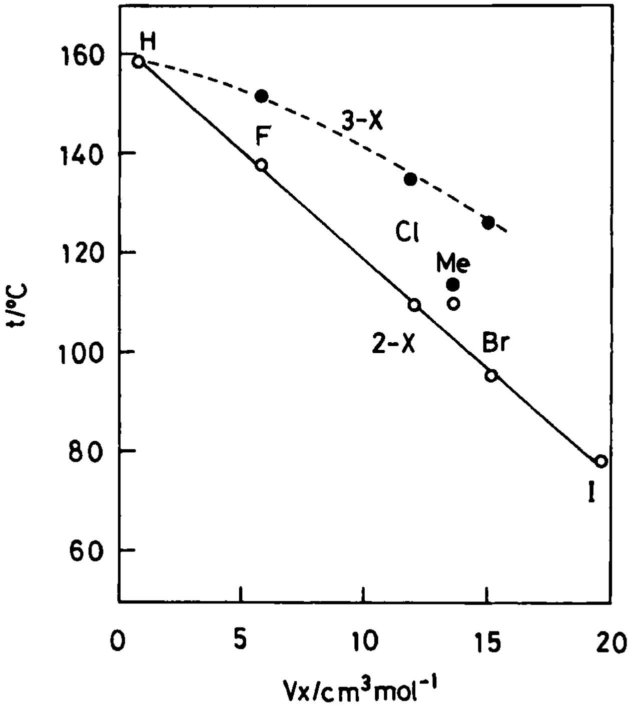

FIGURE 2 Plots of the N-I transition temperature against van der Waals volume of substituent.

depression of the thermal stability. The points for $X$ = 2-Me and 3-Me in the present series as well as in series 1 do not fit in the curves given by the points $X$ = H and halogens. However, the complex situation is illustrated by the fact that, contrary to series 1, the point for $X$ = 3-Me is above that for $X$ = 2-Me.

A metastable smectic A phase is displayed by the 3-F and 3-Cl derivatives among the examined hexyloxy members. Surprisingly, the S-N transition temperature of the former compound (118°C) is higher than the K-N transition temperature of the parent compound (110°C). In order to throw further light on the smectic behavior of the present series, the work was extended to some other homologous members. As to the 3-F and 3-Cl derivatives, a smectic A phase is detectable for the hexyloxy or higher members. Both the transition temperatures and the enthalpy changes increase as the series is ascended. The octyloxy member is the only one for which we could observe a smectic phase among the 3-Br derivatives listed in Table I. The S-N transition temperatures recorded for the octyloxy members are as follows: 133°C for $X$ = F, 124°C for Cl, and 115°C for Br. It must be emphasized that even the last-mentioned temperature is higher than the K-N transition temperature of the parent compound. In fact, the nematic melt of the unsubstituted compound solidified at 90°C. The generation of a smectic A phase by a 3-halogeno substituent was disclosed also for series 1 but the above-mentioned S-N transition temperatures are higher by 20°C or more, suggesting that the flexibility of the benzoyloxy group carrying the lateral substituent is also a favorable factor in stabilizing the smectic phase.

Lateral substituent is known to reduce both the nematic and smectic phase stabilities and the influence on smectic phase stability is nearly always larger because of the particular disruption to the lamellar packing necessary for smectic phases [7, 8]. However, $X$ = F is recognized to be exceptional. Gray and Worrall observed only a small effect upon the smectic thermal stability of 4′-octyloxybiphenyl-4-carboxylic acid. They concluded that the breadth increase is counteracted by the increase in intermolecular interaction arising from the increase in permament polarization on passing from $X$ = H to $X$ = F [2]. The results have been confirmed by the later work on the same compounds by Balkwill *et al.* [9]. It has been stated that 3-fluoro-4, 4″-dipentylterphenyl is very strongly smectogenic because the polar fluoro substituent filling vacant space on the edge of the core strengthens the lateral intermolecular attractions and offsets the smectic-destroying effect of the extra molecular breadth [7]. As a matter of fact, the S-I transition temperature of the parent compound, 4, 4″-dipentylterphenyl is reduced to 185.5°C from 213°C by the lateral fluoro substituent. Therefore, this statement does not mean the enhancement of smectic thermal stability. Accordingly, the depression of the N-I transition temperature accompanied by a large promotion of the S-N transition temperature by incorporating a 3-halogeno substituent found for series 1 and 2 seems to be uncommon.

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