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Mesomorphic behaviour of 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] and related compounds

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DSC and X-ray diffraction studies on a series of 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] are presented. The only mesophase exhibited by the methoxy to hexadecyloxy homologues is of the smectic C type. The reversal of the iminomethyl linkage reduces drastically the incidence of a mesophase; that is, only the first five homologous members exhibit a smectic C phase in the series of 1,3-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates]. Almost all the members in the second series become nematogenic by the chloro substitution at the 4-position of the 1,3-phenylene moiety. In addition, a smectic C phase is observable for the ethoxy to pentyloxy and also the tetradecyloxy and hexadecyloxy members. The second chloro-substituent introduced to the 6-position of the same central ring eliminates completely the smectic C phase and enhances the nematic thermal stability.

1. Introduction

We reported earlier the mesomorphic behaviour of the five-ring systems with an acute-angled configuration such as 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates] and the 2,3-naphthylene analogues [1, 2]. The mesophases appearing in these compounds were shown to be classical nematic and smectic A by establishing continuous miscibilities with reference mesophases. The layer spacings in the smectic A phase measured as a function of the alkyl chain length revealed that the mean tilt angle of the linear three-ring part of the molecule to the layer normal is about 37° and that the molecular core is V-shaped with an angle of about 70° between the long-stretched benzoate legs, in reasonable agreement with the angle suggested by the structural formula. This molecular model accounts for the effects of a methyl group introduced into the 3- or 4-position of the 1,2-phenylene moiety on the mesomorphic properties.

Now we wish to present an extension of our work to compounds with an obtuse-angled configuration; namely, 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] and bis[4-(4-alkoxybenzylideneamino)benzoates] and the 4-chloro- and 4,6-dichloro-derivatives of the latter compounds. About sixty years ago, Vorländer noted that bis[4-(4-methoxyphenylazo)phenyl] isophthalate and 1,3-phenylene bis[4-(4-ethoxyphenylazoxy)benzoate] are mesogenic without specifying

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the phases [3, 4]. The thermal stability of the mesophase was shown to be distinctly lower than that of the corresponding 1,4-phenylene compounds. Recently, Jin *et al.*, reported that bis[4-(4-butylphenylazo)phenyl] isophthalate is not mesogenic [5]. On the other hand, our examination of the phase diagram of a binary system composed of mesogenic 4-(4-nonyloxybenzylideneamino)azobenzene and non-mesogenic 4-[3-(4-dodecyloxybenzoyloxy)benzylideneamino]azobenzene revealed that the latter four-ring compound with an obtuse-angled configuration is potentially smectogenic [6]. More recently, Janietz *et al.*, disclosed the mesomorphic behaviour of aromatic esters containing a 1,3,5-triazine nucleus such as 6-methoxy-2,4-bis[4-(4-propoxyphenyloxycarbonyl)phenoxy]- and 6-methoxy-2,4-bis[4-(4-biphenyloxylcarbonyl)phenoxy]-1,3,5-triazines [7]. The former compound exhibits an enantiotropic nematic phase and the latter an enantiotropic smectic phase.

2. Results and discussion

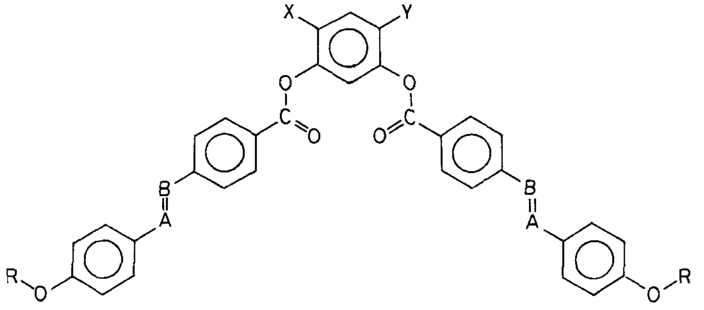
2.1. *1,3-Phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates]* (*I*)

The transition temperatures and the associated enthalpies are listed in table 1. All the homologous members carrying methoxy to hexadecyloxy groups exhibit a thermodynamically stable smectic phase with a fan-shaped texture. The X-ray diffraction patterns recorded for the mesophase are of the smectic A or C phase. The mesophase was identified as a smectic C phase on the basis of the following observations. Attempts to achieve a homeotropic alignment of this phase were unsuccessful. The enthalpy changes observed for the S–I transition, 9 to 28 $\mathrm{kJ\,mol^{-1}}$, are considerably larger than the values compiled by Demus *et al.*, for S_A–I transitions, 2·9 to 12·6 $\mathrm{kJ\,mol^{-1}}$, but are almost within the range covered by S_C–I transitions, 10 to 42·7 $\mathrm{kJ\,mol^{-1}}$ [8]. Miscibility studies involving the hexadecyloxy homologue and ethyl 4-phenylbenzylideneaminobenzoate [C 127 (S_B 105) S_A 132 I] as the standard material showed the existence region of a nematic phase between this smectic phase and the smectic A phase of the latter mesogen. Their layer spacings *d* presented also in table 1 may be approximated by $d=(2{\cdot}50n+1{\cdot}85)$ nm, where *n* is the number of carbon atoms in the alkoxy group. On the other hand, the layer

Table 1. Transition temperatures (°C), associated enthalpies (in parentheses) ($\mathrm{kJ\,mol^{-1}}$), and layer spacing *d* in the smectic C phase (nm) for the 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates].

n†	C		M		S_C		I	*d*/nm
1	•	194 (47)			[•	174 (9·4)]‡	•	
2	•	194 (36)			•	203 (14)	•	
3	•	200 (56)			[•	191 (14)]	•	
4	•	182 (14)	•	185 (16)	•	188 (17)	•	
5	•	171 (16)	•	175 (15)	•	178 (17)	•	3·07
6	•	157 (20)	•	171 (16)	•	175 (20)	•	3·22
7	•	156 (21)	•	163 (12)	•	170 (22)	•	3·65
8	•	156 (22)	•	160 (14)	•	175 (25)	•	3·98
9	•	144 (35)			•	169 (23)	•	4·20
10	•	144 (37)			•	168 (24)	•	4·41
12	•	143 (38)			•	168 (26)	•	4·75
14	•	142 (41)			•	167 (27)	•	5·19
16	•	136 (41)			•	163 (28)	•	5·96

† The number of carbon atoms in the alkyl group.
‡ [ ] denotes a monotropic transition.



I $-A{=}B- = -N{=}CH-$, $X = Y = H$
II $-A{=}B- = -CH{=}N-$, $X = Y = H$
III $-A{=}B- = -CH{=}N-$, $X = Cl$, $Y = H$
IV $-A{=}B- = -CH{=}N-$, $X = Y = Cl$

spacings for the smectic A phase given by the reference compound, i.e. phenyl 4-(4-alkoxyphenyliminomethyl)benzoates is known to be approximated by $d = (0{\cdot}122n + 1{\cdot}96)$ nm [2]. The increment in the present compounds is twice as large as that per methylene group, suggesting that the alkyl chains at the ends of the obtuse-angled molecule are essentially perpendicular to the smectic layer and extend outwards in both directions to the layer boundaries. As the distance between the terminal oxygen atoms may depend upon the configuration of the flexible linking groups, no reliable estimation is possible. Taking 1·96 nm as an effective length of the straight three-ring part of the present molecule, the desired length may be estimated at about 2·75 nm. This distance suggests that the angle between the line joining the terminal oxygen atoms and the smectic layer normal is as large as 48°. It may be interesting to note that this model bears close similarity to the zig–zag conformer of a biforked mesogen found in smectic C mixtures rich in terephthal-bis(4-decylaniline) by Levelut *et al.*, though the molecular core of the biforked mesogen is not angled [9].

An additional more ordered mesophase is observed for the butoxy to octyloxy homologues.

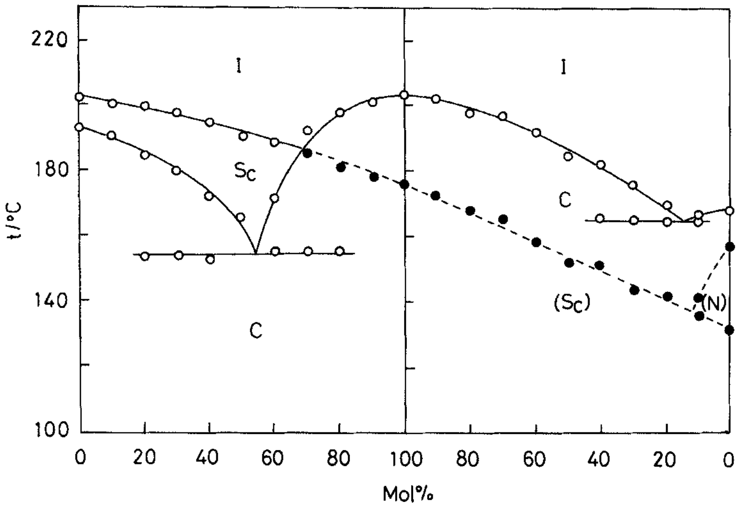
2.2. *1,3-Phenylene bis[4-(4-alkoxybenzylideneamino)benzoates]* (***II***)

Table 2 presents the thermodynamic data for the bis[4-(4-alkoxybenzylideneamino)benzoates. In contrast to the 1,2-phenylene compounds for which the N/S_A–I transition temperature is not much affected by reversal of the iminomethyl group, the incidence of a mesophase is significantly reduced by this structural modification compared to the aforementioned isomeric compounds. The clearing point is depressed by this inversion and only the first five homologues remain mesomorphic. In addition, the phase exhibited by the methoxy, propoxy, and pentyloxy homologues is metastable. The phase diagram of a binary system composed of the [4-(4-ethoxyphenyliminomethyl)benzoate] and the [4-(4-propoxybenzylideneamino)benzoate] is shown in figure 1 (*a*). The smooth curve connecting the enaniotropic transition point in the former compound and the monotropic one in the latter establishes firmly that the mesophases given by these two are of the same nature.

Table 2. Transition temperatures (°C) and associated enthalpies (in parentheses) (kJ mol^{-1}) for the 1,3-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates].

n†	C		S$_C$		I
1	•	219 (44)	[•	169 (5·0)]‡	•
2	•	187 (26)	•	188 (5·4)	•
3	•	203 (47)	[•	177 (8·2)]	•
4	•	162 (14)	•	169 (12)	•
5	•	151 (33)	[•	146 (12)]	•
6	•	137 (330)			•

† The number of carbon atoms in the alkyl group.
‡ [ ] denotes a monotropic transition.



(*a*) (*b*)

Figure 1. Phase diagrams of binary systems composed of (*a*) 1,3-phenylene bis[4-(4-ethoxyphenyliminomethyl)benzoate] and bis[4-(4-propoxybenzylideneamino)benzoate], and (*b*) the latter compound and its 4-chloro-derivative. The open and full circles are the transitions observed in the processes of heating and cooling, respectively.

2.3. *4-Chloro- and 4,6-dichloro-1,3-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates]* (*III*) *and* (*IV*)

It has been concluded by Gray that the smectic state would suffer more than the nematic state by a lateral chloro-substituent though the relative effects depend, to some extent, upon the nature of the molecule into which it is introduced [10]. Indeed, the four enantiotropic smectic phases (S$_C$, S$_B$, S$_3$, S$_G$) exhibited by *N,N′*-bis(4-hexyloxybenzylidene)-1,4-phenylenediamine are completely suppressed by a chloro-substituent introduced to the 2-position of the central ring [11, 12]. Both the melting and clearing points are depressed as much as by 56°C by the substitution and the compound becomes purely nematogenic. Similar but less drastic results were also reported for the 2-methylation of 1,4-phenylene bis(4-alkoxybenzoates) [13]. Therefore, one may hope the emergence of a nematic phase caused by the destabilization of the smectic phase by the introduction of a chloro-substituent into the 1,3-phenylene moiety of the present

Table 3. Transition temperature (°C) and associated enthalpies (in parentheses) (kJ mol^{-1}) for the 4-chloro-1,3-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates].

n‡	C		S_C		N		I
1	•	186 (43)			•	199 (0·3)	•
2	•	173 (51)	[•	138]‡	•	190 (0·8)	•
3	•	165 (38)	[•	132]	[•	148 (0·5)]	•
4	•	143 (38)	[•	129]	[•	143 (0·5)]	•
5	•	141 (46)	[•	105]	[•	119 (0·6)]	•
6	•	121 (26)			[•	118 (0·7)]	•
7	•	121 (38)					•
8	•	105 (53)			•	108 (0·6)	•
9	•	89 (48)			•	100 (0·5]	•
10	•	92 (40)			•	104 (0·6)	•
12	•	96 (48)			•	101 (0·6)	•
14	•	101 (57)	[•	83]	[•	101 (0·7)]	•
16	•	101 (76)	[•	98 (1·7)]	•	104 (1·0)	•

† The number of carbon atoms in the alkyl group.

‡ [ ] denotes a monotropic transition.

compound. If such is the case this moiety must not act as the apex of a V-shaped molecule, but as the central ring of an elongated molecule as suggested in the previous section, even though the molecule is not straight. The thermodynamic data reported in table 3 for the monochloro-derivatives agree, at least, qualitatively with this supposition. The situation unfavourable to the regular stacking of molecules due to the presence of a lateral substituent is clearly demonstrated by the depression of the melting point. All the members from the methoxy to hexadecyloxy homologues but the heptyloxy one are enantiotropically or monotropically nematogenic. An additional metastable mesophase is observable for the following six members; the ethoxy, propoxy, butoxy, pentyloxy, tetradecyloxy, and hexadecyloxy homologues. This phase is of the smectic C type as proved by the phase diagram in figure 1 (*b*) which composed of the propoxy homologue and the corresponding unchlorinated one (the component compound common to figures 1 (*a*) and 1 (*b*)). The maximum temperature of existence of this mesophase is lower by 45°C than that of the parent compound. The S_C–N/I transitions are connected by a straight line, whereas the nematic phase given by the monochloro-derivative is strongly depressed by the addition of the parent compound. A little more than 10 mol % of the parent molecule is enough to eliminate the nematic phase as manifested by the intersection of the two transition point curves. Contrary to the examples cited above, the emergence of the nematic phase must be ascribed mostly to the remarkable promotion of this mesophase and only partly to the destabilization of the smectic C phase by the lateral chloro substituent. Figure 2 presents the phase diagram for binary mixtures of the butoxy homologue with 4-(4-nonyloxybenzylideneamino)azobenzene [C 101 S_B 128 S_A 157 N 164 I]. The appearance of a wide miscibility gap between the smectic phases is in accordance with our phase assignment.

The transition temperatures and associated enthalpies are collected in table 4 for the 4,6-dichloro-derivatives. An enantiotropic nematic phase is the only mesophase observed for all the homologues. The introduction of the second lateral substituent results in the further enhancement of the nematic thermal stability but only by 30°C in the lower homologues and by 10°C in the higher homologues. In contrast to the monochloro-derivatives, the melting point in the lower homologues is also enhanced

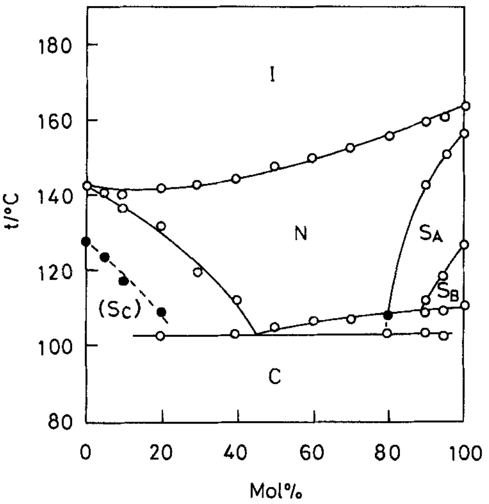


Figure 2. Phase diagram of a binary system composed of 4-chloro-1,3-phenylene bis[4-(4-butoxybenzylideneamino)benzoate] and 4-(4-nonyloxybenzylideneamino)azobenzene. The open and full circles are transitions observed in the processes of heating and cooling, respectively.

Table 4. Transition temperatures (°C) and associated enthalpies (in parentheses) (kJ mol^{-1}) for the 4,5-dichloro-1,3-phenylene bis [4-(4-alkoxybenzylideneamino)benzoates].

n†	C		N		I
1	●	216 (47)	●	230 (1·3)	●
2	●	198 (38)	●	229 (2·3)	●
3	●	164 (36)	●	198 (2·1)	●
4	●	150 (36)	●	187 (2·3)	●
5	●	136 (37)	●	162 (1·7)	●
6	●	130 (48)	●	157 (2·0)	●
7	●	145 (43)	●	146 (1·5)	●
8	●	114 (49)	●	143 (1·8)	●
9	●	101 (44)	●	131 (1·5)	●
10	●	84 (61)	●	132 (1·7)	●
12	●	90 (41)	●	124 (1·6)	●
14	●	99 (51)	●	120 (1·6)	●
16	●	99 (57)	●	115 (1·5)	●

† The number of carbon atoms in the alkyl group.

by the second lateral substituent; therefore, the effects of an increased polarizability and polarity by the second substituent appear to overweigh the steric effects.

2.4. *Miscellaneous compounds*

Bis[4-(4-ethoxyphenyliminomethyl)phenyl] isophthalate melts at 257°C and no accessible mesophase exists. Thus the reversal of the carbonyloxy group appeared to be very unfavourable to the occurrence of any mesophase in the 1,3-phenylene compounds. Therefore, the compound examined by Jin *et al.*, does not seem to be a good choice for their study [5]. Our observation is in conformity with the effects of inverting the carbonyloxy linkages in the 1,4-phenylene compounds studied by Dewar and

Goldberg [14]. 1,4-Phenylene bis[4-alkoxybenzoate) forms the more stable nematic phase than the corresponding bis(4-alkoxyphenyl] terephthalate, but only by 10 to 20°C even though the effects are expected more pronounced in these shorter molecules.

The behaviour of the 4-chloro- and 4,6-dichloro-derivatives of the bis[4-(4-ethoxyphenyliminomethyl)benzoate] was found to be similar to that of the aforementioned isomers. The monochloro-derivative melts to the nematic phase at 162°C and then clears to the isotropic liquid at 193°C. Upon cooling, a smectic phase appears at 151°C. On the other hand, the dichloro-derivative gives a C–N transition at 195°C and an N–I transition at 238°C. No smectic phase is observed for this derivative. In accordance with the behaviour of the unsubstituted compounds, these mesophases are a little more thermodynamically stable than those of the isomeric compounds.

The elimination of the mesophase by the methylation at the 2-position but not at the 5-position of the 1,3-phenylene moiety was demonstrated employing the bis[4-(4-ethoxyphenyliminomethyl)benzoate]. While the former methylated compound melts at 251°C and crystallizes upon cooling without exhibiting a mesophase, the latter melts at 189°C and exhibits a metastable smectic phase below 175°C.

3. Conclusions

The obtuse-angled configuration of the 1,3-phenylene compounds studied in the present work appeared to be favourable to smectic C phase formation. The chloro-substituent introduced into the 4-position of the 1,3-phenylene moiety destabilizes the smectic C phase and leads to the remarkable promotion of the nematic phase, suggesting that the 1,3-phenylene moiety acts as the central ring of an elongated, though not straight, molecule. The mesophase exhibited by bis[4-(4-alkoxybenzylideneamino)benzoates] is considerably suppressed by inversion of the iminomethyl group, whereas it is eliminated by that of the carbonyloxy group.

4. Experimental

4-Alkoxyanilines were obtained commercially or prepared by reactions between 4-nitrophenol and the appropriate 1-bromoalkane, followed by reduction with zinc dust in 75 per cent aqueous ethanol [15]. 4-Alkoxybenzaldehydes were obtained commercially or synthesized by the alkylation of 4-hydroxybenzaldehyde following the method proposed by Gray and Jones [16]. 4-(4-Alkoxyphenyliminomethyl) benzoic acids and 4-(4-alkoxybenzylideneamino)benzoic acids were obtained by the condensation of 4-alkoxyanilines with 4-formylbenzoic acid and of 4-alkoxybenzaldehydes with 4-aminobenzoic acid, respectively. The esterification of resorcinol, 4-chlororesorcinol, and 4,6-dichlororesorcinol with the 4-(4-alkoxyphenyliminomethyl)benzoic acids or 4-(-alkoxybenzylideneamino)benzoic acids by the procedure of Hassner and Alexanian led to the desired compounds [17].

The calorimetric and X-ray diffraction measurements were performed as described in our previous paper [2].

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