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Liquid Crystal Formation in Binary Systems. IX.[1] Effects of Branching of Ester Alkyl Group on the Induction of Liquid Crystals in the Alkyl 4-[4-(Dimethylamino)benzylideneamino]benzoate-4,4′-Dinitroazoxybenzene Systems

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Synopsis. Smectic A liquid crystals are formed not only in systems with normal alkyl esters but also with esters of branched alkyl groups such as *t*-butyl, 1,2-dimethylpropyl, and 1-ethylpropyl.

Branching of a terminal alkyl group has been shown to decrease nematic and smectic thermal stabilities relative to those of the unbranched chain compounds by Gray and Harrison.[2,3] However, the effects of branching on the liquid crystals induced in electron-donor–acceptor systems may not be the same as those found with single mesogenic compounds. Consequently, we decided to examine the effects employing binary systems consisting of nonmesogenic alkyl 4-[4-dimethylamino)benzylideneamino] benzoates as electron donors and nonmesogenic 4,4'-dinitroazoxybenzene as an electron acceptor.

The donor compounds were obtained by fusing equimolar mixtures of *p*-(dimethylamino)benzaldehyde and an appropriate alkyl *p*-aminobenzoate and purifying by repeated recrystallization from ethanol. The methyl, ethyl, two isomeric propyl, four isomeric butyl, five isomeric pentyl, and hexyl esters were prepared for this work. The acceptor compound, hereafter abbreviated as DNAO, is known to be able to produce liquid crystals when it is mixed with *N*-[4-(dimethylamino)benzylidene]-4-ethoxyaniline and related compounds.[4] The measurements were carried out as described in our earlier papers.[1,4]

A 2:1 solid molecular complex melting congruently at 179 °C is formed in the methyl ester–DNAO system. The smectic A phase induced in the composition range from 10 to 40 mol% of DNAO is metastable. The isotropic–smectic A (I-$\mathrm{S_A}$) transition point at the former composition is 138 °C and that at the latter is 156 °C. The broad maximum lies at 173 °C and around 25 mol%.

As is shown in Fig. 1a, a phase diagram of the eutectic type is produced when the ethyl ester is mixed with DNAO. The I-$\mathrm{S_A}$ transition point curve is markedly convex upwards and appears near the eutectic point at 114 °C and 10 mol% and terminates at the intersection with the freezing point curve of DNAO at 147 °C and about 55 mol%. The effects of branching of this alkyl group are demonstrated by the phase diagrams of the isopropyl ester- and the *t*-butyl ester–DNAO systems (see Figs. 1b and 1c). The induced smectic A phases in these two systems are metastable and the maximum temperatures are 132 and 131 °C respectively. A decrease in the transition temperature by the introduction of the first methyl group to the ester ethyl group meets our expectation but, to our surprise, the effect of the second methyl group is essentially nil.

In the propyl ester–DNAO system, a smectic A phase is observable from 15 to 50 mol% (see Fig. 2a). The I-$\mathrm{S_A}$ transition point curve is less convex than that in the ethyl ester–DNAO system, and the maximum is found at 129 °C and around 34 mol%. By 1-methylation, the smectic A phase remains stable only in a small area. The I-$\mathrm{S_A}$ transition point curve reaches its maximum at 111 °C and 29 mol% (see Fig. 2b). The methylation on the penultimate carbon further reduces the thermal stability of the induced mesophase. As is shown in Fig. 2c, the smectic A phase is metastable in this binary system and a nematic phase is also induced on the acceptor-rich side. The maximum temperature of the smectic phase is 103 °C. These observations are in contrast to those made by Gray and Harrison for several series of mesogenic compounds: that is, 1-methylation generally produces the largest decrease in the thermal stability of the smectic A phase, and as the methyl group is moved to the end of the chain, the effect becomes less marked. The anomalous results described

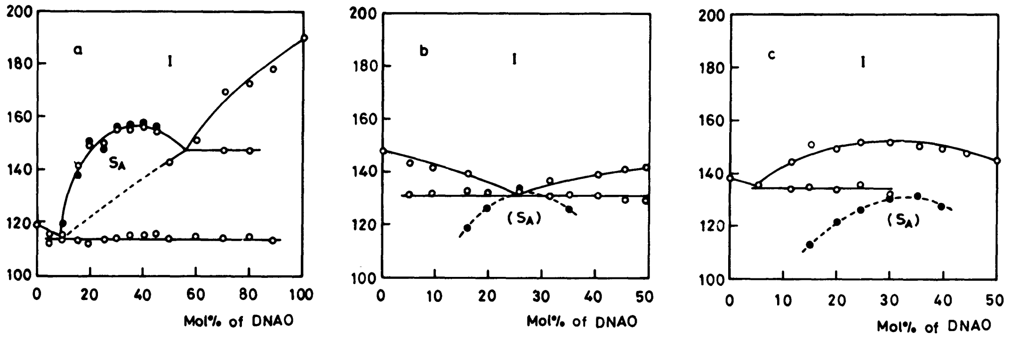

Fig. 1. Phase diagrams of the systems of DNAO with (a) the ethyl ester, (b) the isopropyl ester, and (c) the *t*-butyl ester. The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

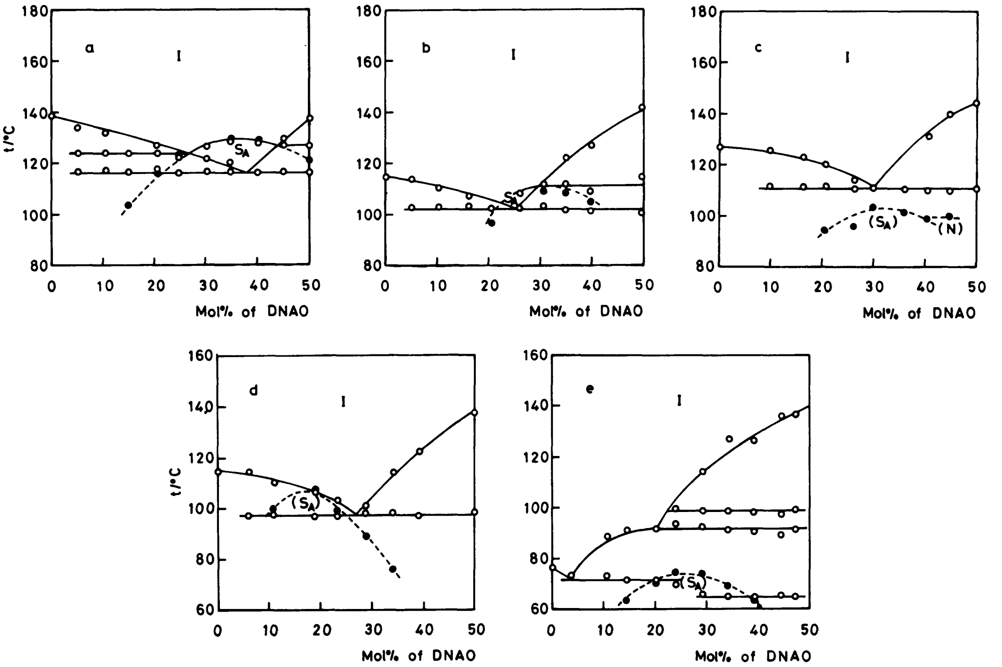

Fig. 2. Phase diagrams of the systems of DNAO with (a) the propyl ester, (b) the 1-methylpropyl ester, (c) the 2-methylpropyl ester, (d) the 1,2-dimethylpropyl ester, and (e) the 1-ethylpropyl ester. As to the open and shaded circles, see the caption of Fig. 1.

above appear to be characteristic of the present binary systems, and are in accord with the effects of the methyl substitution at both the 1 and 2 positions of the ester propyl group (see Fig. 2d). If one considers a 1-methyl group to be added to the isobutyl ester, the substitution raises the maximum I-S_A transition temperature by 3 °C, whereas if the 2-methyl group is regarded as an extra substituent, the temperature is lowered by 5 °C. Moreover, no mesophase could be observed in the neopentyl ester–DNAO system. Figure 2e presents the phase diagram of the 1-ethylpropyl ester–DNAO system. The transition temperature change by 1-ethylation to 74 °C is double that by 1-methylation.

Contrary to the above cases, the effects of methylation on the induced smectic A phase in the butyl ester–DNAO system is normal. The butyl ester and its 2-methyl and 3-methyl derivatives all produce stable smectic A phases when they are mixed with DNAO. The maximum I-S_A transition temperatures are 120, 90, and 111 °C respectively. Finally, it must be noted that the longer the unbranched alkyl group, the maximum I-S_A transition temperature becomes lower: namely, 110 °C with the pentyl ester and 108 °C with the hexyl ester. In the former case, the induced mesophase is metastable in the whole composition range. Thus, even numbers of carbon atoms in the ester alkyl group in the present binary systems tend to produce larger regions of stable existence of induced smectic A phase. This behavior may be, at least partly, ascribed to the marked odd-even alternation of the melting point of the ester as the mesophase is induced in the donor-rich composition range (compare Figs. 1a and 2a).

Although the mechanism of the transition temperature change by chain branching is not well understood even in single mesogenic compounds, branching certainly disturbs smectic order because of a steric interference with neighboring molecules. The anomalous effects observed with the ethyl and propyl esters may be tentatively explained by the difference in molecular length between the donor and acceptor. As the donor and acceptor molecules are arranged side by side in the mesophase, the 1-methyl group may be accommodated, partially at least, within room produced by the acceptor molecule which is shorter than the ester molecules. If the ester molecules are still longer and/or the point of branching is near the end of the chain, the flexible alkyl group is surrounded increasingly by like molecules and may behave as if it is in a single mesogenic compound.

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