Liquid Crystal Formation in Binary Systems. XI.[1] Effects of Branching of Ester Alkyl Group on the Induction of Liquid Crystals in the *N,N,N',N'*-Tetramethylbenzidine–Alkyl 4-(4-Nitrobenzylideneamino)benzoate Systems

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Synopsis. Smectic A liquid crystals are induced in binary mixtures with normal alkyl esters as well as with esters of branched alkyl groups.

In our previous work,[2] the effects of branching of terminal alkyl groups on the liquid crystal induction in electron-donor-acceptor systems were studied employing nonmesogenic alkyl 4-[4-(dimethylamino)benzylideneamino]benzoates and 4,4′-dinitroazoxybenzene. Smectic A liquid crystals were found not only in the systems with the normal alkyl esters but also with the esters of branched alkyl groups such as *t*-butyl, 1,2-dimethylpropyl, and 1-ethylpropyl. These observations are in contrast with what are known for single mesogenic compounds. According to our study on alkyl 4-(4-phenylbenzylideneamino)benzoates, the *t*-butyl and 1-ethylpropyl esters are nonmesogenic.[3] While the thermally stable nematic and smectic A phases in the propyl ester are eliminated by the introduction of methyl groups to the 1- and 2-carbons, the monotropic smectic B phase is stabilized by 4 °C by the substitution. In order to confirm that methyl branching of the alkyl chains of acceptor molecules does result in the same behavioral trends in binary mixtures, a further study was made on the systems composed of nonmesogenic *N,N,N′,N′*-tetramethylbenzidine (TMB) and alkyl 4-(4-nitrobenzylideneamino)benzoates. TMB is known to produce liquid crystals when it is mixed with 4-alkoxy-4-nitro derivatives of *N*-benzylideneaniline.[4]

Experimental

Materials. *N,N,N′,N′*-Tetramethylbenzidine was obtained from Aldrich Chemical Co. and was recrystallized from benzene. The acceptor compounds were prepared by the condensation reaction between *p*-nitrobenzaldehyde and appropriate alkyl *p*-aminobenzoate and purified by repeated recrystallization from ethanol.

Measurements. The calorimetric measurements and visual examinations were carried out as described in our earlier papers.[2,4]

Results and Discussion

The combination of TMB and the ethyl ester gives a phase diagram of the simple eutectic type. The smectic A phase induced in the composition range from 45 to 65 mol% of TMB is stable in a small area as the smectic-isotropic (S-I) transition point curve meets both the freezing point curves of the component compounds near the eutectic point, which is located at 53 mol% and 147 °C. The maximum lies at 152 °C and around 55 mol%. The isopropyl ester forms a 1:1 complex melting incongruently at 144 °C. Metastable smectic A phase appears in the range from 30 to 60 mol%, the maximum temperature being about 148 °C. The *t*-butyl ester complex also produces a peritectic at 151 °C. The maximum of the metastable S-I transition point curve is located at 147 °C. Thus, the branching methyl groups in these two cases enhance the thermal stability of the solid complex but diminish slightly that of the induced smectic A phase.

Figure 1a presents the phase diagram of the propyl ester–TMB system. Unlike the ethyl ester, this ester gives a 1 : 1 solid complex which decomposes to its component compounds at 104 °C. The induced smectic A phase is stable in the range from 25 to 50 mol%; however, it is metastable at the maximum located at about 138 °C and 55 mol%. No solid complex is produced by the *s*-butyl ester (see Fig. 1b). The smectic A phase is formed entirely beneath the freezing point curve of TMB. Although the maximum of the clearing point curve is not well defined, it is certain that the effect of the branching methyl group on the thermal stability of the mesophase is small.

The phase behavior of the isobutyl ester–TMB system shown in Fig. 1c bears a close similarity to that of the propy ester–TMB system. The peritectic is located at 102 °C and the maximum temperature of the induced mesophase is 133 °C. The latter temperature is lower by 5 °C than the corresponding one found for the *s*-butyl ester. Contrary to these findings, it is generally known for single mesogenic compounds that 1-methylation produces the largest decrease in the thermal stability of the smectic A phase and that as the methyl group is moved to the end of the chain, the effect becomes less marked.[5,6] The stabilization of the solid complex by the methyl groups at both the 1- and 2-carbons is significant (see Fig. 1d). The striking feature is nearly the same maximum S-I transition temperature observed for the 1,2-dimethylpropyl ester- and isobutyl ester–TMB systems.

We examined the effect of a branching methyl group introduced to the 1-, 2-, and 3-carbons respectively on the mesophase induced in the butyl ester–TMB system. The butyl and 1-methylbutyl esters yield diagrams of the peritectic type. The smectic A phase is enantiotropic in the former system and is monotropic in the latter. The whole S-I transition point curve is below the freezing point curve of TMB in the diagrams of the simple eutectic type given by the other two esters. Although the clearing point curve is traceable up to 55 mol% of TMB, the maximum appears to be located at a composition a little higher than this. The highest observable temperature is 149 °C for the liquid crystal

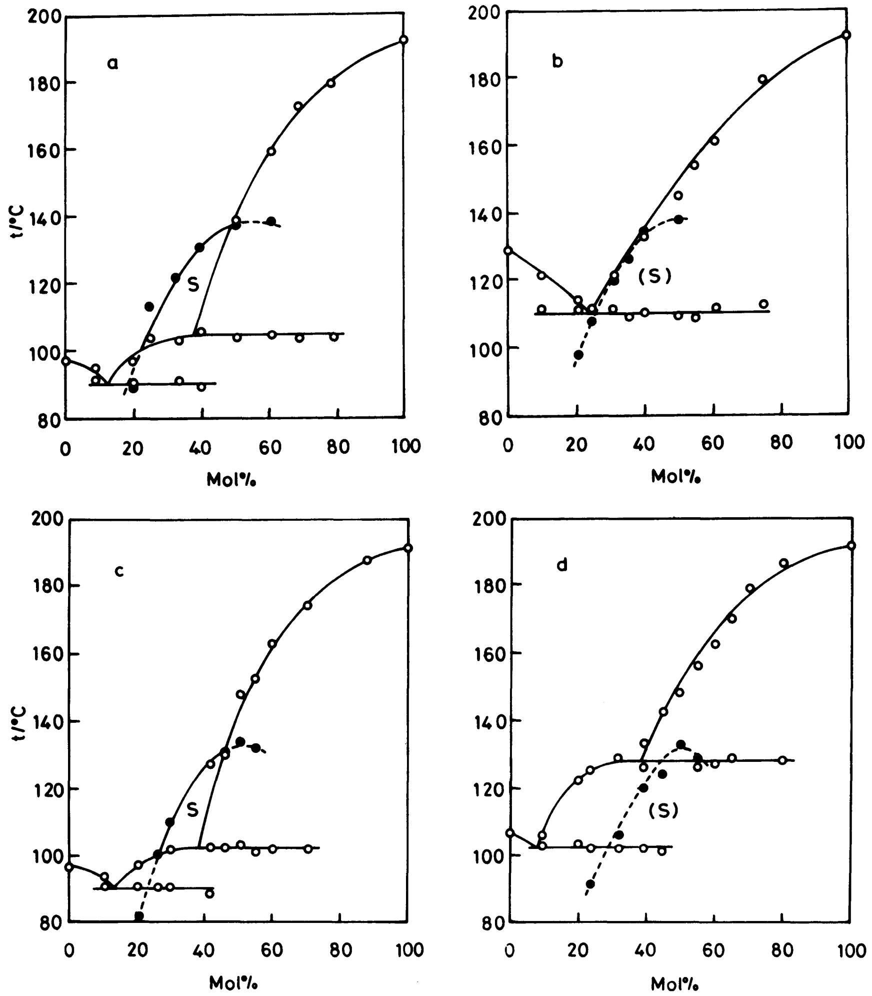

Fig. 1. Phase diagrams of the systems of TMB with (a) the propyl ester, (b) the *s*-butyl ester, (c) the isobutyl ester, and (d) the 1,2-dimethylpropyl ester. The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

given by the butyl ester. It is depressed to 140 °C by 1-methylation, to 134 °C by 2-methylation, and to 138 °C by 3-methylation. The degree of depression by 1- and 2-methyl groups is consistent not only with the tendency found with the propyl ester but also with that reported for the alkyl 4-[4-(dimethylamino)benzylidene-amino]benzoate-4,4′-dinitroazoxybenzene system.2) Thus, the anomalously small effects of 1-methylation of terminal alkyl groups appear to be common to binary liquid crystals and the arguments proposed in the previous paper may also be advanced for them. The 1-methyl group may be accommodated readily within room made available by shorter molecules and cause no serious steric effects when molecules of different lengths are aligned side by side.

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