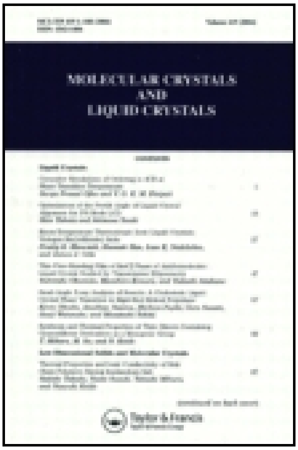

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A Mixture-Induced Nematic Phase

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A Mixture-Induced Nematic Phase†

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We report on an unusual variant in liquid crystal polymorphism where a nematic phase is created from a binary mixture of two compounds, neither one of which in its pure state exhibits the nematic phase. One of the compounds in its pure form exhibits only a smectic A phase which is stabilized by an extended alkyl chain. The other compound in its pure form exhibits a smectic A and a smectic B phase which are stabilized by a terminally substituted halogen. When mixed, a wide-temperature-range nematic is created. This induced nematic is studied by x-rays, differential scanning calorimetry, and by varying the terminal halogen.

INTRODUCTION

Mixture-induced nematic phases have received relatively little attention in the literature, in contrast to mixture-induced smectic phases.[1,2] A number of examples are reported in the literature where a nematic phase was observed in a phase diagram from a binary mixture of two compounds which in their pure form showed no nematic phase,[3–8] but no explanations appear to have been given of why such a phenomenon should occur.

In binary mixtures of 2-fluorenylmethylidene-4′-*n*-dodecylaniline (FC12A) with 4-*n*-butoxybenzylidene-4′-chloroaniline (4O.Cl) we have

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discovered an induced nematic phase over a rather large region in concentration and temperature. One of the compounds, FC12A, in its pure form, exhibits only a smectic A phase which our x-ray studies show it to be of type A_d, with overlapping molecules in a bilayer structure. The other compound, 4O.Cl, in its pure form, also exhibits only smectic phases which our x-ray studies show to be the ordinary smectic A phase (A_1) and, at lower temperatures, the smectic B phase. The layer spacing in the S_A phase is consistent with the molecular length which is considerably shorter than that of FC12A.

In this paper we focus on the induced nematic phase of these materials by examining binary mixtures with other halogen-containing compounds of the 4O.X variety where X = F, Cl, Br and I. The mixtures, as well as some of the pure materials, are well characterized by x-ray diffraction, differential scanning calorimetry and the polarizing microscope.

MATERIALS

The compounds used in this study are shown in Table I. All of these compounds were synthesized by reacting equimolar quantities of the appropriate aldehyde and aniline in absolute ethanol, with molecular sieves (Linde No. 4A) as a dehydrating agent. The reaction was carried out under reflux overnight. The hot solution was filtered to remove the molecular sieves, cooled to 5° and crystals collected. The resulting solid was recrystallized from absolute ethanol to constant clearing point.

TABLE I

Transition temperatures for pure compounds

Compound	C	S_B	S_A	N	I
FC12A[a]	(77.6)[b]	- -	118.0	- -	141.0
4O.F[c]	(36.7)	(58.8)	- -	(60.0)	66.7
4O.Cl[d]	(72.2)	85.1	90.1	- -	91.0
4O.Br	(52.6)	100.0	- -	- -	101.2
4O.I	(46.3)	87.1	- -	- -	113.2

C = liquid crystal to crystal phase transition; S_A = smectic A; S_B = smectic B; N = nematic; I = isotropic liquid.

Temperatures indicate transition temperatures from previous phase to phase indicated.

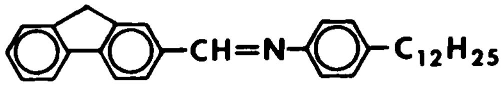
[a] Data from Ref. 9.

[b] Parentheses indicate transition temperature obtained on cooling.

[c] This compound was also reported in Ref. 10, but with a S_A phase rather than a S_B phase.

[d] Also reported in Ref. 10.

A



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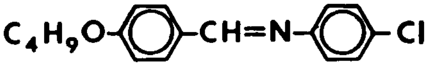

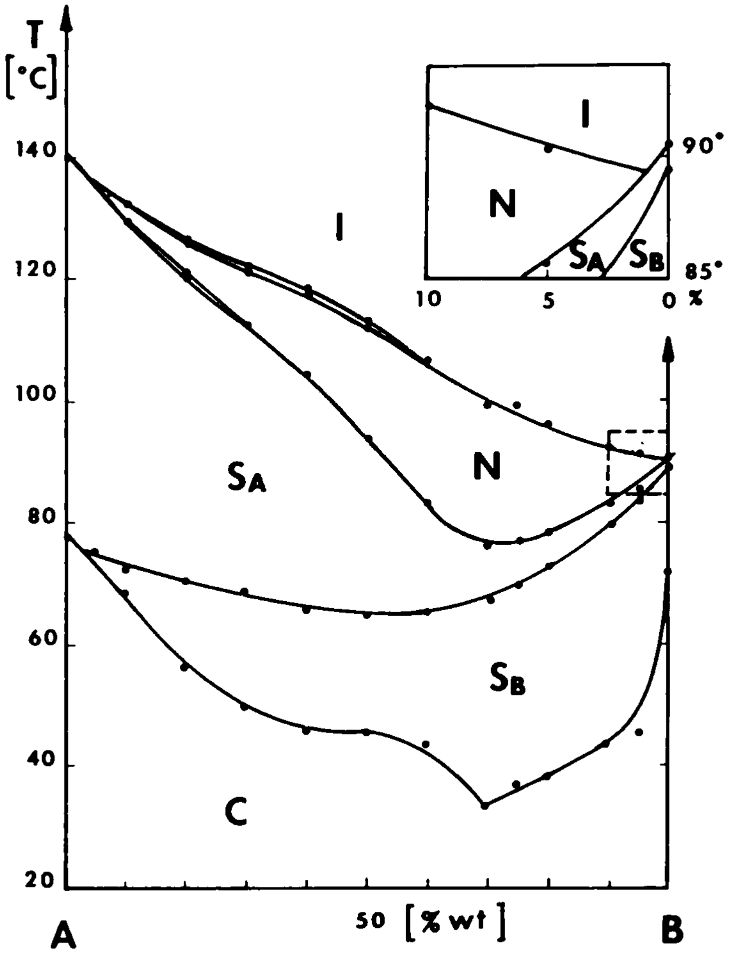

FIGURE 1 Phase diagram for binary mixtures of FC12A and 4O.Cl. The inset shows detail near 100% 4O.Cl (confirmed by the drop contact method).

FIGURE 2 Textures of a contact region with FC12A on the left (smectic A fan texture) and 4O.Cl at the right (in transition from smectic A to smectic B), near 80°C. In the center, one can see the nematic schlieren texture.

EXPERIMENTAL

Binary mixtures were prepared by weight concentration. Phase diagrams were constructed using a hot stage microscope with polarized light for samples of known concentration. In the preparations the substances were placed between a slide and cover glass, without any surface preparation. The textures of N, S_A and S_B phases were not unlike those reported by Demus.[11] Normally, the phase transitions were sharp except in some cases where there were coexisting phases.

The phase diagram for FC12A and 4O.Cl is shown in Figure 1. This system exhibited the largest nematic region with a temperature range of 23° at its widest point and with concentrations nearly spanning the entire range. The details on the extreme right of the phase diagram, expanded in the inset, were confirmed by the drop contact method. With this method one could often see several phases simultaneously in the field of view of the microscope. Figure 2, for example, shows a photograph of the textures taken at 80°C. Upon lowering the temperature the nematic schlieren texture in the center of the field of view vanishes as expected from the diagram of Figure 1.

As seen in Figure 3, a binary mixture of FC12A and 4O.Br is in many respects similar to that of Figure 1 except that the temperature

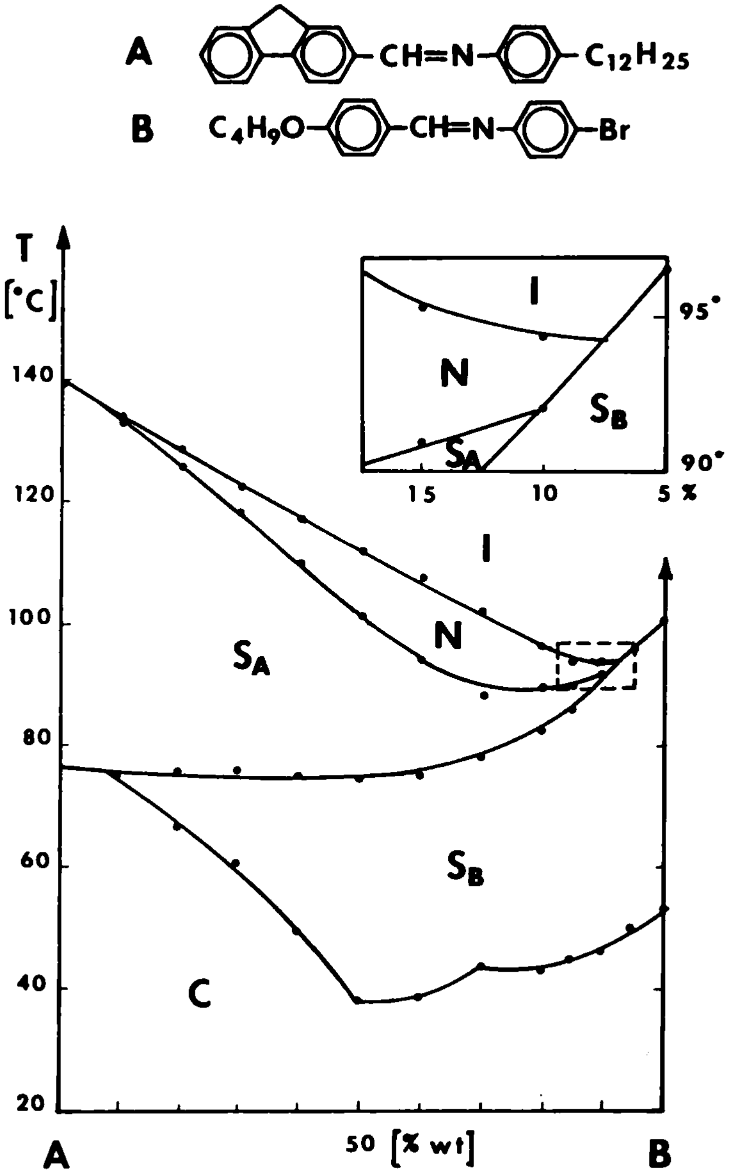

FIGURE 3 Phase diagram for binary mixtures of FC12A and 4O.Br. The inset shows detail near 90% 4O.Br (confirmed by the drop contact method).

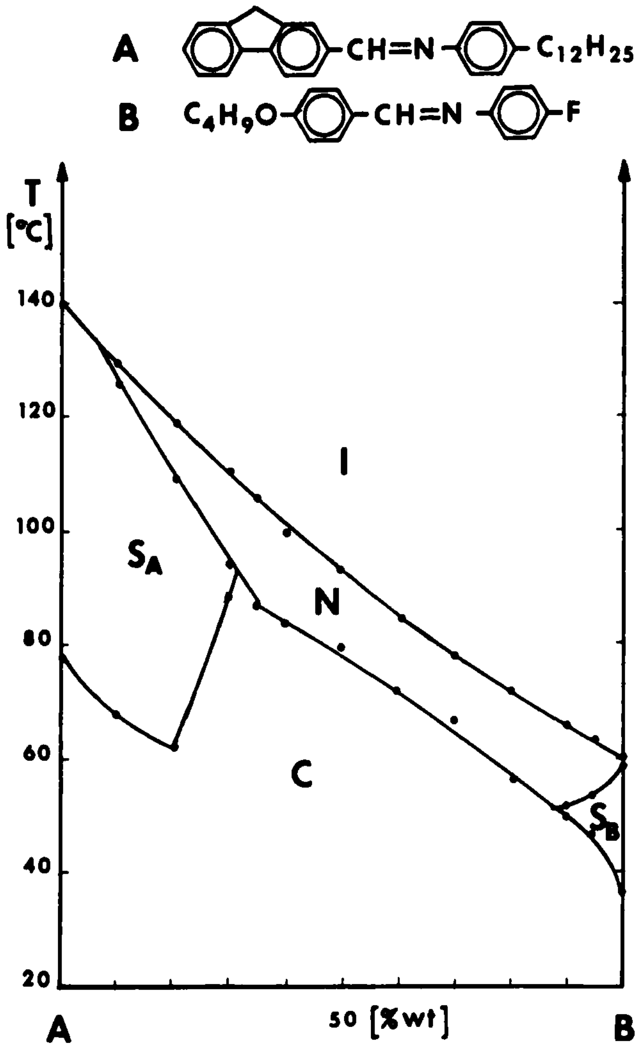

FIGURE 4 Phase diagram for binary mixtures of FC12A and 4O.F.

range of the nematic phase is reduced. It is noted that 4O.Br only contains a S_B phase with an I-S_B phase transition.

Figure 4 shows the phase diagram resulting from mixtures of FC12A and 4O.F. In its pure form 4O.F shows a short range nematic phase. The effect of adding FC12A is to broaden the temperature range of the nematic phase. It does not become as broad, however, as in the

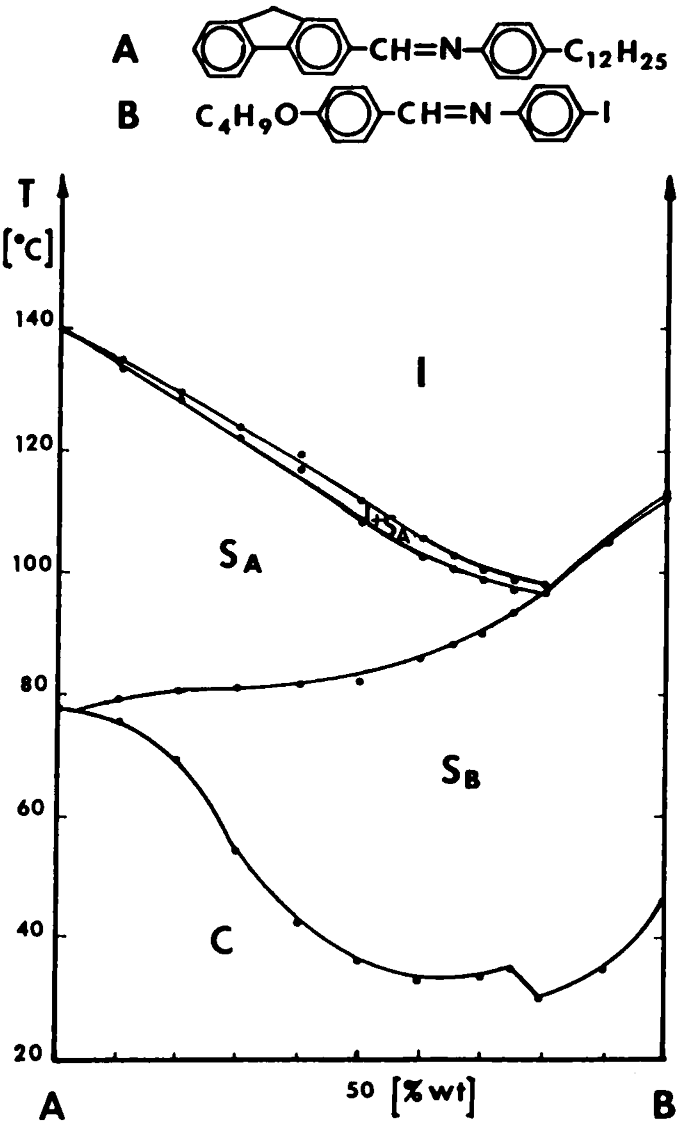

FIGURE 5 Phase diagram for binary mixtures of FC12A and 4O.I.

FC12A/4O.Cl mixture because crystallization intervenes. 4O.F does not possess a S_A phase.

In Figure 5 we show the binary phase diagram of FC12A and 4O.I which shows no induced nematic phase at all. The compound 4O.I shows only a S_B phase in its pure form. The phase diagram of Figure

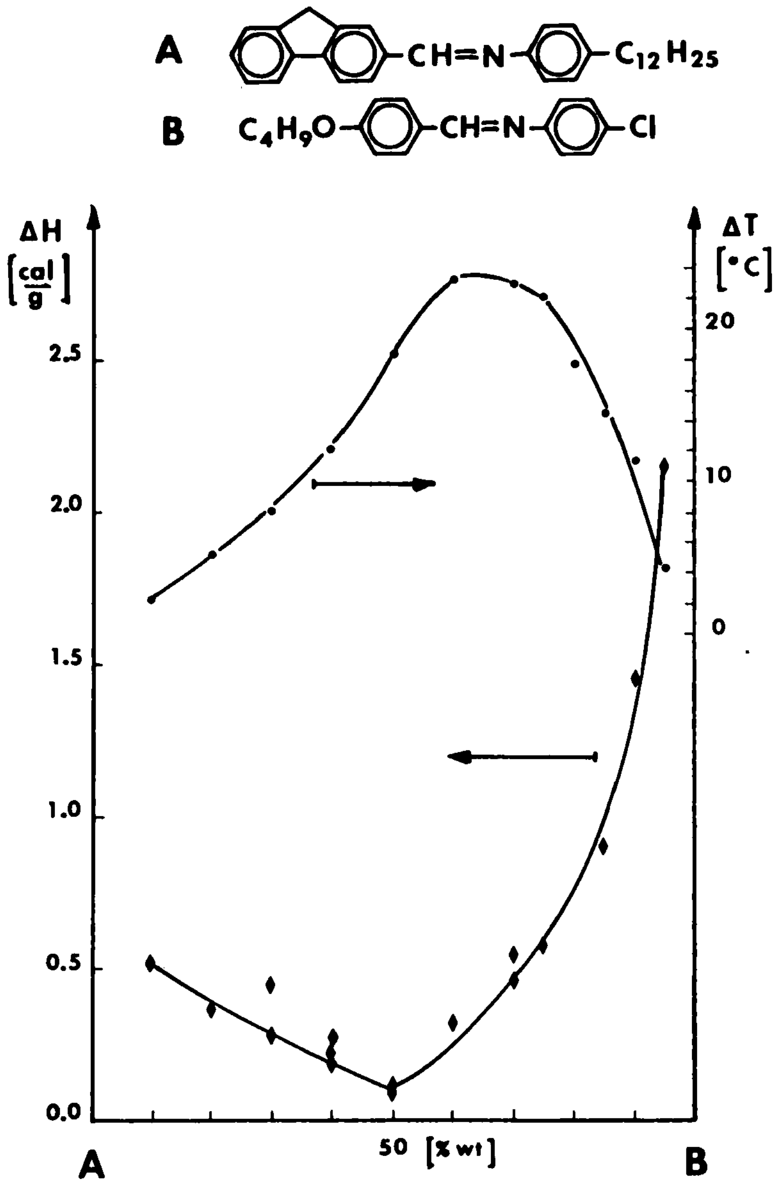

FIGURE 6 Lower curve: ΔH values for nematic to smectic A transition versus concentration for binary mixtures of FC12A and 4O.Cl. Upper curve: range of the nematic phase for binary mixtures of FC12A and 4O.Cl versus concentration.

5 shows a large two-phase I-S_A region, but no nematic phase was evident under the polarizing microscope.

In order to make a more thorough study of the induced nematic we measured the heat of transition for the N-S_A phase transition for mixtures of FC12A and 4O.Cl. Figure 6 shows a plot of the transition enthalpy versus concentration. There appears to be an initial decrease in the heat of transition with increasing 4O.Cl concentration, leading to a broad and not very pronounced minimum. The N-S_A transition is barely visible at 50% of 4O.Cl, indicating that this transition is nearly second order at this concentration. The maximum range of the nematic phase, on the other hand, is near 60% of 4O.Cl.

In a further attempt to elucidate the reasons for the occurrence of the induced nematic, we analyzed the x-ray diffraction patterns of (a) pure 4O.Cl, (b) pure FC12A, and (c) a mixture of 60% 4O.Cl and 40% FC12A. The results were as follows.

a. Pure 4O.Cl. The x-ray diffraction patterns showed all the characteristics of an ordinary smectic A phase, with a layer spacing d_{obs} of 19.4 Å at 90°C (i.e., at 1° below the clearing point). The molecular length l of the molecule (planar all-trans conformation, standard bond lengths and angles) was calculated to be 20.7 Å (at room temperature), which gives[12] l = 20.8 Å at 90°C. With a value of 0.8 for the orientational order parameter S, this gives[12] a value of 19.3 Å for the calculated layer spacing d_{calc}. Thus, the difference between d_{obs} and d_{calc} is only 0.1 Å, which is negligible, confirming that the smectic A phase of 4O.Cl is the ordinary A_1 phase, i.e., an *A* phase with fully overlapping molecules.

b. Pure FC12A. The value of d_{obs} in the smectic A phase at 140°C (i.e., 1° below the clearing point, as in the case of 4O.Cl) was 34.0 Å. For l we obtained 32.4 Å at room temperature, and 32.7 Å at 140°C. Taking again S = 0.8, this gives d_{calc} = 30.3 Å. Thus, $d_{obs} - d_{calc}$ = 3.7 Å. This is a significant difference, indicating that the smectic A phase of FC12A is not an A_1 phase but, rather, an A_d phase, i.e., an *A* phase with only partially overlapping molecules. The amount of overlap is greater, however, than for most other A_d phases reported in the literature: for FC12A, d_{obs}/d_{calc} = 1.12, whereas one usually finds[13] $d_{obs}/d_{calc} \approx 1.45$.

c. Mixture of 60% 4O.Cl and 40% FC12A. The value of d_{obs} in the smectic A phase at 77°C was 24.3 Å. The value of l at room temperature was calculated as l = 0.695 × 20.7 Å + 0.305 × 32.4 Å = 24.3 Å, where 0.695 and 0.305 are the mole fractions of 4O.Cl and FC12A, respectively. This gives l = 24.4 Å at 77°C. With S =

0.8, d_{calc} = 22.6 Å, and $d_{obs} - d_{calc}$ = 1.7 Å. This difference is probably significant, indicating that the *A* phase of this mixture is still an A_d phase, as for pure FC12A, but with an even greater degree of overlap: $d_{obs}/d_{calc} = 1.08$.

DISCUSSION

In this section, we will first examine certain aspects of the phase diagrams presented in Figures 1,3,4, and 5, and then we will analyze in some detail a number of possible explanations for the appearance of the induced nematic phase in mixtures of FC12A with 4O.Cl or 4O.Br.

The phase diagrams

It is clear from the phase diagram in Figure 1 that both FC12A and 4O.Cl have a latent N phase, with N-I transition temperatures only a few degrees below the S-I transition temperatures. This is further confirmed by the following two observations. First, in the homologous series FCnA all members with n = 2 through 10 have a nematic phase.[9] The temperature range of this nematic phase decreases with increasing *n*, and the compound FC12A is only the first compound (with even *n*) without a nematic phase. Second, in the series 4O.X with X = F, Cl, Br, I, the compound 4O.F has a nematic phase (Figure 4), but this phase becomes latent in 4O.Cl and 4O.Br (Figures 1 and 3), becoming more and more suppressed as the halogen atom increases in size. Thus, in this series, the compound 4O.Cl is again only the first member in which the nematic phase becomes latent.

A comparison of the four phase diagrams revealed an interesting similarity between the mixtures in which the halogen is Cl, Br, or I. We have prepared, therefore, a new phase diagram (Figure 7) in which the main features of Figures 1, 3, and 5 are represented together. It turns out that the S_A,N/isotropic transition temperatures are about the same in all three cases, so we have combined them and indicated them by a single line (solid line in Figure 7). The upper boundary of the S_B range (broken lines in Figure 7) shifts upward significantly over essentially the full composition range when going from Cl to Br to I. This, combined with the absence of any significant changes in the S_A,N/isotropic boundary (full line), results in the gradual displacement of the N and S_A phases from the right hand side of the phase diagram when going from Cl to Br to I: the S_A-N boundary (dotted lines in Figure 7) is pushed up significantly when going from Cl to Br, and it disappears entirely when going to I.

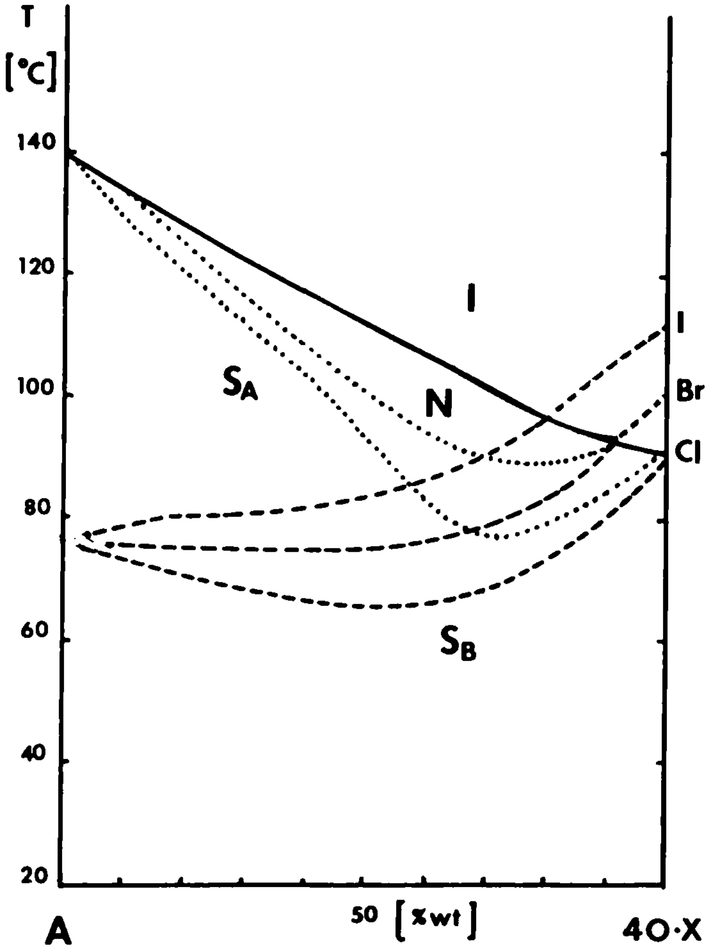

FIGURE 7 Combined phase diagram for the systems FC12A-4O.X with X = Cl, Br, I, showing the phase boundaries between S_B, S_A, N, and I phases (full line: S_A, N/I; broken lines: S_B/S_A, I; dotted lines: S_A/N).

Competing influences stabilizing the smectic phases

In the case of mixtures of FC12A with 4O.Cl or 4O.Br, two stabilizing influences on the smectic phase appear to be of importance: increased chain lengths and para-substituted halogens. The first effect is well known, but the latter, although documented in the literature[10,14] (see also Ref. 15, pp. 131 and 174), is not generally appreciated. The compounds FC12A and 4O.X appear to have smectic phases stabilized by each of these effects, respectively.

As far as the 4O.X compounds are concerned, Table I shows that only 4O.F has a nematic phase, and that the smectic-nematic or smectic-isotropic transition temperatures increase steadily in the order X = F,Cl,Br,I. Thus, the smectic phase in this series of compounds appears to be stabilized by the increase in size of the halogen.

In the homologous series of the FCnA's, as we discussed above, the nematic phase gradually disappears as *n* increases, and has vanished for FC12A. Simultaneously, the range of the smectic A phase increases with *n*. Thus, the smectic A phase in this case is stabilized by increasing the length of the hydrocarbon chain. Such a feature is common in the literature (Ref. 15, p. 207) and was first explained theoretically by McMillan.[16] It is also well known that mixing members of the same homologous series has the approximate effect of averaging the chain lengths.[17] It seems plausible that a similar effect is occurring on the left hand side of the diagram in Figures 1 and 3, as addition of the compound 4O.X effectively shortens the chain, causing the appearance of a nematic phase which increases in range with increasing concentration of 4O.X. The range of the nematic cannot continue to increase as more 4O.X is added, however, since pure 4O.X (X = Cl,Br) shows no nematic phase. On the right hand side of the diagram the range of the nematic must therefore become suppressed.

If the McMillan behavior is indeed occurring on the left hand side of Figure 1, then we would expect a decrease in the heat of transition with increasing concentration of the shorter chained molecule 4O.Cl. Figure 6 does indeed show an initial decrease in the heat of transition with increasing 4O.Cl concentration, and the transition becomes nearly second order at 50% of 4O.Cl. The very steep rise in ΔH on the right hand side of the diagram coupled with the rapid drop in the range of the induced nematic phase illustrates the strong stabilizing effect of the halogen (Cl) on the smectic phase.

We might, therefore, view the induced nematic in Figure 1 (and in Figure 3) as a competition between two smectic stabilizing effects: long chains and terminally para-substituted halogens. This cannot be a general rule, however, as terminally substituted halogens were not involved in several previously reported induced nematic phases.[3-8]

Difference in molecular length

The molecular length of FC12A is 32.4 Å, that of 4O.Cl is 20.7 Å (see above), so the difference in length is 11.7 Å. Such a large difference might be expected to make it difficult for mixtures of these molecules to form smectic layers. Thus, the decreases in the smectic-isotropic or smectic-nematic transition temperatures (i.e., the destabilization of the smectic phase) when 4O.X is added to FC12A or FC12A to 4O.X (Figures 1,3,4,5) could be viewed as a consequence of the large difference in the molecular lengths of the two components.

From the literature reports of the induced nematic phases[3–8] it does indeed appear that molecular length may be relevant to the occurrence of induced nematics, for in all cases the molecular lengths of the components are significantly different. The difference is not always as large as in our case, however.

Different kinds of smectic A phases

Our x-ray studies (see above) indicated that the smectic A phase of FC12A is an A_d phase whereas the smectic A phase of 4O.Cl is an A_1 phase. Thus, it might be suggested that this difference in phase type is the cause for the appearance of the induced nematic phase. From the other cases in the literature,[3–8] however, this does not appear to be a generally applicable argument. Also, Lydon and Coakley[18] found almost ideal mixing behavior for a system consisting of a compound with an A_d phase and one with an A_1 phase.

It should be noted, however, that the two systems with the largest induced nematic ranges reported so far, our Figure 1 and Figure 2c in Ref. 8, were systems in which the two compounds did have different types of A phases (in both cases A_d and A_1). Thus it may well be that this difference in the type of the smectic A phase is a significantly contributing factor for the formation of an induced nematic phase.

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