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Effects of Terminal Substituents on Mesomorphic Properties: Phenyl 4-(4-X-Substituted phenyliminomethyl)benzoate and its Isomeric Compounds

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The nematic-isotropic transition temperature of phenyl 4-(4-X-substituted phenyliminomethyl)benzoate and its seven isomeric compounds carrying only one terminal substituent; i.e., methoxyl, ethoxyl, nitro, or cyano group, has been compared. The temperature is influenced not only by the terminal substituent but also by the arrangement of the linking groups and the effects of these two features are mutually dependent. The efficiency order of substituents for nematic thermal stability was found to be CN > NO_2 > C_2H_5O > CH_3O. The difference in the temperature is as large as 31 to 54°C between the cyano and methoxy derivatives and 23 to 44°C between the nitro and methoxy derivatives. The latter finding is in sharp contrast with the order CH_3O > NO_2, which has been generally quoted. In order to find some clue to the relationship between molecular features and mesomorphic behavior, the compounds were classified into four pairs of the isomeric compounds with the same molecular skeleton, those with a carbonyloxy linking group inverted, and those with an azomethine linking group inverted and their N-I transition temperatures were compared with each other.

Keywords: nematic, terminal substituents, linking groups

INTRODUCTION

A typical mesogenic molecule consists of a two-ring system with two terminal substituents and a central linking group. Each feature is well known to have a significant effect on mesomorphic properties and has been separately discussed in many review articles. As to terminal substituents, Gray compiled the mesomorphic properties of 4-(4-X-substituted benzylideneamino)-4′-methoxy- and -4′-octyloxybiphenyls, 4′-X-substituted biphenyl-4-carboxylic acids, and 2-methylbutyl 4-(4-X-substituted benzylideneamino)cinnamates.[1,2] Strictly comparable data have not been obtained from these four series because some members are not nematogenic. Nonetheless, the orders in the four series are sufficiently similar and he was able

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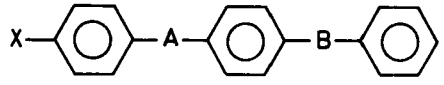
to construct the following order of efficiency in promoting nematic-isotropic (N-I) transition temperatures.

$$Ph > NHCOCH_3 > CN > CH_3O > NO_2$$
$$> Cl > Br > N(CH_3)_2 > CH_3 > F > H$$

This order has been used as guidance in predicting the possible behavior of a compound within a series provided that the series is highly nematogenic.

Recently, Dabrowski *et al.* studied 4-X-substituted phenyl 4-(4-decylcyclohexyl)benzoates and found that the N-I transition temperature of the chloro derivative is lower by 8°C than that of the bromo derivative.[3] Furthermore, Takeda *et al.* noted that 4′-octyloxybiphenyl-4-yl 4-chlorobenzoate exhibits an N-I transition temperature lower by 2°C than its bromo counterpart.[4] While 4-(4-methoxybenzylideneamino)-4′-methoxybiphenyl studied by Gray is transformed from a nematic phase to an isotropic liquid at a temperature higher by 10°C than the nitro analogue, the methoxy derivative studied by Takeda *et al.* has its N-I transition at the same temperature as the nitro analogue.

The above-mentioned inconsistencies suggest strongly that the so-called group efficiency in promoting N-I transition temperature is not quite separable from other features of the molecule. One would obtain some new insight on the group efficiency by examining molecules which are as simple as possible. Because of this reasoning, we worked on compounds carrying only one terminal substituent. To be nematogenic, the molecule must contain, at least, three rings. Employing two asymmetric linking groups, —CH=N— and —COO—, a set of eight isomeric compounds carrying the same terminal groups can be obtained for studying the possible interdependence of the effects of terminal and linking units.



(1) A = —N=CH—, B = —COO—, (2) A = —N=CH—, B = —OOC—,
(3) A = —CH=N—, B = —COO—, (4) A = —CH=N—, B = —OOC—,
(5) A = —OOC—, B = —CH=N—, (6) A = —OOC—, B = —N=CH—,
(7) A = —COO—, B = —CH=N—, (8) A = —COO—, B = —N=CH—,

The N-I transitions for the ethoxy, nitro, and cyano derivatives of all the eight isomer type (1–8), hereafter abbreviated as E, N, and C series respectively, were newly studied. The data for the methoxy derivatives (M series) were taken from our earlier work.[5] According to Gray, 4-ethoxybiphenyl-4′-carboxylic acid exhibits an N-I transition temperature higher by 1.5°C than the methoxy counterpart.[1]

EXPERIMENTAL

All the anilines, benzaldehydes, phenols, and benzoic acids were commercial products. The desired compound was obtained by condensing an aniline with a

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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.[6] The products were recrystallized from ethanol, benzene, or mixtures thereof until constant transition temperatures were recorded.

Calorimetric measurements were carried out as described in a previous paper.[5] The ESR spectra of bis(acetylacetonato)oxovanadium(IV) dissolved in liquid crystals were recorded on a JOEL model JES-FE-1X spectrometer with 100 kHz modulation. The magnetic-field scan was calibrated with Mn^{2+}-doped MgO powder.

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RESULTS AND DISCUSSION

The transition temperatures and the associated enthalpies are listed in Table I. Here, K, N, and I stand for the crystalline, nematic, and isotropic liquid phases, respectively. Each compound will be designated by its terminal group series and the isomer type.

As is expected, the effect of structural variation on the crystal and mesophase stabilities is so significant that the melting point (t_m) in the M series varies in the range from 118 to 153°C and the clearing point (t_{NI}) in the range from 158 to 187°C, respectively. Both the highest melting point and the lowest clearing point are found for isomer 6 so that the temperature range of stable existence of a nematic phase is merely 5°C in this compound. The melting point of isomer 4 is the lowest and the clearing point of isomer 1 is the highest in the M series. Note that the temperature range of 61°C given by the nematic phase of compound M4 is more than ten times that given by compound M6.

It must be emphasized that the above-mentioned variation of the clearing points is more than twice as large as that observed for the monochloro derivatives of the M series.[5] While the addition of a terminal chloro group raises markedly the clearing points, 281 to 293°C, the temperature varies, at most, by 12°C upon changing the arrangement of the linking groups. Moreover, the temperature range of stable existence of a nematic phase is considerably broadened by the second terminal substituent. The widest range of 152°C is given by isomer 8 and the narrowest range of 89°C by isomer 3. However, the ratio of these temperature ranges is less than two. Thus, the mesomorphic properties of the disubstituted compounds are much less variable by the molecular structure than the monosubstituted ones. Therefore, the latter compounds seem to be a better choice, if one wishes to extract the effects of terminal substituents on mesomorphic properties.

It is quite reasonable to find that the behavior of the E series resembles largely that of the M series, but the variation by molecular structure tends to be less significant. Here again, the highest clearing point is given by isomer 1 and the lowest by isomer 6, the difference being 26°C. The widest temperature range of stable existence of a nematic phase (45°C) is observed for isomer 4 and the narrowest (21°C) for isomers 3 and 5. In the E series, the range given by isomer 6 is the second narrowest (22°C). The difference in clearing point between the M and E series is from 6 to 13°C. These values are four to eight times larger than those given by 4-X-biphenyl-4′-carboxylic acids studied by Gray. The variation in the

TABLE I

Transition temperatures and enthalpies of the methoxy (M), ethoxy (E), nitro (N), and cyano (C) derivatives of isomers 1–8

Isomer	t_m /°C	t_{NI} /°C	ΔH_m /kJmol^{-1}	ΔH_{NI} /kJmol^{-1}
		M series[a]		
1	145	187	34	0.3
2	144	184	38	0.4
3	139	174	32	0.4
4	118	179	33	0.5
5	151	173	40	0.3
6	153	158	33	0.5
7	129	177	31	0.4
8	139	170	33	0.6
		E series		
1	160	193	37	0.5
2	146	190	37	0.7
3	161	182	36	0.5
4	143	188	33	0.8
5	161	182	38	0.5
6	145	167	35	0.6
7	147	185	33	0.6
8	143	183	33	1.0

melting point (18°C) is diminished almost by a factor of two by replacing a methoxyl group with an ethoxyl group.

In contrast to the order proposed by Gray, the clearing points in the N series are higher by 23 to 44°C than those in the M series. The former difference is given by isomers 1 and 5, and the latter by isomer 4. In the N series, the highest clearing point is found for isomer 4 and the lowest for isomer 6, the difference being as much as 31°C. The nematic phases in the N series are not very stable with respect to the crystalline phase and the N-I transition is monotropic in the case of compounds N1, N6, and N7. The widest temperature range of stable existence of a nematic phase is 30°C given by isomer 5, which has the lowest melting point in this series, and the second is 18°C given by isomer 4. The variation in the melting point is as large as 54°C in this series.

The clearing point in the C series is in the range from 203 to 233°C, which is

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TABLE I (*continued*)

Isomer	t_m /°C	t_{N-I} /°C	ΔH_m /kJmol^{-1}	ΔH_{N-I} /kJmol^{-1}
		N series		
1	220	(210)[b]	44	0.8
2	200	221	43	0.9
3	201	210	40	0.7
4	205	223	33	0.7
5	166	196	37	0.8
6	197	(192)[b]	31	0.7
7	201	(201)[b]	38	0.8
8	194	199	39	0.7
		C series		
1	183	218	32	0.7
2	179	226	37	0.8
3	174	223	27	0.7
4	164	233	36	0.7
5	134	211	34	0.8
6	185	203	40	0.6
7	160	221	31	0.8
8	152	218	28	0.7

[a] Taken from Ref.5.

[b] Monotropic transitions.

higher by 31 to 54°C compared with that of the counterpart in the M series. In agreement with the observations made for the N series, the highest is given by isomer 4 and the lowest by isomer 6. The widest temperature range of stable existence of a nematic phase (77°C) is exhibited by isomer 5 and the second (69°C) by isomer 4. Isomer 6 exhibits not only the lowest clearing point but also the highest melting point in the C series and in turn the narrowest range of stable existence of the mesophase, 18°C. In this series too, the melting point varies as much as 51°C.

In Figure 1, the N-I transition temperatures observed for the four series are plotted against the isomer type. Although the temperature varies considerably by the arrangement of the linking units in each series, the plots are widely separated from each other, indicating that the effects of the terminal groups are much more dominant than those of the linking groups. The efficiency order of substituents for nematic thermal stability is CN > NO_2 > C_2H_5O > CH_3O in contrast to CN > CH_3O > NO_2 constructed by Gray. Van der Veen found that the anisotropy in

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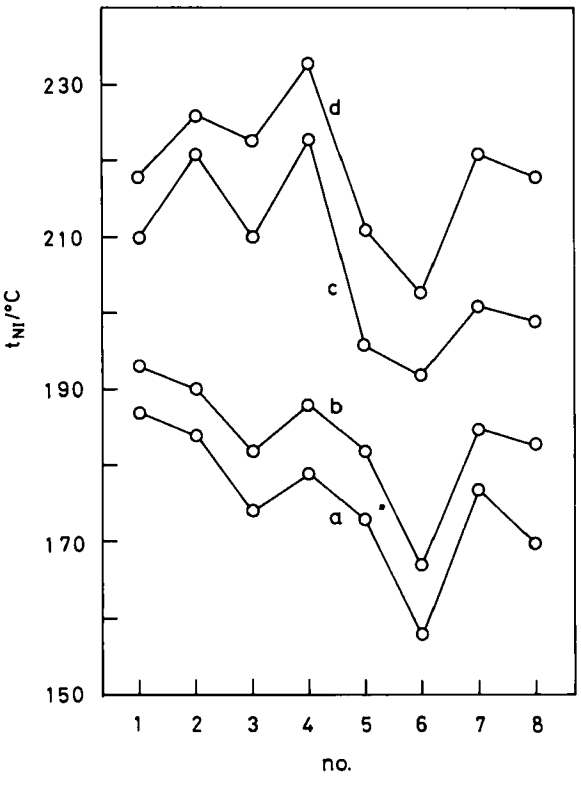

FIGURE 1 Plots of N-I transition temperatures against the number assigned to the isomer type, (a) M series, (b) E series, (c) N series, and (d) C series.

the polarizability for the C_{Ar}—X bonds, where X = F, Cl, CH_3, NO_2, and CN, shows a linear relationship with the N-I transition temperature (in K), in agreement with the molecular statistical theory of Maier and Saupe.[7] Unfortunately, no value is available for the alkoxyl group. The plots for the N and C series, which are parallel to each other, are different from those for the M and E series. This may result from strong molecular association which is of an overlapping head-to-tail nature due to the high dipole moments of these compounds.[8] When two polar molecules are arranged in head-to-tail with quasi-smectic ordering on a local scale, the molecular length is certainly increased and the linearity may be modified, resulting in behavior distinctly different from that in the M and E series. The highest clearing point is given not by isomer 1 but by isomer 4.

Rigidity, linearity, polarizability, and enhancement of polarity by conjugation have been thought to contribute to mesophase stability.[9] The present results concerning eight isomeric compounds may provide some clue to the relationship between molecular features and mesomorphic behavior though the complexity arising from possible molecular association must be kept in mind. Firstly, isomers 1 to 8 are divided into four pairs, each of which shares the molecular skeleton; namely, 1 and 5, 2 and 7, 3 and 6, and 4 and 8. For example, isomers 1 and 5 are derivatives of phenyl 4-(phenyliminomethyl)benzoate with a terminal substituent at a different

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TABLE II

Difference in N-I transition temperature between pairs of isomeric compounds with the same molecular skeleton

Isomer pair	Δt_{NI}/°C			
	M series	E series	N series	C series
1 - 5	14	11	14	7
2 - 7	7	5	20	5
3 - 6	16	15	18	20
4 - 8	9	5	24	15

TABLE III

Difference in N-I transition temperature between pairs of isomeric compounds with the carbonyloxy linking group inverted

Isomer pair	Δt_{NI}/°C			
	M series	E series	N series	C series
1 - 2	3	3	-11	-8
3 - 4	-5	-6	-13	-10
5 - 7	-4	-3	-5	-10
6 - 8	-12	-16	-7	-15

end. As is shown in Table II, all of the differences in N-I transition temperature between such pairs have the same positive sign. Obviously an azomethine group is a more ideal unit for building up a rigid linear structure than an carbonyloxy group. Higher N-I transition temperature is achieved when a terminal substituent, which is the most dominant factor in determining the thermal behavior, is attached to this rigid linear structure. The above comparison thus demonstrates that the rigidity factor is generally important.

Secondly, isomeric pairs with the carbonyloxy linking group inverted are compared in Table III. This way of comparison would delineate the effect of a partial modification of the molecular skeletons with or without the terminal substituents involved. The differences listed in Table III are negative except for 1-2 in the M and E series. It is surprising to see that the inversion of a linking group far from the terminal substituent for the first two pairs in the N and C series affects the N-I transition temperature so much. This may be a manifestation of the molecular association of a partially overlapping head-to-tail nature. Thus, a benzoyloxy group is more favorable to the nematic stability as an end group than a phenyloxycarbonyl group. This phenomenon has been discussed in detail by Dewar and Goldberg in

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terms of conjugation between the terminal substituent and the carboxyl group, resulting in an increase or decrease in polarity, depending upon the electronic nature of the terminal substituent.[10] On the other hand, Malthete *et al.* concluded that permanent dipoles play no major role in the nematic behavior comparing isomeric compounds such as N-(4-cyanobenzylidene)-4-methoxyaniline and N-(4-methoxybenzylidene)-4-cyanoaniline.[11] The crystal and molecular structure of 4-cyanophenyl 4-pentyloxybenzoate has been reported by Baumeister *et al.* and that of the 4-heptylbenzoate by Mandal *et al.*[12,13] Although the linking group (—COO—) plane makes an angle much larger with the cyanophenyl ring than with the carboxylic phenyl ring, the values are quite variable; 90° versus 0° and 62.1° versus 14.7°, respectively. Thus, the stereochemical behavior of phenyl benzoates is not straightforward and not helpful to rationalize our results, possibly because of the rather strong effects of crystal packing.

Another pairwise comparison presented in Table IV shows that a phenyliminomethyl end group is more favorable to the nematic stability than a benzylideneamino group, with a few exceptions. It has been shown that 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°.[14] The lone pair density on the nitrogen atom interacts increasingly with the pi-electron system of the ring by increasing nonplanarity. Hence, the rigid molecular core is more extended if the molecule is terminated by a phenyliminomethyl group. Such substituents as methoxyl and ethoxyl would not alter this feature too much, and the positive values in Table IV are understandably in line with the above discussion. The anomalous behavior found for 1-3 and 2-4 in the N and C series may again imply that these polar molecules are associated.

Finally, it may be worthwhile to point out some peculiarities noted for enthalpies and entropies of N-I transitions. In the M and E series the enthalpy and entropy changes vary by a factor of two by the way of arranging the linking units. The largest values are given by isomers 8 and the smallest by isomers 1. On the other hand, the values in the N and C series remain relatively high through structural modification. Compounds N2 and C2 tend to give the largest transition enthalpies and entropies. In order to demonstrate that a high entropy change at N-I transition

TABLE IV

Difference in N-I transition temperature between pairs of isomeric compounds with the azomethine linking group inverted

Isomer pair	Δt_{NI}/°C			
	M series	E series	N series	C series
1 - 3	13	11	0	-5
2 - 4	5	2	-2	-7
5 - 6	15	15	4	8
7 - 8	7	2	2	3

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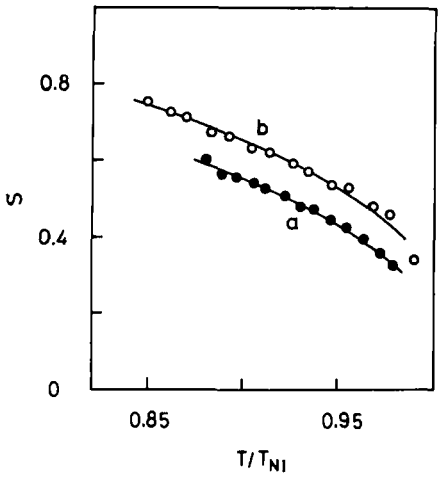

FIGURE 2 Orientational order parameters for the long axis of bis(acetylacetonato)oxovanadium(IV) dissolved in (a) compound E1 and (b) compound E8.

means a high orientational ordering in the nematic phase,[15,16] ESR absorption spectra of bis(acetylacetonato)oxovanadium (IV) dissolved in compounds E1 and E8 were recorded.

The oxovanadium chelate has approximately axial hyperfine and g tensors. Their components, parallel and perpendicular to the V=O bond, are denoted by $A_{\parallel}$ and $A_{\perp}$, and $g_{\parallel}$ and $g_{\perp}$, respectively. Small anisotropies in g tensors may be ignored and the vanadium hyperfine spacings $\langle a \rangle$ in liquid crystals are measured directly from the outermost lines of the eight-line spectra. Then, the order parameter S of the probe for axes orthogonal to the symmetry axis is approximated by

$$S = (a - \langle a \rangle)/(a - A_{\perp})$$

where a is the isotropic hyperfine spacing. The required parameters were determined for the spectra recorded separately in *o*-terphenyl melts and glasses. The paramagnetic probe employed here is known to be ordered to about the same extent as the solvent when it is dissolved in 4,4'-azoxydianisole.[17] The results are summarized in Figure 2. As is expected, the S value observed in compound E8 is invariably higher than that in compound E1, reflecting the higher orientational ordering in the former liquid crystals.

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