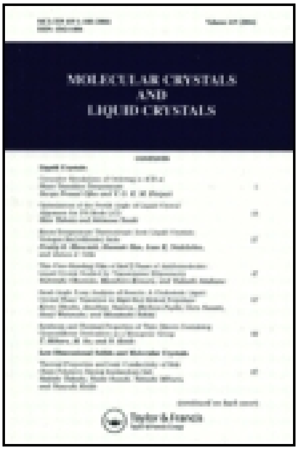

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Effects of Lateral Substituents on Mesomorphic Behavior. I. 4-(Benzylideneamino) phenyl 4-Alkoxybenzoates

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Effects of Lateral Substituents on Mesomorphic Behavior. I. 4-(Benzylideneamino)phenyl 4-Alkoxybenzoates

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Liquid crystalline transition temperatures in 4-(2- and 3-X-benzylideneamino)phenyl 4-alkoxybenzoates, where X = Me or Cl, were examined. Although the two substituents are geometrically similar, they affect the nematic-isotropic transition temperature differently. The transition temperature of the 2-Me derivative is higher by 10 to 15°C than that of the 2-Cl derivative, whereas the reverse is true for the 3-X derivatives, the difference being 14 to 21°C. The 3-halogeno derivatives of the higher homologous members exhibit a smectic A phase which is not observed for the parent compounds.

Keywords: Nematic; smectic; lateral substituent

INTRODUCTION

As early as 1957, Gray *et al.* studied the nematic and smectic thermal stabilities of 4′-alkoxybiphenyl-4-carboxylic acid and its 3′-X-substituted derivatives and showed that when the nematic-isotropic (N—I) transition temperatures are plotted against the molecular diameters, all the points for X = H, F, Me, Cl, Br, I, and NO_2 lie on a smooth, steeply falling curve [1, 2]. Thus, despite the different polarities of the substituents, the main effect appeared to be the increased separation between the long axes of the

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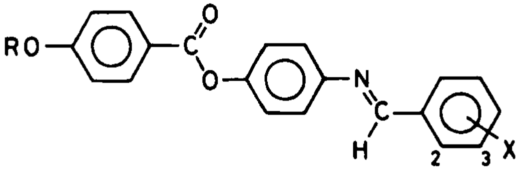
molecules in the nematic melt. On the other hand, both the molecular diameter and the dipole moment of the C—X bond were shown to be important when the smectic-nematic (S—N) or smectic-isotropic (S—I) changes of the same compounds are considered. Later, Gray concluded that the relative effect of a lateral substituent on the nematic and smectic thermal stabilities depends not only on the size and polarity of the substituent but also upon the nature of the molecule into which it is introduced [3]. Osman's work on 1,4-bis (4-trans-pentylcyclohexyl)benzenes revealed that all of the N—I transition temperatures lie on a smooth curve when the temperature is plotted against Bondi's van der Waals volume of the lateral substituent [4]. The substituents employed by this author were halogens and methyl as well as cyano groups. While the effects of lateral substituents on the mesomorphic behavior have been the subject of extensive studies [5], not much attention has been paid to the type of molecular core.

With the hope of evaluating the importance of the molecular core in determining the mesomorphic behavior of laterally-substituted compounds, we planned to examine systematically the liquid crystalline transition temperatures employing isomeric series. This paper, the first in this series, presents results of a study on 4-(2- and 3-X-benzylideneamino)phenyl 4-alkoxybenzoates (1), where X = Me or Cl. Since these two lateral substituents have nearly the same size, a replacement of one by the other should not change appreciably the N—I transition temperatures if the change was a direct result of geometrical modifications introduced to the molecular structure.



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EXPERIMENTAL

All the benzaldehydes and 4-alkoxybenzoic acids were commercially available. Every desired compound was obtained by condensing a benzaldehyde with 4-aminophenol in boiling ethanol and then the resulting Schiff's base with a benzoic acid in chloroform at room temperature by the carbodiimide method [6]. The products were purified by recrystallization from appropriate solvents until sharp constant transition temperatures were achieved. Mesophase identification and transition temperature measurements were accomplished using a Yanaco melting point apparatus, model PV-500V, with the aid of a polarizing microscope (magnification 60×) and also a Rigaku differential scanning calorimeter, model TAS-300 DSC8240D.

RESULTS AND DISCUSSION

The transition temperatures and enthalpy changes of forty-eight compounds are listed in Table I. Here, K, S_A, N and I stand for the crystalline, smectic A, nematic, and isotropic liquid phases, respectively. No smectic phase is observable for the parent compounds (X═H).

As is shown in Figure 1, the N—I transition temperature of the parent compounds is less depressed by 2-Me substitution than 3-Me substitution. The even-membered homolgues of both the 2-Me and 3-Me derivatives give falling transition curves and the odd-membered homologues of the derivatives give rising ones. The difference in temperature between the 2-Me and 3-Me derivatives is merely 10°C at $n=1$ and vanishingly small at $n=8$. In contrast to the methyl derivatives, the N—I transition temperature depression by 3-Cl substitution is appreciably smaller than that by 2-Cl substitution. The separation is as large as 22 to 29°C. Thus, the effects of these two substituents on the N—I transition temperature differ distinctly from each other in the present compounds. Moreover, the hexyloxy, heptyloxy, and octyloxy members of the 3-Cl derivatives are smectogenic. It may be noted that the enthalpy changes associated with the N—I transition are reduced by lateral methyl or chloro substitution. On the other hand, the alternation of N—I transition temperature is enhanced by the introduction of either lateral methyl or chloro substituent.

In order to correlate the depression of the N—I transition temperature with the change in molecular structure, van der Waals volume of the substituents proposed by Bondi and employed by us earlier will be used throughout the present paper [8, 9]. The N—I transition temperatures of the hexyloxy members are plotted against van der Waals volume of substituents in Figure 2. The points for X= H, F, Cl, and Br lie on a smooth curve for each derivative. It may be noted that the curve is concave upwards for the 2-X derivatives and convex upwards for the 3-X derivatives. While the point for the 2-Me derivative is found markedly above the curve, that for the 3-Me derivative is below. In contrast to Bondi's radii, the molecular diameter of

TABLE I Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of 4-(2-X- and 3-X-benzylideneamino)phenyl 4-alkoxybenzoates[a]

n[b]	X	K	S_A	N	I
1	H	.138(27)		. 170(0.4)[d]	.
2	H	.142(35)		. 181(0.8)	.
3	H	.129(43)		. 156(0.6)	.
4	H	.122(39)		. 158(1.0)	.
5	H	.130(40)		. 150(0.6)	.
6	H	.121(43)		. 150(0.7)	.
7	H	.103(42)		. 143(0.7)	.
8	H	. 95(42)		. 144(1.0)	.
1	2-Me	.102(33)		[. 82] [c h]	.
2	2-Me	.120(42)		[. 111(0.4)][c]	.
3	2-Me	. 82(35)		. 88(0.3)	.
4	2-Me	. 95(45)		. 104(0.3)	.
5	2-Me	.107(48)		[. 93(0.3)][c]	
6	2-Me	. 83(44)		. 98(0.4)	.
7	2-Me	. 86(47)		[. 92(0.4)][c]	.
8	2-Me	. 71(42)		. 96(0.3)	.
1	3-Me	.120(34)		[. 72(0.2)][c]	.
2	3-Me	.118(38)		[. 104(0.4)][c]	.
3	3-Me	.106(39)		[. 75(0.3)][c]	.
4	3-Me	.108(50)		[. 95(0.5)][c]	.
5	3-Me	. 85(32)		. 85(0.4)	.
6	3-Me	. 87(34)		. 94(0.3)	.
7	3-Me	. 79(43)		. 88(0.3)	.
8	3-Me	. 71(39)	[. 63(0.4)][c]	. 96(0.5)	.
1	2-Cl	.117(35)		[. 70(0.2)][c e]	.
2	2-Cl	.124(36)		[. 99(0.3)] [c]	.
3	2-Cl	.101(37)		[. 74(0.3)][c]	.
4	2-Cl	.105(32)		[. 91(0.3)][c]	.
5	2-Cl	. 87(42)		[. 78(0.3)][c]	.
6	2-Cl	. 79(27)		. 88(0.3)	.
7	2-Cl	. 90(38)		[. 80(0.3)][c]	.
8	2-Cl	. 74(33)		. 85(0.4)	.
1	3-Cl	.126(35)		[. 98(0.2)][c f]	.
2	3-Cl	.159(47)		[. 121(0.3)][c]	.
3	3-Cl	.125(49)		[. 99(0.3)] [c]	.
4	3-Cl	.111(46)		. 112(0.4)	.
5	3-Cl	. 89(30)		. 106(0.4)	.
6	3-Cl	. 92(33)	[. 76][c g]	. 114(0.5)	.
7	3-Cl	. 82(28)	. 87(0.4)	. 109(0.5)	.
8	3-Cl	. 92(43)	.100(0.5)	. 113(0.5)	.
6	2-F	. 88(26)		. 114(0.6)	.
6	2-Br	. 91(32)		[. 76(0.3)][c]	.
6	3-F	.102(36)	[. 85][c g]	. 139(0.9)	.
7	3-F	. 89(48)	.100(0.4)	. 134(0.7)	.
8	3-F	. 86(26)	.113(1.2)	. 135(1.1)	.
6	3-Br	. 81(46)	[. 67][c g]	. 103(0.6)	.
7	3-Br	. 77(28)	[. 72(0.5)][c]	. 99(0.6)	.
8	3-Br	. 95(50)	[. 89(1.0)][c]	. 102(0.8)	.

[a] The enthalpy changes are in parentheses.

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

[c] Monotropic transition

[d] 139(33) and 170(0.6), [e] 116(31) and 67(0.2), and [f] 130(32) and 104 (0.2) by Matsunaga and Yasuhara (Ref. [7]).

[g] The enthalpy change is too small to be determined.

[h] Microscopic observation.

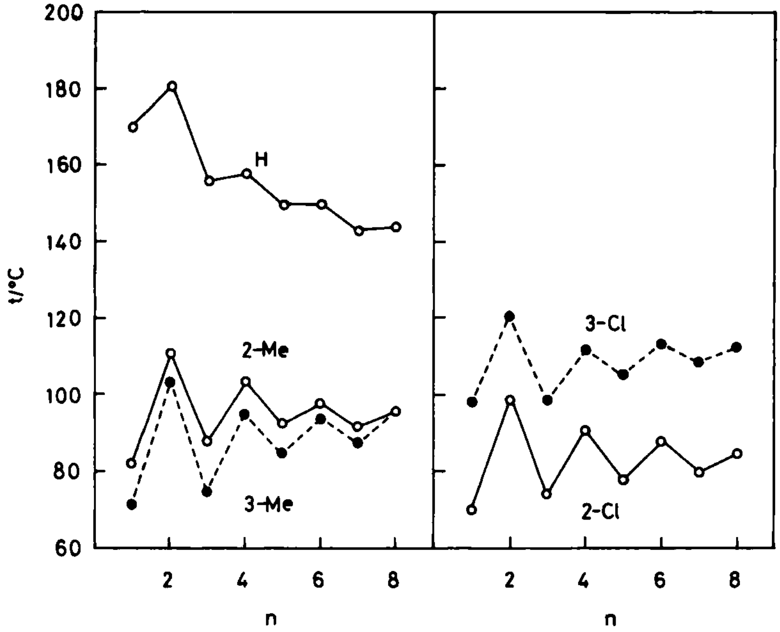

FIGURE 1 Dependence of the N—I transition temperature on the number of carbon atoms (*n*) in the alkyl group.

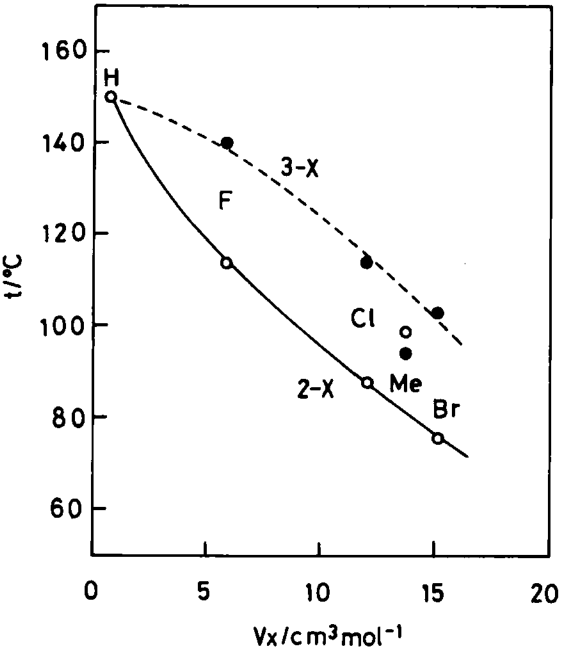

FIGURE 2 Plots of the N—I transition temperature against van der Waals volume of substituent.

3′-chloro-4′-alkoxybiphenyl-4-carboxylic acid estimated by Gray and Worrall is a little larger than that of the corresponding 3′-methyl derivative. If this is the case in our compounds, the point for X = Me in the 2-X derivatives may fit better in the curve employing the molecular diameter instead of van der Waals volume but the deviation has to be enlarged in the 3-X derivatives. Apparently, the relationship similar to that reported by Gray and Worrall and by Osman is not found for the present compounds.

As the effects of the lateral methyl and chloro substituents in the present series are strikingly different, one has to conclude that the change of N—I transition temperature by the incorporation of a lateral substituent cannot be related directly to its size. In other words, the type of molecular core into which a lateral substituent is introduced is as important as the kind of substituent itself in determining the mesomorphic behavior.

It is commonly assumed that the distribution of the centers of mass of the molecules in the nematic phase with respect to a given molecule is spherically symmetric. Such a picture has been shown to be too simple by Leadbetter *et al.* [10]. According to their X-ray diffraction work, the local molecular organization in the nematic phase varies significantly by the type of molecules and short-range structural correlations similar to those of smectic A or C phases can be noted. The extent of short-range ordering is shown to be greater for the higher homologous members. Notably, the repeat distance along the molecular alignment in cyanobiphenyls is about 1.4 times molecular lengths. This distance was interpreted as arising from an overlapping head-to-tail arrangement of molecules, resulting in a quasi-smectic A structure on the local scale.

We included into the present study four compounds having the cyano or nitro group in the place of the alkoxy group. Contrary to the results presented in Figure 1, the N—I transition temperatures of the 2-Me and 3-Me derivatives of the 4-nitro compounds are widely separated; 136°C (enantiotropic) and 116°C (monotropic) respectively. On the other hand, the monotropic N—I transitions of the 2-Cl and 3-Cl derivatives of the 4-cyano compounds are found at essentially an identical temperature, 155°C. Thus, our results suggest that the molecular parameters determining the molecular interactions responsible for the formation of mesophases are strongly interdependent; therefore, anomalous cases would be found for any structure-property relationship of liquid crystals if it was examined in sufficient detail.

It may added that similar studies related to the effects of branching of the ester alkyl chain on the mesomorphic properties of alkyl 4-[4-(4-Xbenzoyloxy)benzylideneamino]benzoates were carried out by one of the present authors [11, 12]. Although the introduction of the first branching methyl group to the ester alkyl chain depresses the N—I transition temperature, the second and/or third groups may either further depress or enhance the temperature, depending upon the nature of terminal substituent X such as CH_3, CH_3O, CN, and NO_2 located far from the ester alkyl group.

A thermodynamically stable smectic A phase is exhibited by the 3-Cl derivatives of the heptyloxy and octyloxy members. It is surprising to see that the S_A—N transition temperature (100°C) of the latter member is higher than the K—N transition temperature (95°C) of the parent compound; in other words, the thermal stability of the smectic A phase is not depressed by the introduction of the lateral chloro substituent but is markedly promoted. Lateral substituents may give rise to not only a decrease in thermal stabilities of the nematic and smectic phases by increasing the lateral separation but also an increase by increasing the polarity and/or polarizability of the molecule. Of these two opposing effects, Gray concluded that the first always predominates unless the substituent does not exert its full breadth-increasing effect [3]. In the present case, the second effect is more important in the smectic A phase although the first predominates in the nematic phase, as indicated in Figure 2.

The two widely-separated curves in Figure 2 may imply that breadth-increasing effect in the smectic phase is also less in the 3-X derivative than in the 2-X derivative. To support these suggestions, we looked into possible metastable smectic A phases appearing from the supercooled nematic melts of the related compounds. No metastable smectic A phase could be detected for the 2-F and 2-Cl derivatives in conformity with the statements by Balkwill *et al.* such as whenever a lateral fluoro substituent points towards the center of the molecular core, smectic phases are eliminated or strongly depressed [13].

In order to supplement the above-mentioned observations on the S—N transition temperature, the heptyloxy and octyloxy members of the 3-F and 3-Br derivatives were also examined. Not only the transition temperature but also the enthalpy change at the S—N transition increase rapidly as the alkyl chain length increases. The S—N transition temperatures of the octyloxy members are as follows: F (113°C) > Cl (100°C) > Br(89°C) > Me (63°C), which are in agreement with the order obtained by Gray and Worrall. However, it must be noted that all the temperatures exhibited by the halogeno derivatives are higher than 87°C where the nematic melt of the parent compound solidified.

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