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Liquid Crystal Formation in Binary Systems. X.1) Potentially Smectogenic Behavior of Some *p*-Disubstituted Benzenes

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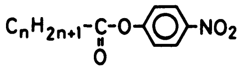
Studies on binary systems with nematogenic *N*-(4-propoxybenzylidene)-4-hexylaniline revealed that 4-nitrophenyl alkanoates, alkyl 4-nitrobenzoates, *N*-(4-nitrophenyl)alkanamides, and *N*-alkyl-4-nitrobenzamides are potentially smectogenic. When the Schiff base is mixed separately with a homologous member from 4-nitrophenyl decanoate to tetradecanoate, a stable smectic A phase is induced and its maximum temperature is about 48 °C. The estimated latent transition points to this mesophase of these benzene derivatives are in the range from −25 to 10 °C. On the other hand, only metastable smectic A phases can be produced with hexyl to dodecyl 4-nitrobenzoates, the maximum temperatures being from 15 to 26 °C. While the metastable smectic B phase of the Schiff base is to some extent stabilized by the addition of the alkanoates, it is drastically depressed by the benzoates. The addition of *N*-(4-nitrophenyl)nonanamide to -dodecanamide produces a stable smectic A phase and also stabilizes the metastable smectic B phase. No smectic A phase is found in mixtures of the Schiff base with *N*-octyl- to *N*-dodecyl-4-nitrobenzamides, and the isotropic or nematic-smectic B transition point curves are almost horizontal indicating that these benzene derivatives have transitions to latent smectic B phases between 10 and 20 °C. Results obtained with some related compounds are also presented.

In one of the earlier papers of this series, we reported the induction of smectic phases by the addition of 4-alkoxynitrobenzenes to *N*-(4-propoxybenzylidene)-4-hexylaniline and the related compounds.2) This Schiff base gives a nematic phase stable between 42 and 63 °C and a metastable smectic B phase below 21 °C. We concluded that the induction of smectic A phases in the above binary mixtures is indicative of the potentially smectogenic behavior of these *p*-disubstituted benzenes even though the upper limit of smectic temperature range is located at about −25 °C for 4-(dodecyloxy)nitrobenzene and lower for the other homologous members. With the hope of finding potentially smectogenic *p*-disubstituted benzenes with higher transition temperatures, we examined the phase diagrams of the binary systems composing of the above Schiff base and 4-nitrophenyl alkanoate (**1**), alkyl 4-nitrobenzoate (**2**), *N*-(4-nitrophenyl)alkanamide (**3**), and *N*-alkyl-4-nitrobenzamide (**4**) respectively. Esters are side chains widely shared by discogenic compounds, whereas amides were rarely studied but chosen for the present work because the $NHCOCH_3$ substituent, which can hydrogen-bond and has a strong dipole, is known to markedly enhance smectic thermal stabilities.3)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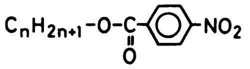
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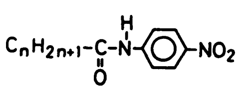
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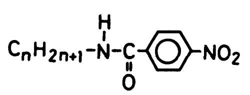
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Experimental

Materials. Homologous series of 4-nitrophenyl alkanoates and *N*-(4-nitrophenyl)alkanamides were obtained by the acylation of 4-nitrophenol and 4-nitroaniline respectively. The products will be referred to as *n*COO, NO_2, and *n*CONH, NO_2 on the basis of the substituents where *n* is the number of carbon atoms in the alkyl group. The alkyl 4-nitrobenzoates and *N*-alkyl-4-nitrobenzamides were prepared by the reaction of 4-nitrobenzoyl chloride on alcohols and alkylamines respectively. They will be abbreviated as *n*OCO, NO_2, and *n*NHCO, NO_2. These disubstituted benzenes were purified by recrystallization, distillation under reduced pressure and/or column chromatography. Hereafter, *N*-(4-propoxybenzylidene)-4-hexylaniline will be denoted by (3O, 6) designating the alkoxyl and alkyl carbon numbers for the substituents.

Measurements. The calorimetric measurements and the identification of the mesophases were made as reported in our previous paper.2)

Results and Discussion

4-Nitrophenyl Alkanoates (nCOO, NO_2). The homologous members from decanoate to tetradecanoate (n=9—13) were examined. Upon mixing with (3O, 6), they produce stable smectic A phases as exemplified by the phase diagrams of the binary systems with each of 10COO, NO_2, and 12COO, NO_2 (see Figs. 1a and b). The open and shaded circles indicate the transitions recorded during the processes of heating and cooling respectively.

The phase diagrams obtained with 9COO, NO_2, and 11COO, NO_2 resemble that given in Fig. 1a; namely, the coexistence of the isotropic and smectic phases occurs over a range of temperature. In contrast, no indication of the two-phase liquid system is found with 12COO, NO_2 or with 13COO, NO_2. The maximum temperature of the smectic A-isotropic transition point curve is not much affected by the alkyl chain length throughout the studied members, that is, 47—48 °C (see Curve a in Fig. 2). It is higher by about 10 °C than the melting points of the first two homologous members, is nearly the same as those of the next two, and is lower by about 10 °C than that of the last. The extrapolation of the transition point curve to 0 mol% of (3O, 6) yields more reliable latent transition temperature when the alkyl chain is shorter as the curve is observable over a wider composition range. Such a tendency is more or less shared by most of the homologous series studied in this paper. The estimated temperature varies from −25

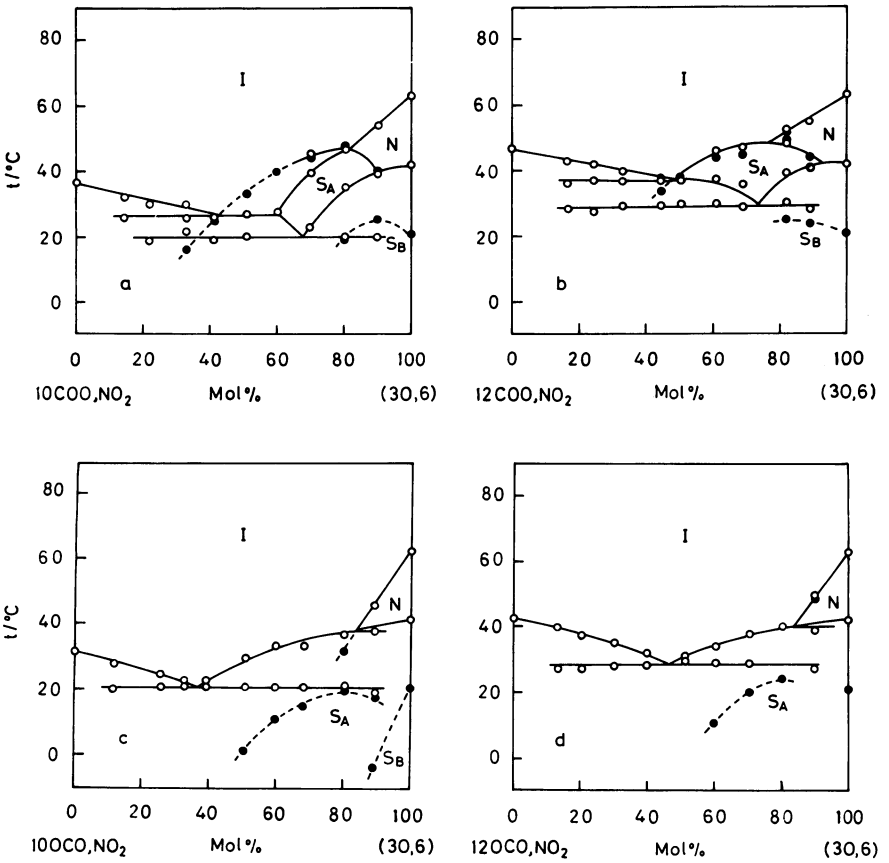

Fig. 1. Phase diagrams of (a) 10COO, NO_2-(3O, 6), (b) 12COO, NO_2-(3O, 6), (c) 10OCO, NO_2-(3O, 6), and (d) 12OCO, NO_2-(3O, 6) systems. The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

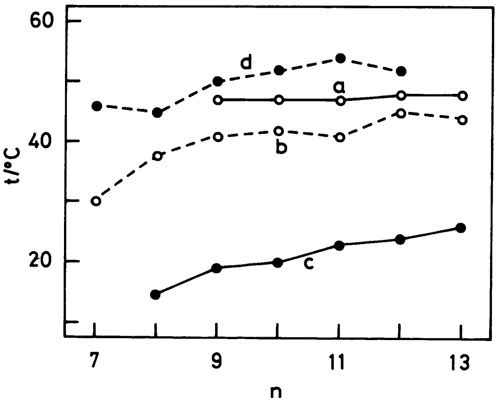

Fig. 2. Plots of the maximum temperatures of the induced smectic A phases against the length of the alkyl chain, *n*, for (a) *n*COO, NO_2-(3O, 6), (b) *n*COO, CN-(3O, 6), (c) *n*OCO, NO_2-(3O, 6), and (d) *n*CONH, NO_2-(3O, 6) systems.

to 10 °C. The values tend to be higher with the higher homologs. They are located below the melting points of *n*COO, NO_2 by 50 to 70 °C. If the isotropic melts were supercooled to such a large extent the appearance of smectic A phases of *n*COO, NO_2 could be achieved; therefore, these 4-nitrophenyl alkanoates may be considered as potential smectogens.

The monotropic smectic B phase of (3O, 6) is also stabilized by the addition of these benzene derivatives. The transition point curves are markedly convex upwards when *n* is even but not so when *n* is odd.

In order to supplement the above results, seven systems consisting of *n*COO, CN, and (3O, 6) were studied. The maximum temperatures of the smectic A-isotropic transition point curves are shown by Curve b in Fig. 2. They are slightly lower than those of the corresponding *n*COO, NO_2-(3O, 6) systems. The extrapolation of the transition point curve to 0 mol% of (3O, 6) also seems to yield lower temperatures; *e.g.*, −30 °C for 10COO, CN *vs.* −25 °C for 10COO, NO_2. As 4-cyanophenyl alkanoates have higher melting points than the 4-nitrophenyl compounds, the induced smectic A phases are metastable except for the cases n=9, 11, and 12. The stabilization of the smectic B phase of (3O, 6) observed with the 4-cyanophenyl esters is more remarkable than that with the 4-nitrophenyl esters. The observation made for the induced smectic A phase is consistent with the order of smectic terminal group efficiency for nitro and cyano groups given by Gray[3] but that made for the monotropic smectic B phase is in the reversed order.

Alkyl 4-Nitrobenzoates (nOCO, NO_2). The homologous series examined extends from the octyl to the tridecyl ester (n=8—13). When these 4-nitrobenzoates are added to (3O, 6), smectic A phases are induced in all the systems. However, they are entirely metastable, the maximum of the isotropic-smectic A transition point curve lying in the range from 15 to 26 °C. Contrary to the alkanoates, the temperature raises with the increase of the alkyl chain length exhibiting a small but definite alternation (see Curve c in Fig. 2). The temperatures observed with 8OCO, NO_2, 9OCO, NO_2, and 11OCO, NO_2 are located above the eutectic points. For the sake of comparison with the effects of the isomeric compounds, the phase diagrams of the decyl and dodecyl ester-(3O, 6) systems are presented in Figs. 1c and d. These esters presumably have the potential to exhibit smectic A phases at temperatures as low as −65 to −40 °C. As is shown in Fig. 1c, the monotropic smectic B phase of the Schiff base shows a drastic depression on addition of 10OCO, NO_2. Furthermore, it must be noted that the slope of the nematic-isotropic transition point curve is much steeper than that observed with the 4-nitrophenyl alkanoates. Thus, the abillity to exhibit mesophases of the 4-nitrobenzoates is undoubtedly inferior to that of the above-mentioned isomerides.

It is worthwhile to note the alternation of the melting points of *n*COO, NO_2, and *n*OCO, NO_2. The former compounds melt at relatively higher temperatures when *n* is odd and the latter exhibit the opposite variation. Therefore, the melting point of *n*COO, NO_2 lies by 15 to 20 °C above that of the corresponding *n*OCO, NO_2 when *n* is odd. The difference is as small as 5 °C when *n* is even.

N-(4-Nitrophenyl)alkanamides (nCONH, NO_2). The replacement of the -O- group in the 4-nitrophenyl alkanoate with an -NH- group brings about a rise in the melting point by 30 to 40 °C depending upon *n*. When $n=9$ or more, the induced smectic A phase is enantiotropic in a certain range of composition and temperature in the binary system with (3O, 6). Even though the maximum temperatures of the transition point curves are in the range from 50 to 54 °C for these systems (see Curve d in Fig. 2), the smectic A phases are observable in the smaller ranges than those found for the *n*COO, NO_2-(3O, 6) systems. For example, the phase diagrams given in Figs. 3a and b may be compared with those in Figs. 1a and b. The observed smectic A-isotropic transition point curves are not long enough to estimate the temperatures for potential smectic A phases but suggest that they are not very different from those estimated for the 4-nitrophenyl alkanoates. As is illustrated in Fig. 3a, the monotropic smectic B phase of (3O, 6) is stabilized by the addition of 10CONH, NO_2.

In order to compare the role of a nitro group and a cyano group in the anilides on the smectogenic behavior, the system comprising 11CONH, CN, and (3O, 6) was included to the present work. The diagram is

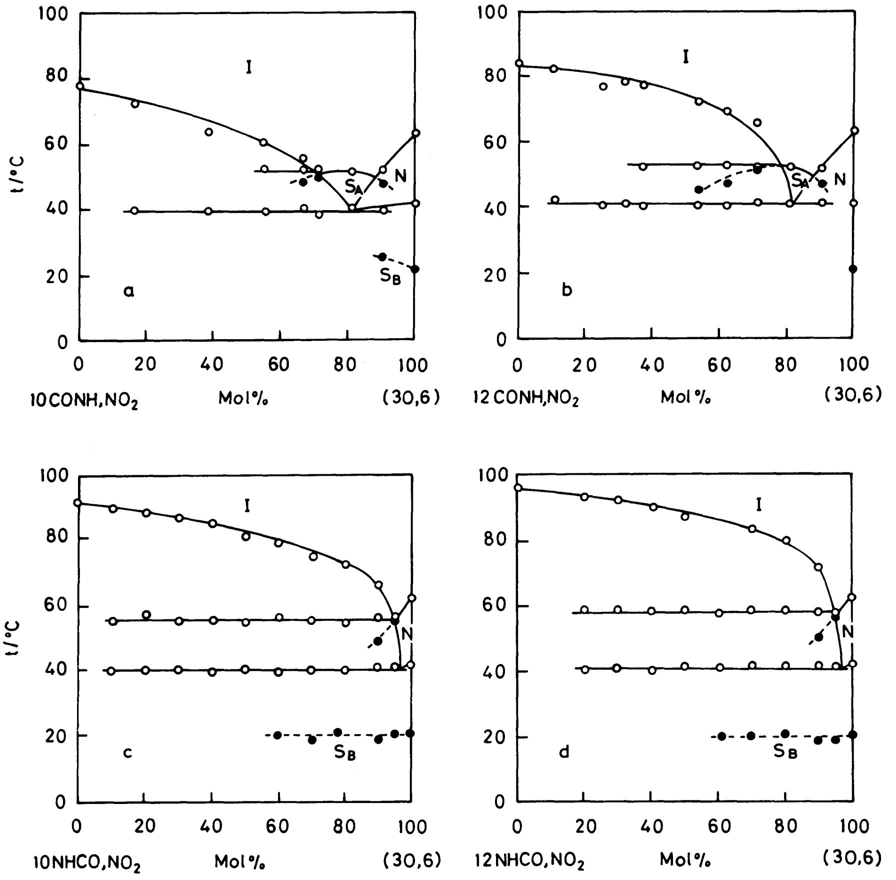

Fig. 3. Phase diagrams of (a) 10CONH, NO_2-(3O, 6), (b) 12CONH, NO_2-(3O, 6), (c) 10NHCO, NO_2-(3O, 6), and (d) 12NHCO, NO_2-(3O, 6) systems. As to the open and shaded circles, see the caption of Fig. 1.

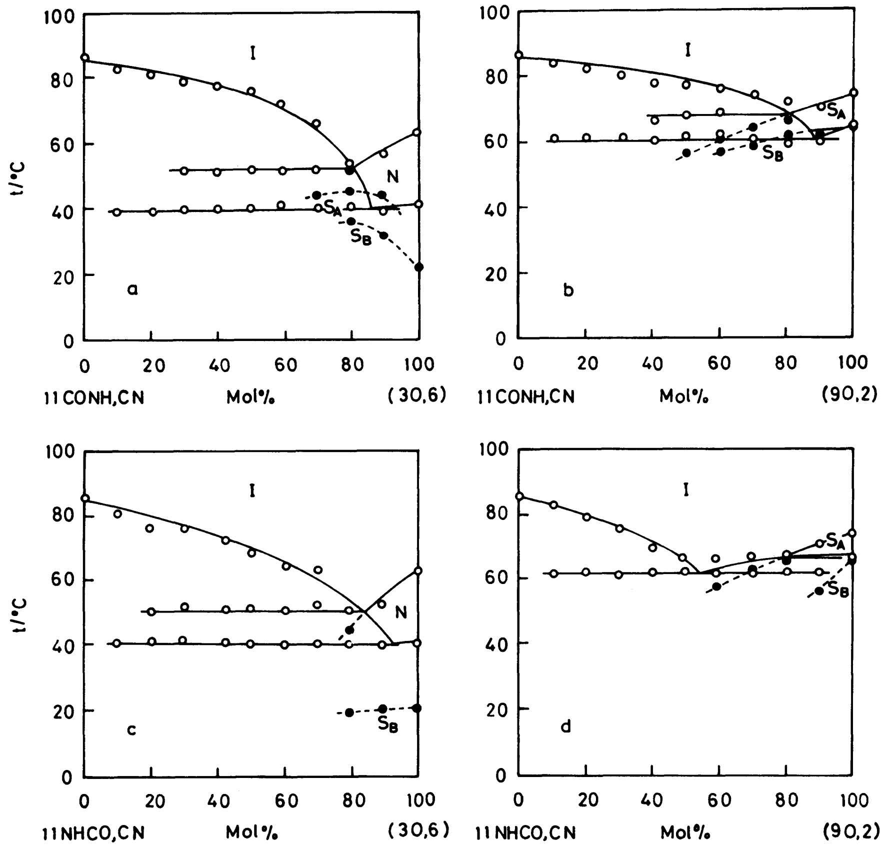

Fig. 4. Phase diagrams of (a) 11CONH, CN-(3O, 6), (b) 11CONH, CN-(9O, 2), (c) 11NHCO, CN-(3O, 6), and (d) 11NHCO, CN-(9O, 2) systems. As to the open and shaded circles, see the caption of Fig. 1.

given in Fig. 4a. A smectic A phase is induced but it is monotropic, the maximum temperature being 46 °C. This observation is in good accord with the tendency found by comparison between *n*COO, NO_2 and *n*COO, CN and also 4-alkoxynitrobenzenes and 4-alkoxybenzonitriles reported in a previous paper.[2] Moreover, it must be noted that the stabilization of the metastable smectic B phase by the cyanoanilide is much greater than that by the corresponding nitroanilide. The maximum temperature achieved by the former compound is 36 °C and that by the latter is 24 °C. This might imply that the 4-cyanoanilide has a potential smectic B phase at a relatively high temperature. This postulate is strongly supported by the phase diagram shown in Fig. 4b, where (3O, 6) is replaced by *N*-(4-nonyloxybenzylidene)-4-ethylaniline, (9O, 2), which exhibits stable smectic A and B phases. The diagram suggests that the latent smectic B phase of 11CONH, CN is located around 30 °C. This temperature is probably higher than that of the latent smectic A phase.

N-Alkyl-4-nitrobenzamides (nNHCO, NO_2). The melting points of the three compounds in this series (*n*=8, 10, and 12) are higher than those of the above isomerides as is seen from Figs. 3c and d. The effect of the change in molecular structure on the liquid crystal behavior is so remarkable that no smectic A phase is found in these mixtures. The monotropic smectic B phase is observable over a composition range as wide as 40 mol%. As the transition point curves are essentially horizontal, these 4-nitrobenzamides should have transition temperatures to latent smectic B phases between 10 and 20 °C. It may be noted that the nematic phase of the Schiff base is rapidly depressed by the presence of *n*NHCO, NO_2.

As is shown in Fig. 4c, the behavior of *N*-undecyl-4-cyanobenzamide is similar to those of the 4-nitrobenzamides described above except for the less drastic depression of the nematic phase and the limited observation of the nematic-smectic B transition point curve. The isotropic or nematic-smectic B transition point curves in Figs. 3c, 3d, and 4c are almost straight; therefore, the reason why no smectic A phase is induced by mixing with (3O, 6) may be ascribed to the absence of the thermal stability enhancement. The phase diagram prepared with (9O, 2) instead of (3O, 6) clearly demonstrates that the 4-cyanobenzamide has a transition point to a latent smectic A phase closely located to that to a latent smectic B phase (compare Fig. 4d with 4c). The observed short smectic A-smectic B transition point curve is concave upwards.

N-(4-Nitrobenzylidene)alkylamines (nN=CH, NO_2). Finally, we studied the effects of the addition of *N*-(4-nitrobenzylidene)alkylamines (*n*=9—13) as a series of the compounds involving a double bond linkage in the substituent. All the homologous members can induce smectic A phases exhibiting maximum temperatures from 40 to 41 °C. As is shown in Fig. 5, the com-

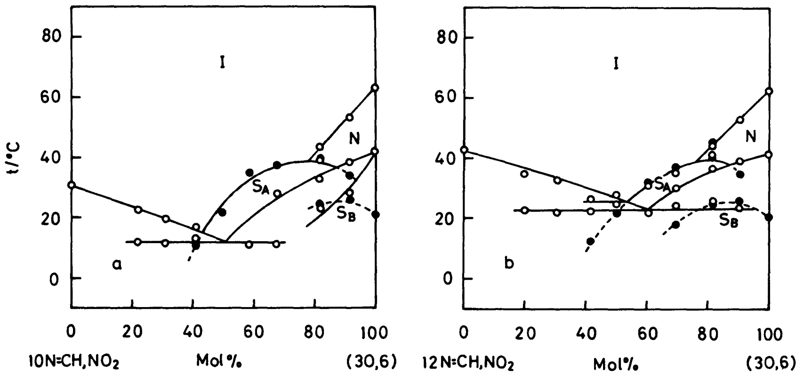

Fig. 5. Phase diagrams of (a) 10N=CH, NO_2–(3O, 6) and (b) 12N=CH, NO_2–(3O, 6) systems. As to the open and shaded circles, see the caption of Fig. 1.

position range of the stable smectic A phase is fairly wide. The monotropic smectic B phase is appreciably stabilized. However, the latent smectic phases of these compounds are probably located at temperatures as low as −50 to −40 °C.

The above results emphasize that the particularly high transition temperatures to latent smectic phases can be achieved with the benzamides and anilides. As the suitability of the terminal substituent for liquid crystal formation may be at its most significant in simple systems we decided to extend our examination of thermal properties to a number of benzene derivatives carrying two or three of these terminal groups; namely, $C_nH_{2n+1}NHCO$ and $C_nH_{2n+1}CONH$. Some novel mesomorphic compounds have been discovered by this approach. Their properties will be the subject of the forthcoming papers.

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