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Effects of Lateral Substituents on the Mesomorphic Properties of *N*-[4-(4-Methoxybenzoyloxy)benzylidene]aniline and Its Isomeric Compound

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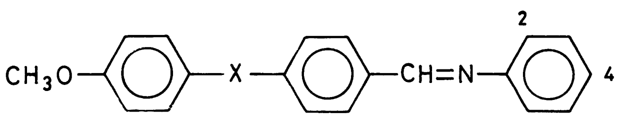
Synopsis. The nematic phases exhibited by the title compounds carrying a hydroxyl or cyano group at the 2-position of the aniline moiety are thermally more stable than expected on the basis of the relationship between the nematic–isotropic transition temperature of the corresponding halogeno derivatives and the van der Waals volume of the substituents.

The effects of lateral substituents on the mesomorphic properties have been the subject of extensive studies by many workers.[1] For example, Gray et al. examined the thermal behavior of 4-[(4-alkoxybenzylidene)amino]biphenyls and 4,4′-bis[(4-alkoxybenzylidene)amino]biphenyls with methyl or halogeno-substituents in the 2-position of the biphenyl core, and showed that both the smectic–nematic and the nematic–isotropic transition temperatures decrease smoothly with increasing the molecular breadth.[2,3] Moreover, Osman's recent work on 1,4-bis(4-*trans*-pentylcyclohexyl)benzenes revealed that all of the nematic–isotropic transition temperatures lie on a smooth curve when the temperature is plotted against the van der Waals volume of the lateral substituent.[4] The substituents employed by the latter author were halogens and methyl as well as cyano groups.

However, experience has shown that the effects of a substituent on the mesomorphic properties vary with the type of parent system, and also that a steric factor cannot account for all of the observed effects regarding terminal substituents; therefore, the above-mentioned relationship may not hold for other types of compounds. Indeed, we found that the nematic–isotropic transition temperatures of *N*-[4-(4-methoxybenzoyloxy)-benzylidene]-2-hydroxy and 2-cyanoanilines (**1**) deviate appreciably from a smooth curve constructed by those of the corresponding halogeno derivatives. Similarly, marked deviations were also observed with a series of isomeric compounds, 4-methoxyphenyl 4-[4-(2-substituted phenyliminomethyl)]benzoates (**2**).



(**1**) X = -CO-O- (**2**) X = -O-CO-.

Experimental

The Schiff bases were prepared and then esterification was carried out, following the procedure of Hassner and Alexanian, to obtain the desired compounds.[5] Microscopic and calorimetric examinations were made, as described in a previous paper.[6]

Results and Discussion

The van der Waals volumes of substituents at the 2- or 4-position of the aniline moiety, the transition temperatures, and the associated enthalpy changes of compounds **1** and **2** are presented in Tables 1 and 2, respectively. For a comparison, the corresponding 4-substituted compounds were included in our examination. All of the van der Waals volumes of the substituents were taken from Bondi's work, except for that of the hydrogen atom (0.7 $cm^3 mol^{-1}$), which was calculated concerning the basis of a van der Waals radius of hydrogen of 0.100 nm, a C–H bond length of 0.110 nm, and a van der Waals radius of carbon of 0.170 nm.[7] Here, K, N, and I stand for the crystalline, nematic, and isotropic liquid phases, respectively.

As is shown in Fig. 1, plots of the N–I transition temperature of the parent compounds and their 2-halogeno derivatives against the van der Waals volume of the substituent give smooth curves. The curve for series 1 is slightly concave upwards, whereas the curve for series 2 is slightly convex upwards. Contrary to what has been reported for the above-mentioned cases, the transition temperatures of the hydroxy and cyano derivatives in the present series deviate markedly from a smooth relationship.

In the case of *N*-(2-hydroxy-4-methoxybenzylidene)-4-butylaniline, the hydroxyl group does not exert its

Table 1. Van der Waals Volume ($cm^3 mol^{-1}$) of Substituent,[a] and Transition Temperatures (°C) and Enthalpy Changes ($kJ mol^{-1}$) of Compounds **1**[b]

Substituent	V	K		N		I
H[c]	0.7	·	129 (31)	·	177 (0.4)	·
2-F[c]	5.8	·	135 (39)	·	145 (0.3)	·
2-OH	8.0	·	140 (35)	·	153 (0.3)	·
2-Cl[c]	12.0	·	129 (34)	[·	118 (0.3)]	·
$2-CH_3$[c]	13.7	·	150 (41)	[·	121 (0.2)]	·
2-CN	14.7	·	162 (39)	[·	144 (0.5)]	·
2-Br[c]	15.1	·	140 (34)	[·	105 (0.2)]	·
2-I[c]	19.6	·	133 (36)	[·	81 (0.2)]	·
4-F[c]	5.8	·	131 (32)	·	255 (0.8)	·
4-OH	8.0	·	202 (35)	·	305[d]	·
4-Cl[c]	12.0	·	172 (27)	·	285 (1.6)	·
$4-CH_3$[c]	13.7	·	129 (28)	·	278 (1.1)	·
4-CN	14.7	·	180 (38)	·	324 (0.8)	·
4-Br[c]	15.1	·	187 (38)	·	280 (0.9)	·
4-I[c]	19.6	·	202 (21)	·	274 (0.4)	·

a) Taken from Ref. 7. b) The last values are in parentheses. The braced quantities represent monotropic transitions. c) Taken from Ref. 8. d) Approximate decomposition temperature.

Table 2. Van der Waals Volume (cm^3 mol^{-1}) of Substituent,$^{a)}$ and Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **2**$^{b)}$

Substituent	V	K		N		I
H$^{c)}$	0.7	.	151 (40)	.	173 (0.3)	.
2-F	5.8	.	118 (31)	.	152 (0.3)	.
2-OH	8.0	.	174 (43)	[.	161 (0.2)]	.
2-Cl$^{c)}$	12.0	.	129 (35)	.	132 (0.3)	.
2-CH$_3$	13.7	.	142 (41)	[.	129 (0.2)]	.
2-CN	14.7	.	171 (44)	[.	149 (0.5)]	.
2-Br	15.1	.	143 (38)	[.	119 (0.3)]	.
2-I	19.6	.	146 (38)	[.	97 (0.2)]	.
4-F	5.8	.	146 (36)	.	251 (0.8)	.
4-OH	8.0	.	226 (56)	.	330$^{d)}$	.
4-Cl	12.0	.	168 (39)	.	284 (0.8)	.
4-CH$_3$	13.7	.	149 (36)	.	275 (0.9)	.
4-CN	14.7	.	204 (36)	.	276 (0.6)	.
4-Br	15.1	.	169 (42)	.	280 (0.7)	.
4-I	19.6	.	193 (46)	.	274 (0.5)	.

a) Taken from Ref. 7. b) The last values are in parentheses. The braced quantities represent monotropic transitions. c) Taken from Ref. 6. d) Approximate decomposition temperature.

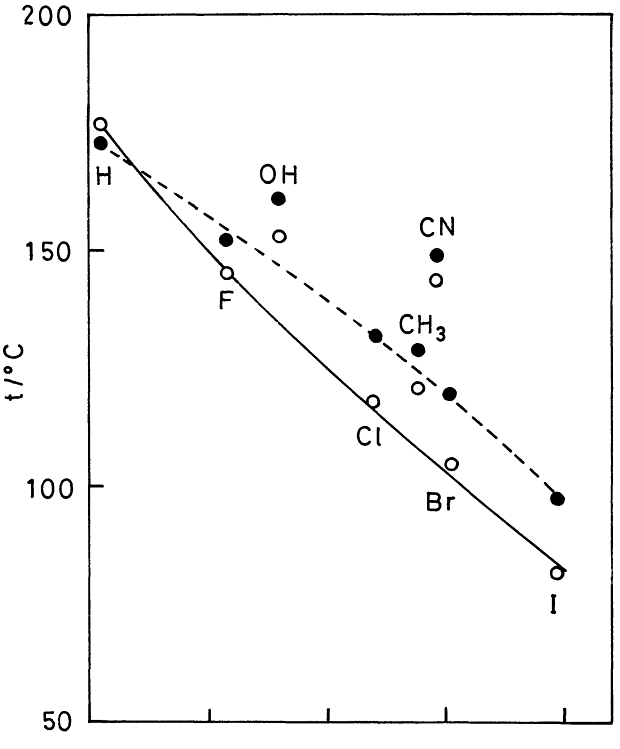


Fig. 1. Plots of the N–I transition temperature of compounds **1** (○) and of compounds **2** (●) against the van der Waals volume of substituents at the 2-position.

full breadth effect, and gives rise to an enhancement of the N–I transition temperature because it is held in the *cis*-position through intramolecular hydrogen bonding.$^{9)}$ Similarly, we found that the transition temperatures of 4-(2-hydroxybenzylideneamino)phenyl 4-methoxybenzoate (193 °C) and 4-methoxyphenyl 4-(2-hydroxybenzylideneamino)benzoate (181 °C), which are isomeric with compounds **1** and **2**, are higher than those of their parent compounds (171 °C and 159 °C, respectively). For the 2-hydroxy derivatives of the present series too, an intramolecular hydrogen bonding is conceivable but stabilization of the nematic phase is clearly less significant. The same group at the 4-position is subject to intermolecular hydrogen bonding and gives rise to a promotion of the mesophase if the structural criteria for liquid crystallinity are satisfied.$^{10,11)}$ The present 4-hydroxy derivative gives the highest, or the second-highest, N–I transition temperature in each series.

The terminal cyano group is well-known to give rise to an antiparallel correlation of molecular dipoles, which often results in higher N–I transition temperatures than with a comparable nonpolar substituent. As a matter of fact, the 4-cyano derivative gives the highest clearing point among compounds **1**, but the fourth among compounds **2**. The deviation of the N–I transition temperature from a smooth curve suggests that dipolar attractive forces due to a lateral cyano group cannot be ignored compared with dispersive forces in influencing the nematic thermal stability of our compounds.

A relatively small deviation of the N–I transition temperature of the methyl derivative in series 1 from a smooth curve cannot be ascribed to dipolar attractive forces and remains to be clarified.

The effects of terminal substituents on the mesomorphic behavior are certainly not simple. For example, even in the case of halogeno derivatives the nematic thermal stability increases in the order F, I, Br, Cl and cannot be explained in terms of either molecular length or van der Waals volume. It is likely that all of the factors applicable to the terminal substituents should, more or less, be considered for the lateral substituents. Apparently, the simple relationship reported by previous authors does not provide a general interpretation of the effects of lateral substituents on the N–I transition temperatures.

References

1) K. J. Toyne, "Thermotropic Liquid Crystals," ed by G. W. Gray, John Wiley, Chichester (1987), pp. 47—57.

2) D. J. Byron, G. W. Gray, A. Ibbotson, and B. M. Worrall, *J. Chem. Soc.*, **1963**, 2246.

3) S. J. Branch, D. J. Byron, G. W. Gray, A. Ibbotson, and B. M. Worrall, *J. Chem. Soc.*, **1964**, 3279.

4) M. A. Osman, *Mol. Cryst. Liq. Cryst.*, **128**, 45 (1985).

5) A. Hassner and V. Alexanian, *Tetrahedron Lett.*, **1978**, 4475.

6) Y. Matsunaga and K. Yasuhara, *Mol. Cryst. Liq. Cryst.*, in press.

7) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

8) H. Hasegawa, T. Masuda, Y. Matsunaga, S. Seo, and K. Yasuhara, *Bull. Chem. Soc. Jpn.*, **62**, 2875 (1989).

9) I. Teucher, C. M. Paleos, and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **11**, 187 (1970).

10) D. C. Schroeder and J. P. Schroeder, *J. Org. Chem.*, **41**, 2566 (1976).

11) H. Takeda, Y. Sakurai, S. Takenaka, H. Miyake, T. Doi, and S. Kusabayashi, *Chem. Lett.*, **1989**, 1335.