3230 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 3230—3234 (1983) [Vol. 56, No. 11

Liquid Crystal Formation in Binary Systems. VIII.[1] Induction of Smectic Phases by the Addition of 4-Alkoxynitrobenzene or 4-Alkoxybenzonitrile to *N*-(4-Propoxybenzylidene)-4-hexylaniline

Eiji Chino and Yoshio Matsunaga*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received April 25, 1983)

When 4-alkoxynitrobenzenes are mixed with *N*-(4-propoxybenzylidene)-4-hexylaniline, smectic A phases which are not found with the component compounds, are produced. The liquid crystals are stable if the number of carbon atoms in the alkoxyl group is eight or more, the maximum temperature being 49 °C with dodecyloxyl group, but they are entirely metastable if the number of carbon atoms is six or less. The extrapolation of the partly-observed smectic A-isotropic transition point curve indicates that 4-(dodecyloxy)-nitrobenzene has a latent transition point at about −25 °C and that all the examined *p*-disubstituted benzenes are potentially smectogenic. Smectic A phases are also induced by the addition of 4-alkoxybenzonitriles to the above Schiff base. The transition to the induced mesophase is enantiotropic when the alkoxyl group is decyloxyl or dodecyloxyl. The replacement of the propoxyl group in the Schiff base with an ethoxyl group makes the induced smectic A phases thermally less stable. The change is drastic when the alkoxyl group in the *p*-disubstituted benzene is hexyloxyl or shorter.

We reported in earlier papers,[2–5] that nematic and smectic liquid crystals can be induced by mixing a nonmesogenic electron donor and a nonmesogenic electron acceptor of the type 4-X-C_6H_4-Z-C_6H_4-Y-4. The appearance of mesophases in these binary systems was attributed to the thermal stabilization of the potential mesophases of the component compounds by the charge-transfer interaction introduced by mixing. It is generally believed that monomeric *p*-disubstituted benzenes are not mesogenic. However, the possibility that they are potentially mesogenic cannot be excluded. The observation of a smectic phase in the 4,4′-bis(hexyloxy)azoxybenzene–4-(hexyloxy)nitrobenzene system covering the range as wide as 70 mol% reported by Schroeder and Schroeder[6] may be indicative of the potentially smectogenic behavior of 4-alkoxynitrobenzenes. We report here that the potential liquid crystal behavior of 4-alkoxynitrobenzenes and 4-alkoxybenzonitriles are readily demonstrable by the induction of new mesophases in the binary systems. For this purpose, we employed *N*-(4-propoxybenzylidene)-4-hexylaniline, which gives a nematic phase stable between 42 and 63 °C and a metastable smectic B phase below 21 °C, and its related compounds as the other components.[7]

Experimental

Materials. *N*-(4-Propoxybenzylidene)-4-hexylaniline, hereafter abbreviated as (3O, 6) designating the alkoxyl and alkyl carbon numbers for the substituents, was prepared by a condensation reaction between 4-propoxybenzaldehyde and 4-hexylaniline. The Schiff bases (2O, 6), (3O, 4), and (9O, 3) were similarly prepared. A homologous series of 4-alkoxynitrobenzenes was obtained by the alkylation of 4-nitrophenol following the procedure reported by Gray and Jones.[8] The compounds will be referred to as *n*O, NO_2 on the basis of the substituents where *n* is the number of carbon atoms in the alkoxyl group. By replacing 4-nitrophenol with 4-hydroxybenzonitrile, the 4-alkoxybenzonitriles, *n*O, CN, could be obtained.

Measurements. The calorimetric curves were recorded on a Rigaku Thermoflex differential scanning calorimeter equipped with a low-temperature unit. The heating and cooling rates in this work were 3 °C $\min^{-1}$. The mesophases were identified by examining the texture with the aid of a polarizing microscope and by studying the continuous miscibility with the reference mesophases given by (9O, 3).

Results and Discussion

4-Alkoxynitrobenzenes, n*O,* NO_2. The even carbon number homologs up to $n=12$ were examined. Induced smectic A phases were observed in all the mixtures with (3O, 6). The phase diagrams of the binary systems containing each of 2O, NO_2, 6O, NO_2, and 10O, NO_2 are shown in Fig. 1. The open and shaded circles indicate the transitions recorded during the processes of heating and cooling respectively.

In Fig. 1a, the smectic phase found in the composition range from 61 to 87 mol% of (3O, 6) shows a texture different from the smectic B phase of (3O, 6); therefore, the induction of a smectic A phase by mixing is highly probable. This conclusion is confirmed by a study of the phase diagram of the pseudo-binary system consisting of the 81 mol% mixture (shown by an arrow in Fig. 1a) and (9O, 3). The latter compound gives a smectic A phase stable between 71.5 and 84 °C and also a smectic B phase stable between 48 and 71.5 °C.[9] The results presented in Fig. 1b firmly establish that the monotropic transition observed at 24 °C in the 81 mol% mixture is from a supercooled nematic phase to a smectic A phase. The smectic B phase exhibited by (3O, 6) appears to be drastically destabilized by the addition of 2O, NO_2.

The smectic A phase induced in the 4O, NO_2-(3O, 6) system covers the composition range from 50 to 82 mol% of (3O, 6), the maximum being located at 29 °C and near 80 mol%. This temperature is higher by 12 °C than that of the eutectic point. The transition temperature of (3O, 6) from the nematic phase to the smectic B phase is not much lowered by the addition of 4O, NO_2. At 89 mol% of (3O, 6) the supercooled nematic phase is transformed into the smectic B phase at 16 °C.

The compound 6O, NO_2 melts at 26 °C, the lowest among the melting points of *n*O, NO_2 examined. The

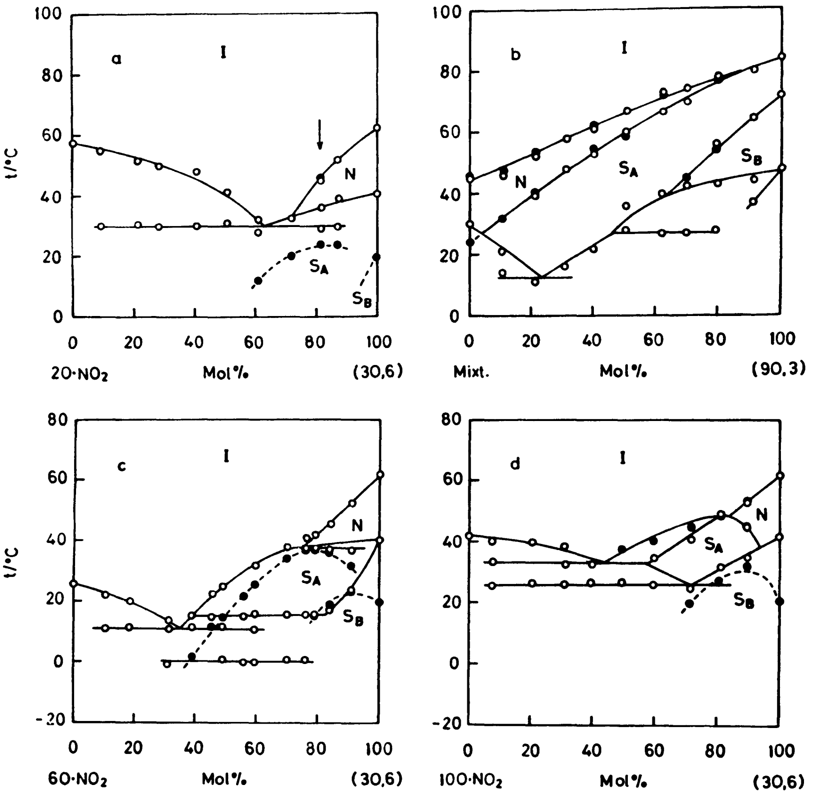

Fig. Phase diagrams of (a) 2O, NO_2-(3O, 6), (b) its 81 mol% mixture-(9O, 3), (c) 6O, NO_2-(3O, 6), and (d) 10O, NO_2-(3O, 6) systems. The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

system with (3O, 6) exhibits a smectic A phase in the range from 39 to 91 mol% of (3O, 6). Around 78 mol%, the transition point curve reaches its maximum of 38 °C. The stabilization of the smectic B phase by 6O, NO_2 is also noted in this binary system. The monotropic transition at 91 mol% is found at 24 °C (see Fig. 1c).

The smectic A liquid crystals in the systems with each of 8O, NO_2, 10O, NO_2, and 12O, NO_2 can exist as stable phases. As the three phase diagrams are of the same type, they are exemplified by that of the 10O, NO_2-(3O, 6) system (see Fig. 1d). The transition between the isotropic liquid and the smectic A phase does not occur at a fixed temperature, that is, there is a range over which the isotropic liquid and the smectic A phase coexist. The smectic A-smectic B transition point curve is markedly convex upwards. As summarized in Fig. 2, the maximum smectic A-isotropic transition temperature against chain-length plot (see Curve a) shows a continued rise up to $n=10$ and then levels out. This change is of a common type for relationships known for homologous series of mesogenic compounds.[10]

The nematic-isotropic transition point curve is convex upwards in Fig. 1a, while the corresponding ones in the other systems are essentially straight (see Figs. 1c and 1d). Nevertheless, the latent transition point estimated for nO, NO_2 by the extrapolation to 0 mol% of (3O, 6) cannot be accurate since the observed fragment is not long enough. To a rough approximation, it is about −50 °C when $n=4$ and about −20 °C when $n=12$. If one similarly extrapolates plot of the smectic A-isotropic transition points against the composition, the latent smectic A-isotropic or -nematic transition point of nO, NO_2 may be estimated. Unfortunately, the plot is far from linear and the available points are limited to a high mol% range. By guess, one might infer about −60 °C for 6O, NO_2 and between −30 to −20 °C for 10O, NO_2 and 12O, NO_2: therefore, these temperatures are for transitions from smectic A phase to nematic phase.

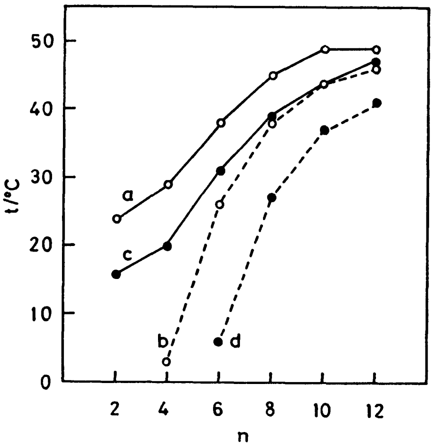

Fig. 2. Plots of the maximum temperatures of the induced smectic A phases against the length of the alkyl chain, n, for (a) nO, NO_2-(3O, 6) (b) nO, NO_2-(2O, 6), (c) nO, CN-(3O, 6), and (d) nO, CN-(2O, 6) systems.

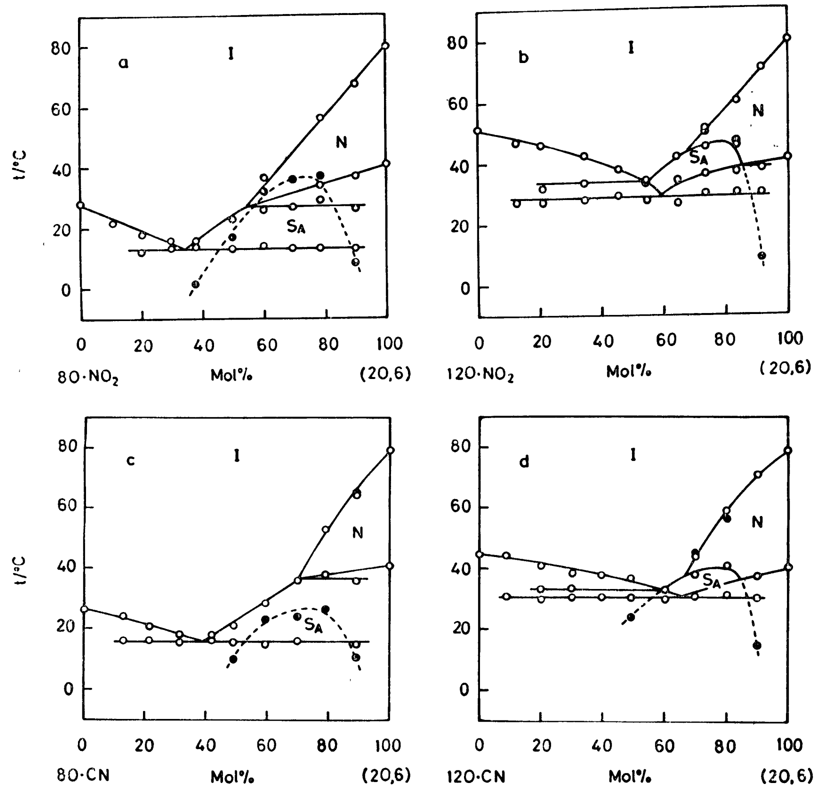

Fig. 3. Phase diagrams of (a) 8O, NO_2-(2O, 6), (b) 12O, NO_2-(2O, 6), (c) 8O, CN-(2O, 6), and (d) 12O, CN-(2O, 6) systems. As to the open and shaded circles, see the caption of Fig. 1.

The potential liquid crystal behavior of nO, NO_2 is supported also by the work on the systems with (2O, 6). The compound (2O, 6) is known to be nematogenic.[7] The mesophase is stable between 40.5 and 79.5 °C. Except for 2O, NO_2, smectic A phases are induced in all the combinations. The maximum smectic A-isotropic transition temperatures are given in Fig. 2 (see Curve b). Because of the steep rise between $n=4$ and 6 and that between $n=6$ and 8, Curve b lies far below Curve a at $n=2$ but the two approach to each other at $n=12$. Only when $n=10$ and 12, does the induced mesophase have a region of stable existence. The phase diagrams of the systems with each of 8O, NO_2 and 12O, NO_2 are presented in Fig. 3. The latent smectic A-nematic transition point of 8O, NO_2 may be estimated to be about −50 °C. As the smectic A phase induced in the 4O, NO_2-(2O, 6) system covers only the range from 70 to 80 mol% of (2O, 6), we studied further the system with (3O, 4). This mesogen exhibits a nematic phase stable between 41 and 58 °C and also a smectic B phase appearing from the supercooled nematic phase at 23.5 °C.[7] In the mixture with 4O, NO_2, the smectic A phase can be seen in the range from 50 to 90 mol% of (3O, 4), the maximum lying at 20 °C and about 75 mol%. Although the maximum temperature is lowered by 9 °C compared with that found in the corresponding system with (3O,6), there is no significant difference between the extent of the observable composition range. The latent smectic A phase of 4O, NO_2 may be located at a temperature as low as −70 °C. When 2O, NO_2 is mixed with (3O, 4), a smectic A phase is induced in the range from 70 to 88 mol%. In general, the stabilization of the smectic A phase by mixing with N-(4-alkoxybenzylidene)-4-alkylaniline appears to decrease in this order: (3O, 6)>(3O, 4)>(2O, 6).

4-Alkoxybenzonitriles, nO, CN. As exemplified by the binary systems consisting of (3O, 6) and each of 2O, CN, 6O, CN, and 10O, CN, these p-disubstituted benzenes are also potentially smectogenic. In Fig. 4a, the appearance of a new mesophase is indicated by the two monotropic transitions at 91 mol% of (3O, 6). The phase diagram of the pseudo-binary system, the 81 mol% mixture-(9O, 3), establishes that the newly-appeared phase is of the smectic A type (see Fig. 4b). The temperature range where this mesophase is observable is lower by 8 to 10 °C than that found in the 2O, NO_2-(3O, 6) system.

By mixing with (3O, 6), the compound 4O, CN produces a metastable smectic A phase covering the range from 40 to 90 mol%. The maximum temperature lies at 20 °C near 80 mol%. The transition to the smectic B phase located at 11 °C and 77 mol% may imply that the latent smectic B phase is thermally more stable than the smectic A phase when extrapolated to pure 4O, CN. It may be added that 4O, CN has the lowest melting point, 18.5 °C, among the 4-alkoxybenzonitriles employed in this work.

The phase diagram for the 6O, CN-(3O, 6) system is shown in Fig. 4c. In this system, the smectic A-smectic B transition point curve exhibits a maximum at about 90 mol% and 27 °C but the observation of the smectic B phase is limited to the range above 80 mol%.

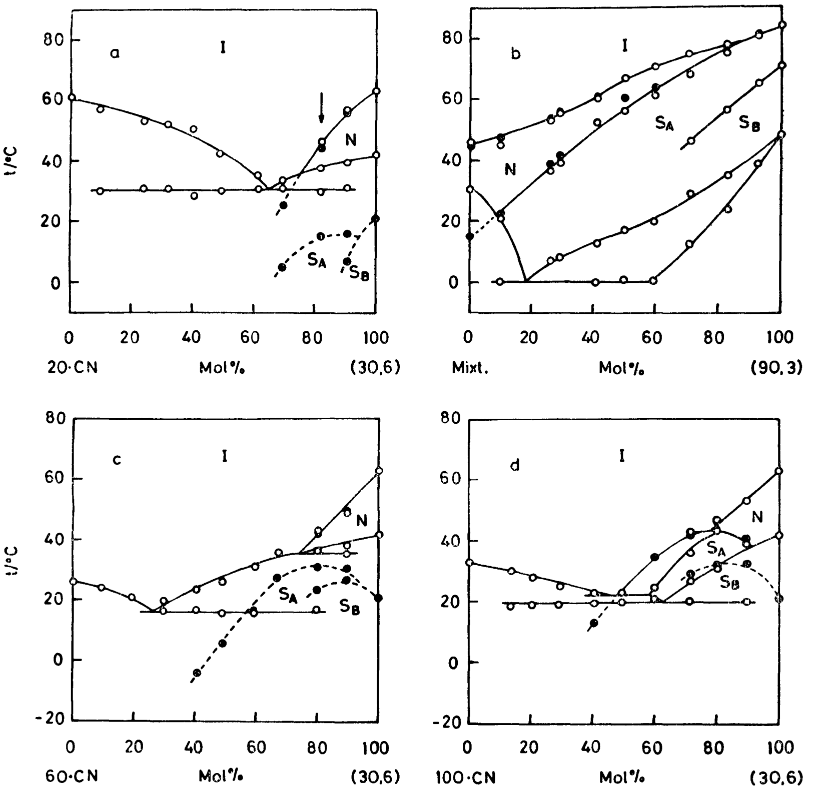

Fig. 4. Phase diagrams of (a) 2O, CN-(3O, 6), (b) its 81 mol% mixture-(9O, 3), (c) 6O, CN-(3O, 6), and (d) 10O, CN-(3O, 6) systems. As to the open and shaded circles, see the caption of Fig. 1.

With 8O, CN the stabilization of the smectic phases is appreciable. The maximum of the monotropic isotropic-smectic A transition point curve is at 39 °C and almost coincides with the horizontal line extending from the intersection between the isotropic-nematic transition point curve and the freezing point curve of (3O, 6). The smectic B phase is observable above 70 mol% with the maximum at 29 °C and about 85 mol%.

As is shown in Fig. 4d, a stable smectic A phase is found in the 10O, CN-(3O, 6) system. The compound 12O, CN also produces a diagram of the same type when it is mixed with (3O, 6). Although the diagram given in Fig. 4d bears a close similarity to that in Fig. 1d, it must be noted that the stabilization of smectic B phase with benzonitrile is more pronounced than that with nitrobenzene.

In Fig. 2, Curve c gives the plot of the maximum temperature of the smectic A-isotropic transition point curve against *n*. The temperature is 16 °C at $n=2$ and steadily increases to 47 °C at $n=12$.

Smectic A phases could be observed by mixing (2O, 6) with 6O, CN, 8O, CN, 10O, CN, and 12O, CN; however, only with the last benzonitrile the liquid crystal can be stable in a small region (see Figs. 3c and 3d). The maximum transition temperature in the *n*O, CN-(2O, 6) system is shown by Curve d in Fig. 2. The value is 6 °C at $n=6$ and 41 °C at $n=12$. Contrary to the 2O, NO_2-(3O, 4) system, the compound 2O, CN gives no smectic A phase when mixed with (3O, 4); however, the thermal stabilization of the smectic B phase is extensive and is observed to 78 mol% of (3O, 4), the temperature at this composition being 0 °C. When 4O, CN is employed with (3O, 4), a metastable smectic A phase appears in the range from 55 to 80 mol% of (3O, 4). The transition occurs at 16 °C at the upper limit and no maximum is located for this composition.

In conclusion, 4-alkoxynitrobenzenes and 4-alkoxybenzonitriles are potentially smectogenic. This potential liquid crystal behavior is possibly common to a wide range of *p*-disubstituted benzenes. The induction observed in the present systems may be partly attributed to the electron-donor-acceptor interaction as indicated by the pale yellow color developed on mixing and also may be partly due to a dipole-dipole interaction. As described above, the smectic A phases induced are observable mostly above 50 mol% of the Schiff base. This limitation may be ascribed to the relatively low latent transition temperatures of the *p*-disubstituted benzenes. In order to estimate the latent transition temperatures, it seems highly desirable to obtain essentially straight transition point curves in the binary systems with reference mesogens. With such systems, the effects of terminal substituents on liquid crystal behavior may be firmly established because of the simplicity of molecular structure. Attempts along this line are now in progress.

The present work was partly supported by a Grant-in-Aid for Scientific Research No. 543001 from the Ministry of Education, Science and Culture.

References

1) Part VII, M. Fukui and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **55**, 3707 (1982).

2) K. Araya and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **53**, 3079 (1980).

3) K. Araya and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **54**, 2430 (1981).

4) K. Araya and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **55**, 1710 (1982).

5) K. Araya, N. Homura, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **55**, 1953 (1982).

6) J. P. Schroeder and D. C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).

7) G. W. Smith, Z. G. Gardlund, and R. J. Curtis, *Mol. Cryst. Liq. Cryst.*, **19**, 327 (1973).

8) G. W. Gray and B. Jones, *J. Chem. Soc.*, **1954**, 1467.

9) C. Weygand and R. Gabler, *Naturwissenschaften*, **27**, 28 (1939). These authors have noted the appearance of two smectic phases. Our identification was made on the basis of the texture by thermal microscopy.

10) G. W. Gray and P. A. Winsor, "Liquid Crystals and Plastic Crystals," Ellis Horwood, Chichester (1974), Vol. 1, pp. 116—125.