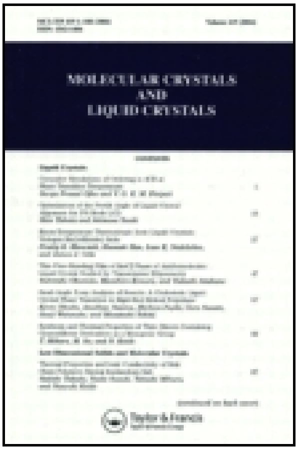

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Mesomorphic Behavior of 1,2-Phenylene Bis[4-(4-alkoxybenzylideneamino)benzoates

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Mesomorphic Behavior of 1,2-Phenylene Bis[4-(4-alkoxybenzylideneamino)benzoates]

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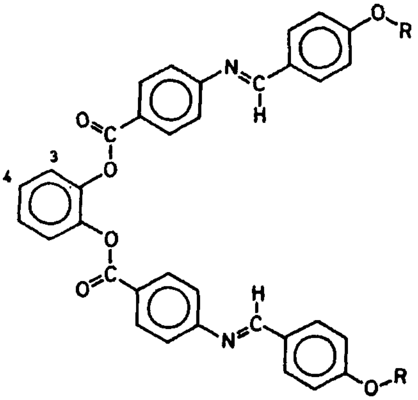
A series of 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates] has been prepared in order to establish that the nonlinear molecular structure is not necessarily incompatible with mesophase formation. The phases appearing in the methoxy and ethoxy derivatives are classical nematic. While the propoxy to octyloxy derivatives display a smectic A phase, as well as a nematic phase, the higher homologous members are purely smectogenic. Although the introduction of a methyl group to the 3-position of the central phenylene ring eliminates the nematic phase, the thermal stability of the smectic A phase is not much affected. The 4-methylation promotes both the nematic and smectic A phases. A metastable smectic B phase is observed in many members of these three series. The above-mentioned behavior closely resembles that given by the corresponding methyl derivative of phenyl 4-(4-alkoxybenzylideneamino)benzoate.

Keywords: nematic, smectic, fused twins, methyl substitution

INTRODUCTION

Vorländer is well-known by his rule about the chemical structure of liquid crystals; that is, the liquid-crystalline state is obtainable by an utmost linear shape of the molecules.[1] However, he was also the first to describe mesogenic compounds with



(1)

nonlinear molecular structure such as bis(4-methoxyphenylazophenyl) isophthalate and 1,2-phenylene bis(4-ethoxyphenylazoxybenzoate).[2,3] The mesophase given by the latter compound in the temperature range from 164 to 213°C was noted to be nematic in a recent review article by Demus.[4] The compound was classified by this reviewer into fused twins. Owing to our interest in nonlinear disubstituted benzene derivatives carrying two sufficiently long stretched mesogenic units, we have examined the thermal behavior of 1,2-phenylene bis[4-(4-alkoxybenzylideneamino) benzoates] (*1*) and also the 3- and 4-methyl-1,2-phenylene compounds.

EXPERIMENTAL

4-(4-Alkoxybenzylideneamino)benzoic acids were obtained by condensing the 4-alkoxybenzaldehydes and 4-aminobenzoic acid. The esterification of catechol and 3-methyl and 4-methylcatechols with the 4-(4-alkoxybenzylideneamino)benzoic acids by the procedure of Hassner and Alexanian produced the desired compounds.[5]

TABLE I

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates][a]

n$^{b)}$	K	S_B	S_A	N	I
1	. 180 (55)			. 191 (0.3)	.
2	. 191 (60)			[. 188 (0.4)]$^{c)}$	.
3	. 151 (54)		[. 95 (---)]$^{c)}$	. 168 (0.1)	.
4	. 169 (44)		[. 127 (0.6)]$^{c)}$	. 173 (0.3)	.
5	. 128 (39)	[. 64 (2.4)]$^{c)}$	. 149 (3.0)	. 168 (0.2)	.
6	. 135 (44)	[. 60 (2.4)]$^{c)}$	. 151 (2.3)	. 168 (0.3)	.
7	. 115 (40)	[. 63 (2.6)]$^{c)}$	. 164 (3.3)	. 169 (0.5)	.
8	. 104 (50)	[. 57 (2.1)]$^{c)}$	. 170 (4.6)	. 172 (0.4)	.
9	. 72 (52)	[. 56 (2.6)]$^{c)}$	. 173 (6.1)		.
10	. 126 (91)	[. 51 (---)]$^{c)}$	. 175 (6.3)		.
12	. 76 (90)		. 177 (6.3)		.
14	. 78 (69)		. 178 (6.0)		.
16	. 82 (85)		. 174 (7.7)		.

[a] The latter values are in parentheses.

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

[c] The transition is monotropic.

Some phenyl and 3-methyl and 4-methylphenyl 4-(4-alkoxybenzylideneamino) benzoates were prepared in a similar manner in order to employ as the reference mesogenic compounds. Microscopic observations and calorimetric and X-ray powder diffraction measurements were made as described in a previous paper.[6] The phase diagrams were determined by the calorimetric curves of mixtures at every ten mol%.

RESULTS AND DISCUSSION

The transition temperatures and the associated enthalpy changes of 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates] are presented in Table I. Here, K, S_B, S_A, N, and I stand for the crystalline, smectic B, smectic A, nematic, and isotropic liquid phases respectively. The mesophases were classified on the basis of the microscopic examination; namely, the nematic phase by a schlieren texture, the smectic A and B phases by fan textures. The smectic A phase appearing in the process of heating tends to be homeotropic. As is depicted in Figure 1, the observed nematic phases are stable in all of the homologous members except for the ethoxy derivative. While the propoxy to octyloxy derivatives exhibit a stable nematic phase, as well as a smectic A phase, the higher homologous members are purely smectogenic. The N-S_A transitions in the first two members are monotropic and are

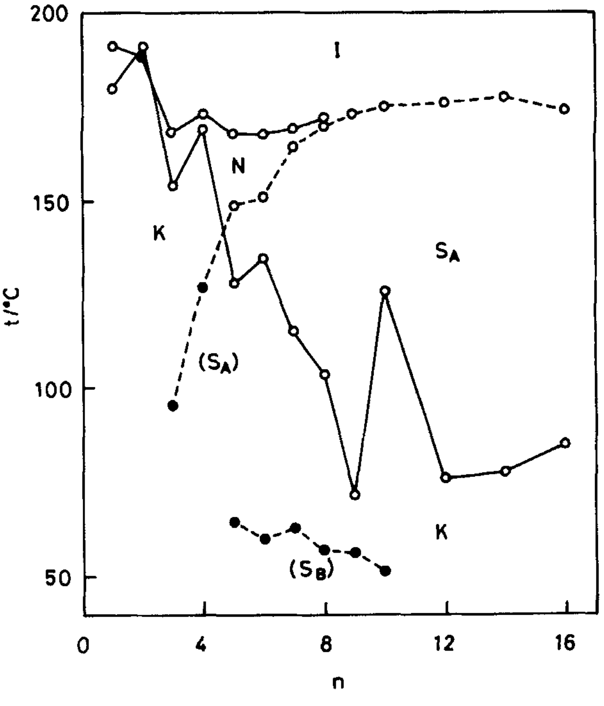


FIGURE 1 Plot of transition temperatures against the number of carbon atoms in the alkyl group (n) for 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates].

represented by shaded circles in this figure. A metastable smectic B phase appears in all of the members from the pentyloxy to decyloxy derivatives.

It is very interesting to point out that the mesomorphic behavior of the present compound agrees qualitatively with that of the corresponding phenyl 4-(4-alkoxybenzylideneamino)benzoate. For example, the hexyloxy derivative in the latter series melts at 103°C, forming a smectic A phase. This mesophase is transformed into a nematic phase at 143°C and then into an isotropic liquid at 161°C. Moreover, a smectic B phase appears at 64°C when the smectic A phase is supercooled.

The X-ray diffraction patterns recorded for the smectic A phase consist of a sharp inner peak and a diffuse outer one, supporting the assignment. The former peak is accompanied by weak peaks assignable to the second- and third-order reflections. The layer spacing increases linearly with increasing the alkyl chain length (from 2.29 nm in the pentyloxy derivative to 4.08 nm in the hexadecyloxy derivative). The increment of 0.158 nm per carbon atom in the alkyl group is larger than that expected for the full length of a single alkyl chain. The extrapolation of the layer spacings to n = 0 gives 1.55 nm which is certainly much shorter than the

TABLE II

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of 3-methyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates][a]

n[b]	K		S_B		S_A		I
1	.	174 (50)					.
2	.	179 (51)					.
3	.	154 (35)			[.	140 (6.2)][c]	.
4	.	143 (34)			.	157 (8.3)	.
5	.	133 (36)	[.	91 (2.5)][c]	.	162 (9.8)	.
6	.	103 (41)	[.	90 (3.1)][c]	.	162 (9.3)	.
7	.	112 (28)	[.	88 (2.6)][c]	.	165 (9.2)	.
8	.	111 (48)	[.	92 (2.9)][c]	.	168 (10)	.
9	.	100 (34)	[.	91 (2.2)][c]	.	173 (9.6)	.
10	.	98 (39)	[.	91 (2.6)][c]	.	172 (12)	.
12	.	100 (48)	[.	91 (2.4)][c]	.	173 (12)	.
14	.	102 (55)	[.	86 (2.0)][c]	.	170 (12)	.
16	.	103 (66)			.	167 (12)	.

[a] The latter values are in parentheses.
[b] The number of carbon atoms in the alkyl group.
[c] The transition is monotropic.

length expected for a single stretched molecular core (phenyl (4-hydroxybenzylideneamino)benzoate), indicating that the core and also the whole molecule are inclined to the layer normal. Therefore, the building units of the mesophase must be dimers in which the twin molecules are aligned in antiparallel.

Table II presents the thermodynamic data of the 3-methyl-1,2-phenylene compounds. As is shown in Figure 2, the introduction of a 3-methyl group to the central phenylene ring completely eliminates the nematic phase, even though the melting point is depressed by the methylation in the lower homologous members. The thermal stability of the smectic A phase is appreciably enhanced by the methylation in the lower homologous members (45°C in the propoxy derivative), but is slightly diminished in the higher members (7°C in the hexadecyloxy derivative). The smectic B phase is invariably stabilized by the methylation and is observable in the pentyloxy to tetradecyloxy derivatives. Nevertheless, the phase remains metastable in all of the members because the melting point of the higher members is also generally promoted by the methylation.

The nematic phase appearing in phenyl 4-(4-alkoxybenzylideneamino)benzoates is also eliminated when a methyl group is introduced to the 3-position of the phenyl group. For example, the hexyloxy derivative melts at 77°C, and the resulting smectic A phase is directly transformed into an isotropic liquid at 117°C. On the other hand, the 2-methylation eliminates the smectic phases; namely, the K-N and N-I transition temperatures in the hexyloxy derivative are located at 95°C and 125°C

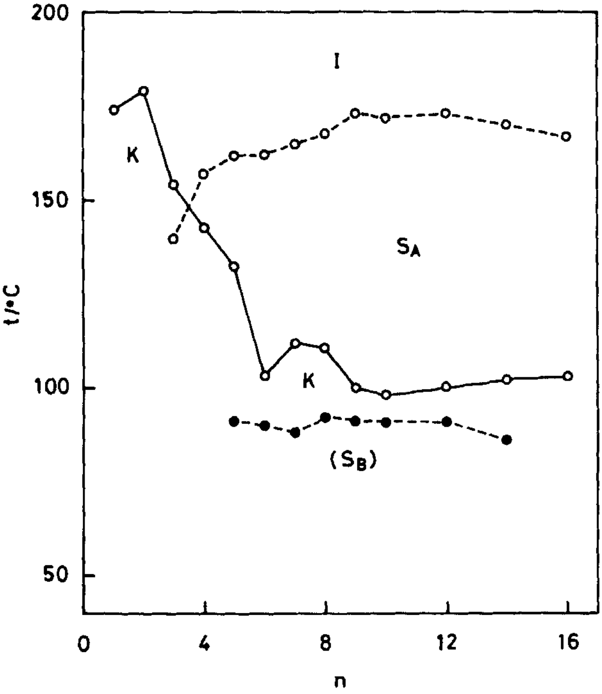


FIGURE 2 Plot of transition temperatures against the number of carbon atoms in the alkyl group (n) for 3-methyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates].

TABLE III

Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of 4-methyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates][a]

n[b)]	K		S_B		S_A		N		I
1	.	118 (36)					.	217 (0.2)	.
2	.	155 (36)					.	206 (0.2)	.
3	.	144 (37)					.	195 (0.3)	.
4	.	120 (36)			.	138 (1.4)	.	194 (0.4)	.
5	.	133 (44)			.	160 (2.4)	.	185 (0.4)	.
6	.	125 (39)	[.	56 (2.8)][c)]	.	173 (2.5)	.	185 (0.7)	.
7	.	83 (26)	[.	64 (3.0)][c)]	.	181 (4.3)	.	185 (0.8)	.
8	.	89 (42)	[.	64 (2.9)][c)]	.	185 (6.1)			.
9	.	95 (43)	[.	66 (2.8)][c)]	.	187 (7.0)			.
10	.	109 (49)	[.	62 (2.7)][c)]	.	190 (8.0)			.
12	.	104 (47)	[.	56 (2.5)][c)]	.	190 (8.9)			.
14	.	80 (85)			.	186 (9.6)			.
16	.	93 (56)			.	183 (10)			.

[a] The latter values are in parentheses.
[b] The number of carbon atoms in the alkyl group.
[c] The transition is monotropic.

respectively. The resemblance in the effects of 3-methylation on the mesomorphic properties between the fused twin and the reference mesogen implies that the mean geometric orientation of the substituent relative to the director (the layer normal in the case of smectic A phase) is similar to each other.

The thermodynamic data of the 4-methyl-1,2-phenylene compounds are summarized in Table III and the transition temperatures are plotted against the number of carbon atoms in the alkyl group in Figure 3. Contrary to the cases presented in Figure 2, both the nematic and smectic A phases are promoted by 4-methylation in the whole series. Because the melting point in the methoxy to butoxy derivatives is greatly lowered, the temperature range of stable existence of the nematic phase is appreciably extended by 4-methylation. The metastable smectic B phase does not change its stability by this substitution and is observed for the hexyloxy to dodecyloxy derivatives. The behavior of the fused twins again resembles to that given by the reference mesogen carrying a 4-methyl group; that is, the hexyloxy

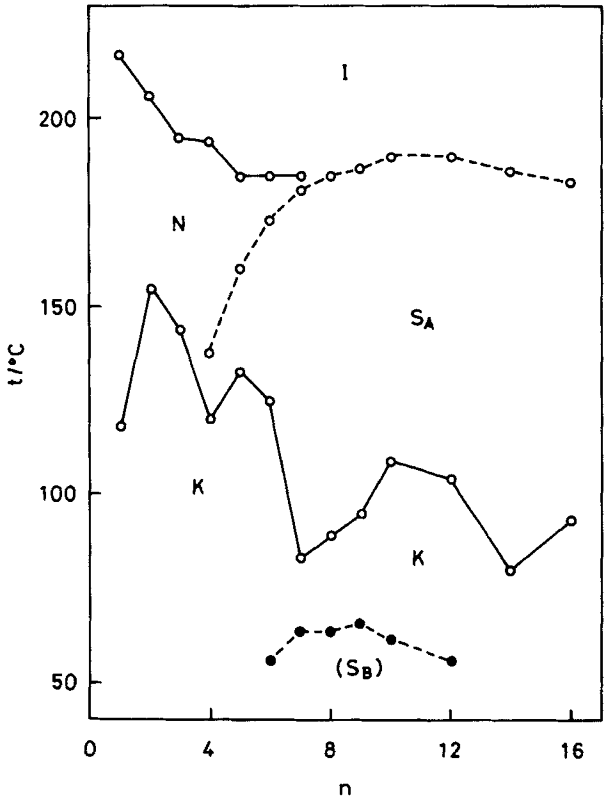


FIGURE 3 Plot of transition temperatures against the number of carbon atoms in the alkyl group (n) for 4-methyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates].

derivative melts at 92°C and is transformed into a smectic A phase. The S_A-N transition occurs at 157°C and the N-I transition at 228°C. Thus, the 4-methylation stabilizes the smectic A phase by 14°C and the nematic phase as much as by 67°C. Therefore, the preferred orientation of the fused twin molecule may be such that the substituent is located, more or less, along the director.

The plots of the layer spacings in the smectic A phases in the 3-methyl- and 4-methyl-1,2-phenylene compounds against the number of carbon atoms in the alkyl group give the slopes of 0.155 and 0.161 nm per methylene group which essentially agree with that given by the unmethylated compounds. The values extrapolated to n = 0 are increased by methylation to 1.73 nm and 1.71 nm respectively.

The above-mentioned classification of mesophases was firmly supported by the existence of complete miscibility in the phase diagrams of binary systems consisting of some representative twins and the reference compound. For example, Figure 4 presents the binary system between phenyl (4-hexyloxybenzylideneamino)benzoate and the hexyloxy derivative of the 4-methyl-1,2-phenylene compound. The diagram gives continuous S_B-S_A, S_A-N, and N-I transition curves which are convex upwards.

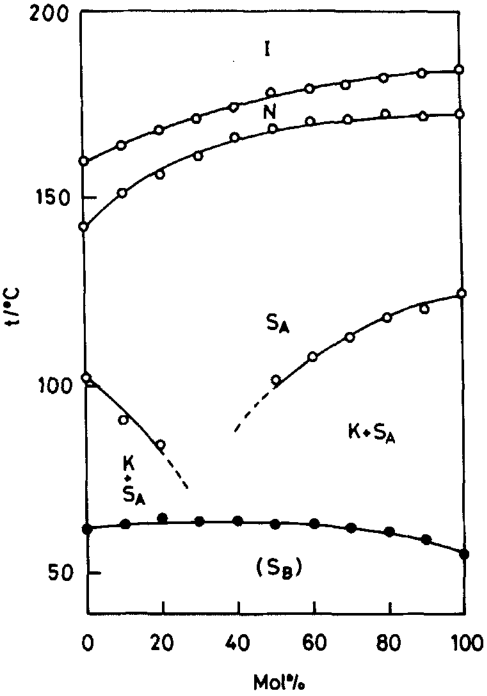


FIGURE 4 Phase diagram of the binary system consisting of phenyl 4-(4-hexyloxybenzylideneamino)benzoate and 4-methyl-1,2-phenylene bis[4-(4-hexyloxybenzylideneamino)benzoate]. The former compound is located on the left-hand side.

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