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Mesomorphic Properties of Dialkyl *N,N′*-[1,4-Phenylenebis(methylidyne)]bis[4-aminobenzoates]

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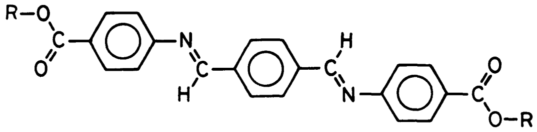
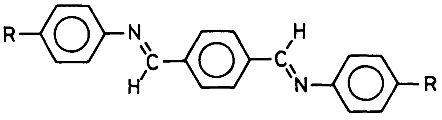
The mesomorphic behavior of fourteen dialkyl *N,N′*-[1,4-phenylenebis(methylidyne)]bis[4-aminobenzoates] has been examined by optical microscopy and differential scanning calorimetry in order to make a comparison with the behavior of *N,N′*-[1,4-phenylenebis(methylidyne)]bis[4-alkylanilines] and to study the effects of branching of the ester alkyl groups. Among the results obtained, the following may be particularly important: (1) the unbranched alkyl ester is generally less polymesomorphic than the corresponding alkyl compound, (2) mesophase(s) is completely eliminated by the 1-methylation, and (3) the 3-methylbutyl, 3-methylpentyl, and 4-methylpentyl esters are more polymesomorphic than the unbranched alkyl esters.

The mesomorphic properties of organic compounds are highly sensitive to changes in chemical structure; therefore, a systematic study of closely related compounds is desirable in order to elucidate the relationship between the structural parameters and the thermal stabilities of various mesophases. This paper presents our work on dialkyl *N,N′*-[1,4-phenylenebis(methylidyne)]bis[4-aminobenzoates] which have the general structure given below (**1**) and are closely related to that of *N,N′*-[1,4-phenylenebis(methylidyne)]bis[4-alkylaniline] (**2**), well-known for their smectic polymorphism.[1,2] For example, the propyl compound exhibits the smectic H, G, C, and A phases as well as the nematic phase, and the hexyl compound exhibits the smectic G, F, C, and A phases as well as the nematic phase.[2] Therefore, we may be able to find various types of the mesophase in the compounds to be studied. Indeed, Arora et al. have shown that the dibutyl ester exhibits smectic C and A phases as well as the nematic phase.[3] Secondly, we were interested in extending our work on the effects of the branching of the ester alkyl chain on the mesomorphic properties to diesters in which the effects may be more appreciable than in the monoester. The bis(2-methylbutyl) ester has been known to show only the nematic phase, through the work of Coates et al.[4]



(**1**)



(**2**)

Experimental

Materials. Alkyl *p*-aminobenzoates were obtained by reactions between *p*-nitrobenzoyl chloride and alcohols, followed by reduction with iron powder and dilute hydrochloric acid, as described by Adams et al., or with zinc dust in 75% aqueous ethanol.[5,6] The Schiff's bases were prepared by condensing terephthalaldehyde with the alkyl *p*-aminobenzoates in boiling ethanol or benzene, employing a small amount of acetic acid as a catalyst.

Measurements. Microscopic observations and calorimetric measurements were made as described in our previous paper.[7] Phase diagrams were determined by the calorimetric curves for binary mixtures in order to identify the smectic phases.

Results and Discussion

The transition temperatures and enthalpy changes are listed in Table 1 for the fourteen esters examined in this work. Here, K, S, N, and I stand for crystalline, smectic, nematic, and isotropic liquid phases, respectively. The seven unbranched alkyl esters are given in section a in this table.

The methyl and ethyl esters are purely nematogenic. Because of the thermal decomposition near the clearing point the enthalpy change in the former ester could not be measured. Both their melting and clearing points are much higher than those of the corresponding alkyl compounds, respectively. The appearance of the smectic H phase in the temperature range from 126 to 150 °C reported by Neubert and Maurer was not supported by Wiegeleben et al.

The propyl ester is transformed into an isotropic liquid at a temperature almost the same as that of the propyl compound (260 °C by Neubert and Maurer and 255 °C by Wiegeleben et al.). The temperature range of the smectic A phase is a little wider than that of the corresponding alkyl compound (26 to 30 °C). The three other smectic phases given by the propyl compound, H, G, and C, are not detectable in this ester.

Thus, the clearing point of the ester is reduced as the ester alkyl group becomes longer and a profound alternation of the transition temperature is exhibited by higher homologous members. The transformation of the butyl ester from the nematic phase to an isotropic liquid occurs at a lower temperature than the corresponding alkyl compound; namely, 209 versus 235 °C.[1,2] Similarly, the smectic A and C properties are decreased compared with those in the alkyl compound. The difference in their thermal stabilities is in the following order: $S_C > N > S_A$. Therefore, a large depression of the smectic A phase in the hexyl and heptyl esters may explain the absence of nematic properties in these two members. It must be noted that all of the mesophases appearing below the smectic C in the alkyl compounds are eliminated by the change of the terminal substituent from the alkyl to the alkoxycarbonyl group.

Turning now to the branched alkyl esters, the thermal properties are given in section b in Table 1. According to the systematic studies by Gray and Harrison, all of the branched chain esters have lower liquid crystal stabilities than the unbranched chain esters.[8] Especially, the branching methyl group occupying the 1 position greatly reduces the thermal stability and, as the methyl group is moved towards the end of the chain, the transition temperature rises again. In addition to the information given in table, the esters carrying the following alkyl groups were studied: isopropyl, *t*-butyl, 1-methylbutyl, 1,2-dimethylpropyl, 1-methylbutyl, and 1-methylpentyl. No mesophase was found for these esters, indicating that the liquid crystalline behavior in the present series dramatically suffers as the result of a branching methyl substituent on the 1 position in the alkyl chain.

The nonmesomorphic behavior of the neopentyl ester in the present series is in sharp contrast with the observation made for the corresponding ester in the 4-(4-phenylbenzylideneamino)benzoate series.[7] In the latter, the N–I transition temperature of the propyl ester remains at 133 °C by the introduction of a methyl group at the 2 position and is depressed only by 8 °C by the second methyl group. This remarkable discrepancy strongly supports our previous view that the effects of the branching of the alkyl chain on mesomorphic properties greatly vary with the features of the molecular structure.

The N–I transition temperature of the 2-methylpropyl ester is lower by 17 °C than that of the unbranched propyl ester. The smectic A phase observed for the latter compound is lost by the

Table 1. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **1**[a]

Alkyl group	K		S_G		S_B		S_C		S_A		N		I
a. Unbranched													
CH_3	.	243 (53)									.	339 (—)	.
CH_2CH_3	.	210 (31)									.	295 (0.21)	.
$CH_2CH_2CH_3$	.	153 (39)							.	199 (0.21)	.	258 (0.38)	.
$CH_2CH_2CH_2CH_3$[b]	.	92 (32)					.	137 (—)	.	190 (0.84)	.	209 (0.38)	.
$CH_2CH_2CH_2CH_2CH_3$	.	100 (34)							.	206 (1.3)	.	216 (0.46)	.
$CH_2CH_2CH_2CH_2CH_2CH_3$	.	113 (27)					.	148 (—)	.	189 (2.9)			.
$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	.	92 (41)					.	140 (—)	.	196 (4.5)			.
b. Branched													
$CH_2CH(CH_3)_2$	.	157 (40)									.	241 (0.42)	.
$CH_2CH(CH_3)CH_2CH_3$[c]	.	131 (29)									.	183 (0.29)	.
$CH_2CH_2CH(CH_3)_2$	.	113 (24)					.	140 (0.33)	.	158 (0.33)	.	170 (0.29)	.
$CH_2CH(CH_3)CH_2CH_2CH_3$	.	115 (39)									.	175 (0.21)	.
$CH_2CH_2CH(CH_3)CH_2CH_3$	.	100 (20)	.	106 (0.04)	.	133 (0.71)			.	145 (0.59)	.	147 (0.33)	.
$CH_2CH_2CH_2CH(CH_3)_2$	.	109 (56)					.	140 (0.25)	.	160 (0.92)	.	170 (1.0)	.
$CH_2CH(CH_3)CH_2CH_2CH_2CH_3$	.	101 (37)									.	146 (0.25)	.

a) The latter quantities are in parentheses. b) 91 (38), 134 (—), 185 (0.88), and 203 °C (0.46) by Arora et al.[3] c) 123 (17) and 184 °C (0.21) by Coates et al.[4]

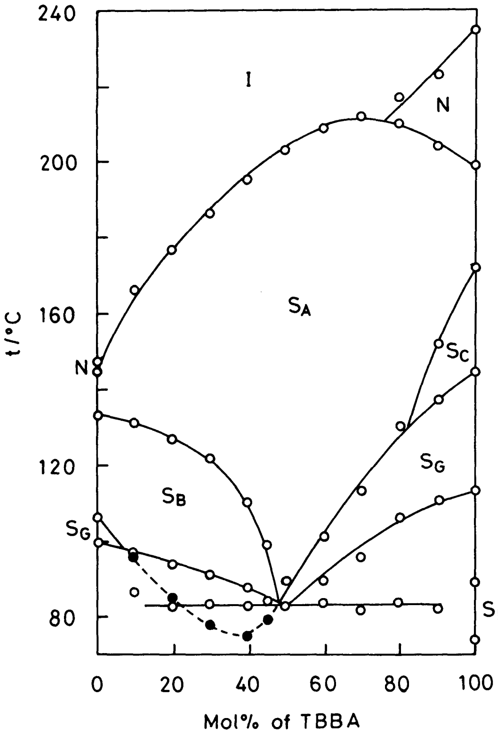


Fig. 1. Phase diagram of the binary system consisting of compound **1** with R=3-methylpentyl and TBBA (compound **2** with R=butyl). The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

introduction of a methyl group at the 2 position.

When the branching methyl group is located at the 2 or 3 position in the butyl ester, the change in the transition temperature is rather unusual. Contrary to what is generally known,[8–11] the 2-methylbutyl ester gives an N–I transition temperature higher by 13 °C than the 3-methylbutyl ester. The latter compound exhibits smectic A and C phases, both of which are characteristic of the butyl ester. While the smectic A behavior is depressed by as much as 32 °C, the smectic C behavior is a little bit promoted by the branching methyl group.

The branching at the 2 or 3 position of the pentyl ester presents very interesting features. The N–I transition temperature of the 2-methylpentyl ester is higher by 28 °C than that of the 3-methylpentyl ester. Although the former ester exhibits only the nematic phase, the latter gives polymesomorphic changes. It must be pointed out that the smectic B phase shown by the 3-methylpentyl ester is not observable for the unbranched pentyl ester. In order to supplement the identification made by the microscopic observation, a phase diagram of the binary system with the butyl compound (TBBA) was prepared.[12] This reference compound is known to exhibit the smectic H, G, C, and A phases and the nematic phase.[2] As is shown in Fig. 1, the eutectic point is found at 50 mol% and 83 °C. Since the smectic A phase is stabilized by mixing, only parts of the N–I transition temperature curve are observable. Nevertheless, it is easily seen that the temperature varies monotonously with the composition. The thermal stabilities of the other smectic phases of TBBA, especially those of the smectic C and H phases, are drastically reduced by the addition of the ester. The intermediate smectic phase in the ester is clearly different from any smectic phase given by the reference compound and was identified to be of the smectic B type by a microscopic observation of the texture. This assignment is in accordance with one of the possible sequences of appearance for three smectic phases.[13] On the other hand, the low-temperature smectic phase is apparently miscible with the smectic G phase of TBBA, even though the smectic B–smectic G transition temperature curve shows a deep minimum.

By a shift of the methyl group from the 3 position to the 4 position, the nematic phase is stabilized by 23 °C and the smectic A phase by 15 °C. The above-mentioned effects of the branching methyl group on the N–I transition temperature of the pentyl ester indicates that the temperature changes alternately in the present series as the branching methyl group moves from the odd to even position in the chain. One may recognize such an alternation, even in the N–I transition temperatures of the methyl-substituted pentyl 4-(4-cyanobenzylideneamino)cinnamates reported by Gray and Harrison;[8] however, it was not detectable in our earlier series of alkyl 4-(4-alkoxybenzylideneamino)benzoates.[10] Thus, the magnitude may markedly depend on the features of the molecular structure. Because of the presence of two alkyl groups, the alternation in the present series may be so large that one cannot miss it. However, monoesters exhibiting similar changes will be provided by the forthcoming papers. The present ester exhibits the smectic C phase, which is not known for the unbranched pentyl ester.

Finally, we add that the 2-methylhexyl ester is purely nematogenic, while the unbranched hexyl ester is purely smectogenic. The appearance of the nematic phase by a partial destruction of the smectic A phase by a branching methyl group has been amply demonstrated in the present author's previous studies.[7,10,11]

References

1) M. E. Neubert and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, **43**, 313 (1977).

2) A. Wiegeleben, L. Richter, J. Deresch, and D. Demus, *Mol. Cryst. Liq. Cryst.*, **59**, 329 (1980).

3) S. L. Arora, J. L. Fergason, and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **10**, 243 (1970).

4) D. Coates, K. J. Harrison, and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **22**, 99 (1973).

5) R. A. Adams, E. K. Rideal, W. B. Burnett, R. L. Jenkins, and E. E. Dreger, *J. Am. Chem. Soc.*, **48**, 1758 (1926).

6) W. E. Kuhn, *Org. Synth.*, Coll. Vol. II, 447 (1943).

7) Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **104**, 353 (1984).

8) G. W. Gray and K. J. Harrison, *Mol. Cryst. Liq. Cryst.*, **13**, 37 (1971).

9) G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **104**, 335 (1984).

10) Y. Matsunaga and N. Miyajima, *Bull. Chem. Soc. Jpn.*, **57**, 1413 (1984).

11) Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **116**, 207 (1985).

12) As the trivial name, terephthal- or terephthalylidenebis(*p*-butylaniline) has been widely used, TBBA is the abbreviation in accord with that used in the references.

13) D. Demus, S. Diele, S. Grande, and H. Sackmann, "Advances in Liquid Crystals, Vol. 6," ed by G. H. Brown, Academic Press, New York (1983), p. 11.