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Mesomorphic Properties of 4-[3,4-Bis(4-alkoxybenzoyloxy)benzylideneamino]azobenzenes and Related Compounds

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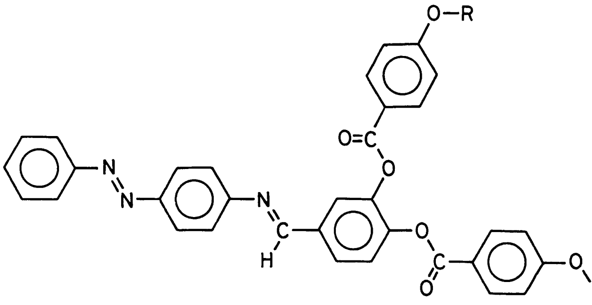
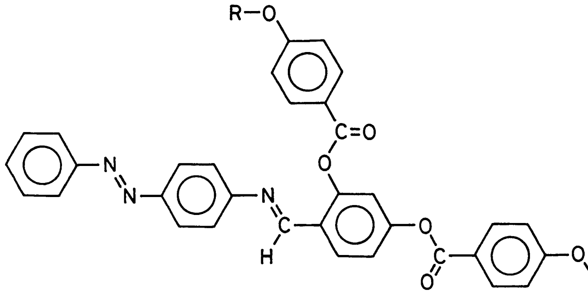
The mesomorphic properties of a homologous series of 4-[3,4-bis(4-alkoxybenzoyloxy)benzylideneamino]azobenzenes have been studied by differential scanning calorimetry and microscopy. While the nematic phases exhibited by the ethoxy and propoxy homologues are metastable, those exhibited by all of the butoxy-to-hexadecyloxy homologues exhibit the temperature range of stable existence. A metastable smectic A-phase is observed for the tetradecyloxy and hexadecyloxy homologues. Among the examined 4-[2,4-bis(4-alkoxybenzoyloxy)benzylideneamino]azobenzenes, only the dodecyloxy and tetradecyloxy members are nematogenic. Their clearing points are located at more than 30 °C below the melting points. 4-(Benzylideneamino)azobenzene and its 3-(4-dodecyloxybenzoyloxy) derivative are nonmesogenic; however, the phase diagrams of binary systems with 4-(4-nonyloxybenzylideneamino)azobenzene revealed that the addition of a 3-(4-dodecyloxybenzoyloxy) group to the former molecule depresses the virtual nematic behavior, but promotes the smectic A behavior. A further addition of the same group at the 4-position drastically raises the nematic-isotropic transition temperature.

Systematic studies on the influence of lateral substitutents on the mesomorphic properties of rod-like molecules indicated that only relatively small ones allow the persistence of the liquid crystalline state.[1–3] However, Weissflog and Demus discovered that some molecules with a long alkyl group, and even with an aromatic branch bound to the middle moiety of a rod-like molecule, can form mesophases.[4–7] The compounds of the latter type include 4-nitrophenyl 2,5-bis(4-octyloxybenzoyloxy)benzoate and 4′-ethoxy-3-[*N*-(4-ethoxyphenyl)iminomethyl]-4-(4-methoxybenzoyloxy)azobenzene. The former compound exhibits a stable smectic A-phase covering the temperature range from 96 to 164 °C, whereas the latter exhibits a metastable nematic phase, the transition into an isotropic liquid of which is located far below the melting point (73 °C vs. 160 °C). A single-crystal X-ray analysis performed on the azobenzene derivative disclosed that the molecule is in a bifurcated shape. The phenyliminomethyl branch is markedly bent from the nearly linear three-ring basic fragment, but is almost coplanar with the azobenzene moiety.

More extensive synthetic studies concerning closely-related compounds were carried out by Takenaka et al.[8–10] Tris(4-alkoxyphenyl) 1,2,4-benzenetricarboxylates were shown to exhibit a metastable nematic phase when the alkyl group is heptyl or octyl and a smectic A-phase as well as a nematic phase when the alkyl group is nonyl or decyl.[8] 4-Cyanophenyl 3,4-bis(4-alkoxybenzoyloxy)benzoates, in which the alkyl group is from pentyl to octyl, are nematogenic. Among these members only the hexyl compound gives a nematic phase with a temperature range of stable existence. A metastable smectic A-phase was observed for the heptyl-to-decyl homologues.[9] The 4-alkoxylphenyl esters of the same acid are also nematogenic when the alkyl group is butyl-to-nonyl. The nematic–isotropic transitions in the hexyl compound and the higher homologous members are enantiotropic. The nonyl compound shows a metastable smectic-A phase in addition to a nematic phase. Thus, many 1,2,4-benzene derivatives comprising four-rings are mesogenic; however, the mesophase–isotropic transitions are known to be mostly monotropic. Consequently, we prepared a series of 4-[3,4-bis(4-alkoxybenzoyloxy)benzylideneamino]azobenzene (**1**) and the related compounds (**2**), both of which have a linear four-ring basic fragment, and studied their liquid-crystalline behavior. In order to clarify the effects of an aromatic branch on the mesomorphic properties, the thermal behavior of 4-[3-(4-alkoxybenzoyloxy)benzylideneamino]azobenzenes (**3**) were also examined.



(**1**)



(**2**)

Experimental

Materials. Equimolar amounts of 4-aminoazobenzene and

3-hydroxybenzaldehyde or 2,4- or 3,4-dihydroxybenzaldehyde were dissolved in ethanol, and then a few drops of acetic acid were added. The precipitated orange-colored 4-(benzylideneamino)azobenzene derivative was collected by filtration and washed first with ethanol and then with hexane. Compounds **1** were obtained by the reaction of 4-(3,4-dihydroxybenzylideneamino)azobenzene with 4-alkoxybenzoic acids in chloroform, following a procedure of Hassner and Alexanian.[11] Found: C, 76.61; H, 8.10; N, 4.79%. Calcd for $(C_{12}H_{25}OC_6H_4CO_2)_2C_6H_3\text{-}CH{=}N\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_5$: C, 76.56; H, 8.00; N, 4.70%. Compounds **3** were similarly prepared. In order to synthesize compounds **2**, the esterification of 4-(2,4-dihydroxybenzylideneamino)azobenzene had to be carried out by the reaction with 4-alkoxybenzoyl chloride in boiling benzene by the addition of pyridine.

Measurements. The transition temperatures and associated enthalpy changes were measured by means of a Rigaku Denki Thermoflex differential scanning calorimeter. Phase diagrams were determined by the calorimetric curves of mixtures.

Results and Discussion

The mesomorphic transition temperatures and associated enthalpy changes of compounds **1** are summarized in Table 1. Here, K, S_A, N, and I stand for crystalline, smectic A, nematic, and isotropic liquid phases, respectively. In spite of the presence of an aromatic lateral branch, all of the ethoxy-to-hexadecyloxy homologues were found to be mesogenic. The N–I transition temperature gradually decreases with increasing the alkyl chain length throughout this series. The mesophases given by the ethoxy and propoxy compounds are metastable, whereas those given by the butoxy-to-hexadecyloxy compounds have a temperature range of stable existence. Thus, the presence of the 4-(phenylazo)phenyliminomethyl group in the molecule greatly enhances the thermal stability of the mesophases, compared with those reported by other workers.[5–10] They show a marble texture characteristic of nematic phases formed by rod-like molecules. The temperature ranges of stable existence given by the octyloxy homologue and the later members of the series are about 30 °C. In addition, a metastable smectic phase exhibiting a fan texture is observable with the tetradecyloxy and hexadecyloxy homologues.

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

$n^{b)}$	K		S_A		N		I
2	·	181(43)			[·	160(0.4)]	·
3	·	176(52)			[·	141(0.4)]	·
4	·	145(40)			·	147(0.4)	·
5	·	126(51)			·	135(0.4)	·
6	·	107(55)			·	136(0.4)	·
7	·	110(61)			·	132(0.4)	·
8	·	102(59)			·	131(0.4)	·
9	·	99(68)			·	127(0.4)	·
10	·	91(67)			·	125(0.5)	·
11	·	82(65)			·	121(0.5)	·
12	·	82(73)			·	121(0.6)	·
14	·	91(78)	[·	76(0.4)]	·	115(0.7)	·
16	·	100(80)	[·	88(0.5)]	·	113(0.8)	·

a) The enthalpy changes are in parentheses. Brackets indicate monotropic transitions. b) The number of carbon atoms in the alkyl group.

As is shown in Fig. 1, the nematic phase of the dodecyloxy compound is completely miscible with the nematic phase of 4-(4-nonyloxybenzylideneamino)azobenzene, indicating that the mesophase is classical nematic, in spite of the molecular shape being far from rod-like. The latter compound has been reported to give the following transitions: K 109.5 S_B 126 S_A 156 N 162 I.[12] The present conclusion is in a sharp contrast with our previous finding that *N*,*N'*-dialkanoyl-2,5,6-trimethyl-4-alkanoyloxy-1,3-benzenediamines (the molecular shape of which is supposed to resemble, to some degree, that of the present series) is discotic nematic.[13] The smectic A- and B-phases of the reference mesogen are considerably destabilized upon mixing. The S_A–N transition point curve intersects with the melting point curve of the reference compound at 108 °C and 68 mol% and the S_B–S_A transition point curve at 111 °C and 92 mol%. Fitting Van Hecke's equation, $T{=}\Delta H_{AV}/\Delta S_{AV}$, to the diagram using the entropy ratio as a parameter suggests that the virtual S_A–

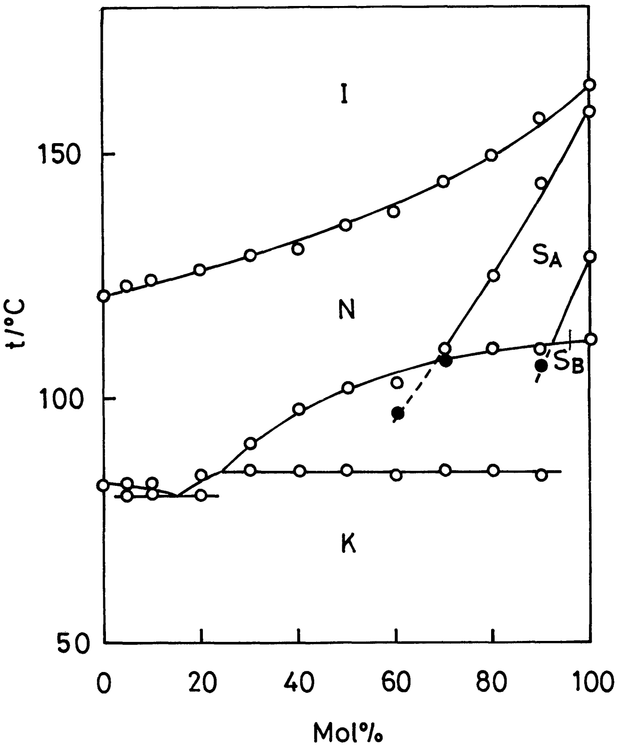


Fig. 1. Phase diagram of the binary system consisting of 4-[3,4-bis(4-dodecyloxybenzoyloxy)benzylideneamino]azobenzene and 4-(4-nonyloxybenzylideneamino)azobenzene. The latter compound is located on the right-hand side. The open and shaded circles are transitions recorded in the processes of heating and cooling respectively.

Table 2. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **2** and **3**$^{a)}$

$n^{b)}$	K		N		I
		Compounds **2**			
10	·	109(61)			·
11	·	98(65)			·
12	·	105(64)	[·	73(0.5)]	·
14	·	106(70)	[·	71(0.6)]	·
16	·	108(72)			·
		Compounds **3**			
6	·	131(71)			·
10	·	114(75)			·
12	·	107(82)			·

a) The enthalpy changes are in parentheses. Brackets indicate monotropic transitions. b) The number of carbon atoms in the alkyl group.

N transition of the dodecyloxy compound is located at about 35 °C.[14] It may be noted that the destabilization of the ordered smectic phase is more drastic than that of the non-ordered one.

Table 2 presents the thermal properties of series **2** and **3**. For the former series, only the decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, and hexadecyloxy members were studied. The melting point tends to be higher than that of the corresponding member of series **1**. A metastable mesophase is detectable only with dodecyloxy and tetradecyloxy compounds. Judging from the magnitude of the enthalpy change at the clearing point, the mesophase is undoubtedly nematic. The transition is located more than 30 °C below the melting point. In other words, the N–I transition temperature is depressed by 41 or 48 °C by the shift of the 4-alkoxybenzoyloxy branch from the 3-position to the 2-position of the benzylideneamino moiety. This mesomorphic behavior of compound **2** may be ascribed to the difference in the rigidity between the specific moieties of the linear four-ring basic fragment located close to the 4-alkoxybenzoyloxy branch. While the more-or-less planar 4-(phenylazo)phenyliminomethyl group is favorable for an enhancement of the thermal stability of the mesophase (as seen earlier), the 4-alkoxybenzoyloxy branch at the 2-position in compound **2** is not allowed to adopt configurations relaxed well from the Y-shape because of the rigidity of the afore-mentioned group. On the other hand, the two 4-alkoxybenzoyloxy groups at the 3- and 4-positions may easily take configurations less deviated from the rod-like shape by rotating rather freely around the C–O and C–C single bonds.

All of the three examined members of compounds **3**, the molecule of which has a bent, is not mesogenic at all. In order to explore the potential mesogenic properties, we studied the phase diagrams of binary systems comprising the dodecyloxy homologue and the corresponding member of series **1**, as well as the afore-mentioned reference compound, 4-(4-nonyloxybenzylideneamino)azobenzene. In the former system, which shows a eutectic point at 75 °C and 37 mol% of compound **3**, the thermal stability of the mesophases given by the reference compound is so diminished that the N–I transition point curve meets the melting point curve of compound **1** at 78 °C and 27 mol%.

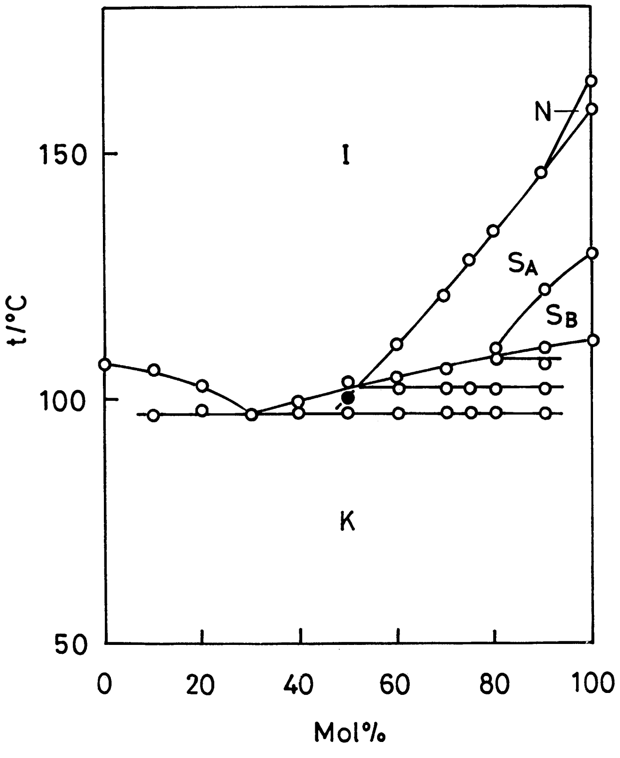


Fig. 2. Phase diagram of the binary system consisting of 4-[3-(4-dodecyloxybenzoyloxy)benzylideneamino]azobenzene and 4-(4-nonyloxybenzylideneamino)azobenzene. The latter compound is located on the right-hand side. As to the open and shaded circles, see the caption of Fig. 1.

The phase diagram given by the latter system is presented in Fig. 2. The nematic phase disappears upon the addition of 10 mol% of compound **3**; therefore, the N–I transition point curve is only our eye guide drawn so as to be consistent with the curve in the former system. The $\mathrm{S_A}$–I transition point curve intersects with the melting point curve of the reference compound at 102 °C and 52 mol% and the $\mathrm{S_B}$–$\mathrm{S_A}$ transition point curve at 108 °C and 79 mol%. The virtual $\mathrm{S_A}$–I transition of compound **3** may be located at about 60 °C by the extrapolation of the transition point curve, which is slightly concave upwards, observable down to 50 mol% of the reference compound to 0 mol%.[14] This temperature is undoubtedly higher than the $\mathrm{S_A}$–N transition temperature estimated for the corresponding member of series **1**. In contrast to the $\mathrm{S_A}$–I transitions, the $\mathrm{S_A}$–$\mathrm{S_B}$ transitions seem to form a curve that is slightly convex upwards. Thus, the introduction of a 4-(4-dodecyloxybenzoyloxy) group to the molecule of compound **3** leads to very significant stabilization of the

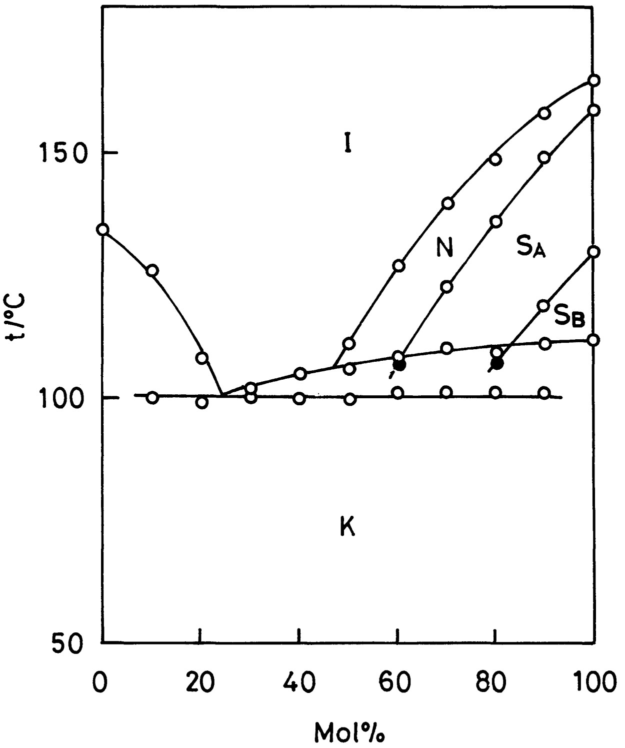


Fig. 3. Phase diagram of the binary system consisting of 4-(benzylideneamino)azobenzene and 4-(4-nonyloxybenzylideneamino)azobenzene. The latter compound is located on the right-hand side. As to the open and shaded circles, see the caption of Fig. 1.

nematic phase and a relatively small destabilization of the smectic A-phase. If we consider that the dodecyloxy homologue of series **1** is formed by the introduction of a (4-dodecyloxybenzoyloxy) group to the 3-position of 4-[4-(4-dodecyloxybenzoyloxy)benzylideneamino]azobenzene, the depression of the N–I transition by the branching is as much as 157 °C, since this linear four-ring compound exhibits transitions, K 142 N 277 I.

Fig. 3 presents a phase diagram of a binary system comprising nonmesogenic 4-(benzylideneamino)azobenzene, the common moiety of all the compounds studied here, and 4-(4-nonyloxybenzylideneamino)azobenzene. The N–I transition is enantiotropic above 47 mol%, the S_A–N transition above 61 mol%, and the S_B–S_A transition above 83 mol%. The maximum temperatures of both the virtual nematic and smectic phases of 4-(benzylideneamino)azobenzene may be located near or below 0 °C.[14] A comparison of the present diagram with the one in Fig. 2 strongly suggests a depression of the N–I transition temperature, as well as a promotion of the S_A–N or S_A–I transition temperature by the introduction of a 3-(4-dodecyloxybenzoyloxy) group to this common moiety. Therefore, if a mesogenic compound could be obtained employing molecules with an obtuse-angled configuration one would speculate that it tends to be smectogenic rather than nematogenic. The mesomorphic properties of 1,3-phenylene bis[4-(4-alkoxybenzylideneamino)benzoates] and their related compounds will be the subject of a forthcoming paper.[15]

References

1) J. Byron, G. W. Gray, and B. M. Worrall, *J. Chem. Soc.*, **1965**, 3706.

2) W. R. Young, I. Haller, and D. C. Green, *J. Org. Chem.*, **23**, 3707 (1972).

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

4) W. Weissflog and D. Demus, *Mol. Cryst. Liq. Cryst.*, **129**, 235 (1985).

5) S. Diele, W. Weissflog, G. Pelzl, H. Manke, and D. Demus, *Liq. Cryst.*, **1**, 101 (1986).

6) W. Weissflog and D. Demus, *Liq. Cryst.*, **3**, 275 (1988).

7) U. Baumeister, Z. Kosturkiewicz, H. Hartung, D. Demus, and W. Weissflog, *Liq. Cryst.*, **7**, 241 (1990).

8) S. Takenaka, Y. Masuda, and S. Kusabayashi, *Chem. Lett.*, **1986**, 751.

9) S. Takenaka, H. Morita, M. Iwano, S. Kusabayashi, T. Ikemoto, Y. Sakurai, and H. Miyake, *Mol. Cryst. Liq. Cryst.*, **166**, 157 (1989).

10) S. Takenaka, Y. Masuda, M. Iwano, H. Morita, S. Kusabayashi, H. Sugiura, and T. Ikemoto, *Mol. Cryst. Liq. Cryst.*, **168**, 111 (1989).

11) A. Haussner and V. Alexanian, *Tetrahedron Lett.*, **1978**, 4475.

12) D. Demus and H. Sackmann, *Z. Phys. Chem.* (*Leipzig*), **238**, 215 (1968).

13) H. Kawada and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **63**, 1691 (1990).

14) G. R. Van Hecke, *J. Phys. Chem.*, **89**, 2058 (1985).

15) T. Akutagawa, Y. Matsunaga, and K. Yasuhara, to be published elsewhere.