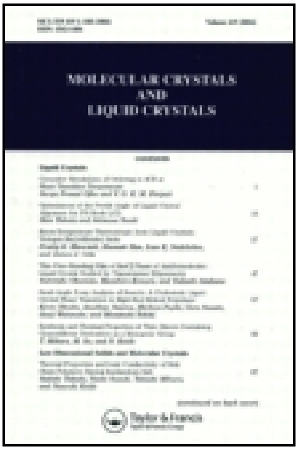

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The Re-entrant Nematic, Enhanced Smectic A Phases and Molecular Composition

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The Re-entrant Nematic, Enhanced Smectic A Phases and Molecular Composition

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Phase diagram and X-ray studies of mixtures of 8OCB (cyanooctyloxybiphenyl) and 4O8 (butyloxybenzilidene octylaniline) and 8OCB and 6OCB (cyanohexyloxybiphenyl) demonstrate:

1. 4O8 molecules inhibit the pairing of the 8OCB molecules. One 4O8 molecule is attributed with the breakup of one 8OCB pair.
2. The maximum pressure at which the smectic A phase is stable increases as the number of 8OCB pairs decreases.
3. The temperature at which the smectic A phase is stable is maximum when the mixture is most polar [no 8OCB pairs at all]. For these mixtures, there is no nematic phase.
4. There is no smectic A phase when all of the 8OCB molecules are paired.
5. When the nematic-smectic A transition temperature of the mixture approaches the nematic-isotropic transition temperature of the pure compound, the nematic phase is completely suppressed.

Assuming that the smectic A order parameter is coupled to the nematic order parameter and the coupling depends on temperature and composition, a Landau description is formulated which qualitatively summarizes all of these results.

I INTRODUCTION

Although binary mixtures of liquid crystals usually exhibit phase diagrams of the simple eutectic type, there are exceptions. One exception is the re-entrant nematic phase diagram,[1] others are phase diagrams showing induced or enhanced smectic mesomorphism.[2] In this latter case, two dissimilar components (e.g. one polar, the other nonpolar)[3] exhibiting only the nematic

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phase in their respective pure state, will form the smectic A phase when mixed. The other exception, the nematic-smectic A re-entrant nematic phenomenon, occurs in mixtures of cyano compounds (hence polar) which form molecular associations[4–8] thereby converting a polar, high temperature system (where there are few associations) to a nonpolar, low temperature one (where there are many). This temperature dependence of associations has been proposed as the mechanism triggering the re-entrant nematic phase[7,8] as explained in the next paragraph.

A comparison of compounds which are not too different shows that the nematic–smectic A transition temperature, T_{NS}, is greater the more polar the compound. It is hypothesized then, that for systems whose degree of "polarness" depends on temperature, the nematic–smectic A transition temperature will also depend upon temperature. For example, in the case of the cyano compounds, at high temperatures there are relatively few anti-parallel pairs of molecules.[9] The system is therefore quite polar due to the 4.5 debye dipole associated with the nitrile bond.[4] In contrast, an anti-parallel pair of these molecules is not polar since the dipoles cancel.[7,8] With decreasing temperature, the number of pairs, N, increases and T_{NS} decreases while the system transforms from a "polar" ensemble to a "nonpolar" one. These ideas can apply equally well to the pure compounds where the re-entrant nematic has also been observed at one atmosphere.[10–13] A model has been proposed for the variation of T_{NS} with N which accounts for both the re-entrant nematic phase and the reappearance at even lower temperatures of a second smectic A phase.[8]

Now, it is known that the stability of the smectic A phase of cyano compounds is enhanced (i.e. T_{NS} increases) when mixed with nonpolar molecules.[3,14] Here, I propose, that (for a specific case) this is because the nonpolar molecules inhibit the pairing of the polar molecules. This could account for the relationship found by Engelen *et al.*[14] between the smectic A layer spacing and the maximum transition temperature of their mixtures.

To demonstrate this effect, I will present results similar to Ref. 16 which I found studying mixtures of 8OCB [cyanooctyloxybiphenyl, $M_\omega = 307$] and 4O8 [butyloxybenzilidene octylaniline, $M_\omega = 366$]. 8OCB is polar when unpaired but forms antiparallel pairs as evidenced by the size of the smectic A layer spacing. It is about 1.5 times the molecular length. It also exhibits the re-entrant nematic phase in the pure state under pressure and at one atmosphere when mixed with its shorter homologue 6OCB [cyanohexyloxybiphenyl, $M_\omega = 279$]. 4O8 is nonpolar and does not form molecular associations. Its pressure temperature phase diagram is quite unexceptional.

Let N be the number of anti-parallel pairs formed by 8OCB, M be the number of unpaired 8OCB molecules and O the number of 4O8 molecules; then, the layer spacing, d, observed in a mixture (assuming that the volume of the mixture is simply the sum of the volumes of each component)[9] of x mole fraction of 4O8 is:

$$d = \frac{(NL_p + ML_s + OL_0)}{(N + M + O)}, \tag{1a}$$

where the L's refer to the lengths of the appropriate unit. For example, a molecular model[7] gives $L_p = 32.3$ Å for an anti-parallel 8OCB pair, $L_s = 24.0$ Å for a single 8OCB molecule and $L_0 = 28$ Å for the 4O8 molecule. If T is the total number of molecules, then from Eq. (1), we deduce:

$$\frac{N}{T} = \left[\frac{L_s - d(x) + x(L_0 - L_s)}{2L_s - L_p - d(x)}\right]. \tag{2a}$$

By measuring $d(x)$, one can extract N/T as a function of x. In fact, if the size and the number of participants of the molecular association, and, the size of the single molecule are known, Eq. (1) can be used to measure N even for a pure compound. A similar analysis will be made for the 8OCB–6OCB mixtures. In particular, it will be shown that the composition showing the maximum stability of the S_A phase has no nematic phase and corresponds to a molecular ensemble of no pairs at all whereas the complete destabilization of the A phase corresponds to a completely paired ensemble. In addition, it will be seen that the maximum pressure at which the smectic A phase is stable, P_M, increases as the number of pairs decreases.

Finally, by assuming simply that the smectic A order parameter is coupled to the nematic order parameter, a Landau theory is proposed which summarizes all of these results.

II EXPERIMENTS AND OBSERVATIONS

The materials used have been discussed in the introduction. They are: 8OCB, 4O8 and 6OCB. All were purchased and used without further purification.

A The phase diagram at one atmosphere

Figure 1 shows the phase diagram at one atmosphere of the 4O8–8OCB mixtures (to the right of the pure 8OCB line) as well as the 6OCB–8OCB mixtures (to the left)[15] for comparison. As can be seen, the 4O8–8OCB phase diagram is quite complex and deserves some discussion.

In the figure, the two phase regions are all marked except where they were too narrow. The phases were determined using an optical microscope equipped with a Mettler hot stage. The abscissa is simply the mass percent C of 4O8.

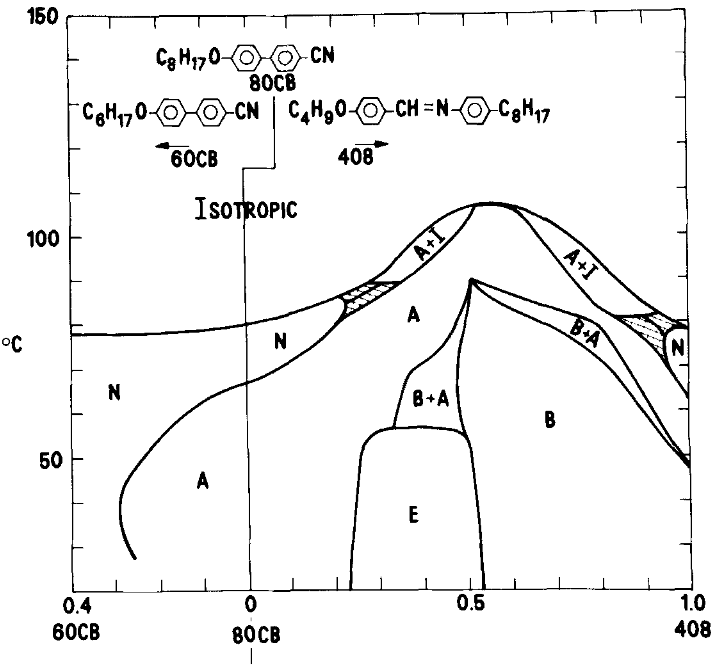

FIGURE 1 The phase diagrams at one atmosphere of mixtures of 4O8 in 8OCB (to the right) and 6OCB in 8OCB (to the left). The abscissa is the mass ratio of 4O8 in (4O8 + 8OCB) for the 4O8-8OCB mixtures and the mass ratio of 6OCB in (6OCB + 8OCB) for the 6OCB-8OCB mixtures.

1) For concentrations C between 25 % and 53 % of 4O8, there is an induction of the smectic E phase. The E–B transition is 50°C for the 51 % mixture but only 29°C for the 53 % one. The induced E–B line is practically vertical as is the smectic A-induced E line.

2) For $35\% \leqslant C \leqslant 50\%$, a very wide (B + A) two phase region is observed. This is deduced from the persistence of transition bars throughout the entire area marked B + A for this range of concentrations. For the 53 % mixture, the transition bars whisked through the preparation within a few hundredths of a degree.

3) The nematic phase is suppressed when T_{NS} is equal to the nematic isotropic transition temperature in the pure compound.

4) The maximum temperature at which the smectic A phase was stable occurred for the 53 % and 61 % mixtures. As will be shown (in Section C), a minimum in the layer spacing was found for these compounds corresponding to the fact that there are no 8OCB pairs in these mixtures.

5) Although the two smectic A phases are shown as being just miscible,

they may not be. It is very difficult to determine whether the small temperature range between 80°C and 83°C for the 80% 4O8 mixture was entirely and uniquely smectic A. On the other hand, there is no question that the two nematic phases are immiscible.

6) Amusing behavior is observed in the regions that are crosshatched and which border on the three phases: isotropic, nematic and smectic A. For example, cooling a 30% 4O8 mixture from the isotropic phase, one observes first smectic A bâtonnets growing in the isotropic liquid. Upon continued *cooling*, nematic drops (round) start forming in the isotropic liquid. The bâtonnets cease to grow at this point and end up being enveloped by the nematic phase. They appear as bâtonnet fossils in the nematic. Cooling still further the whole sample becomes smectic A.

B Pressure temperature phase diagram

These measurements were made using an optical pressure bomb[16] and an optical microscope. The sample is contained in a flexible cavity between two *c*-cut sapphire windows. Plexoil or octoil *S*, is compressed by a piston driven by a stepping motor. A YSI temperature controller regulates the temperature of the bomb (which is contained in an oven) to better than 0.1°C. The pressure is determined from the resistance of a manganin coil immersed in the pressurizing fluid and can be determined with a precision of 10 bars.

Figure 2 shows the dependence of T_{NS} on pressure for dilute mixtures. Even though the entire phase diagram has been studied for representative mixtures at 10% intervals across Figure 1, they will not be shown here as they are in general rather complicated for $C > 50\%$ with pure 4O8 being the sole exception (Figure 3). In Figure 2, the numbers parameterizing the curves are x_M = [# molecules 4O8]/[total # molecules] = mole fraction $= C/(C(1 - R) + R)$ where R is the molecular weight ratio of 4O8 to 8OCB. As can be seen, only a small amount of 4O8 ($x_M = 0.07$) increases the stability of the smectic A phase to above 4 kbars. P_M, the maximum pressure at which the smectic A phase is stable is linear in x_M for these mixtures, i.e. in Figure 4, $x_1 \equiv x_M$.

Also shown in Figure 4 is the linear dependence of P_M for the 8OCB–6OCB mixtures. Here P_M is linear in x_2 where x_2 is proportional to the number of additional pairs formed by 8OCB for $x_{6\mathrm{OCB}} > 0$, i.e.

$$x_2 = 2x_{8\mathrm{OCB}}x_{6\mathrm{OCB}} - (x_{6\mathrm{OCB}})^2 \tag{3}$$

where $x_{8\mathrm{OCB}}$ is the mole fraction of 8OCB and the squared term recognizes that 6OCB also pairs with itself. As we will show in the next section, in the pure state, 95% of pure 8OCB is paired. 6OCB efficiently scavenges the unpaired biphenyls so that the 37% mixture is completely dimerized. Figure

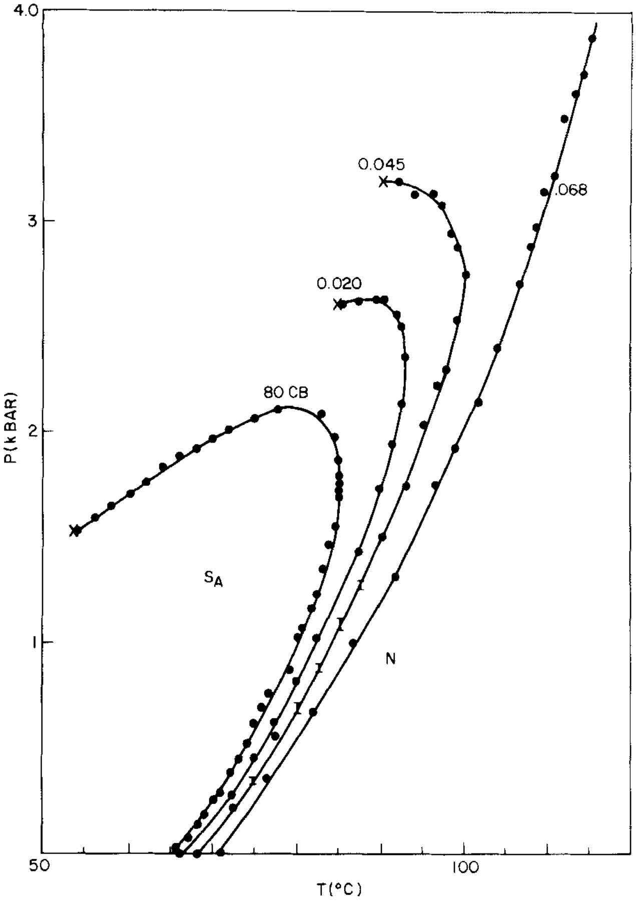

FIGURE 2 Pressure-Temperature phase diagram for mixtures of 4O8 and 8OCB for the nematic-smectic A phase only. P_M is the maximum pressure at which the smectic A phase is stable. P_M increases for increasing concentration of 4O8 in 8OCB. The x's mark the points where the sample crystallized. The number parameterizing the curves is mole fraction of 4O8.

1 shows the system is no longer polar enough to support a smectic A phase when the concentration of 6OCB exceeds 30%.

C X-ray measurements

In order to perform these measurements, representative mixtures from Figure 1 were loaded into thin quartz capillaries and their diffraction observed using a 6 kwatt rotating anode and a linear detector.[17] The temperature, monitored by a thermocouple, was controlled to better than 0.1°C using the

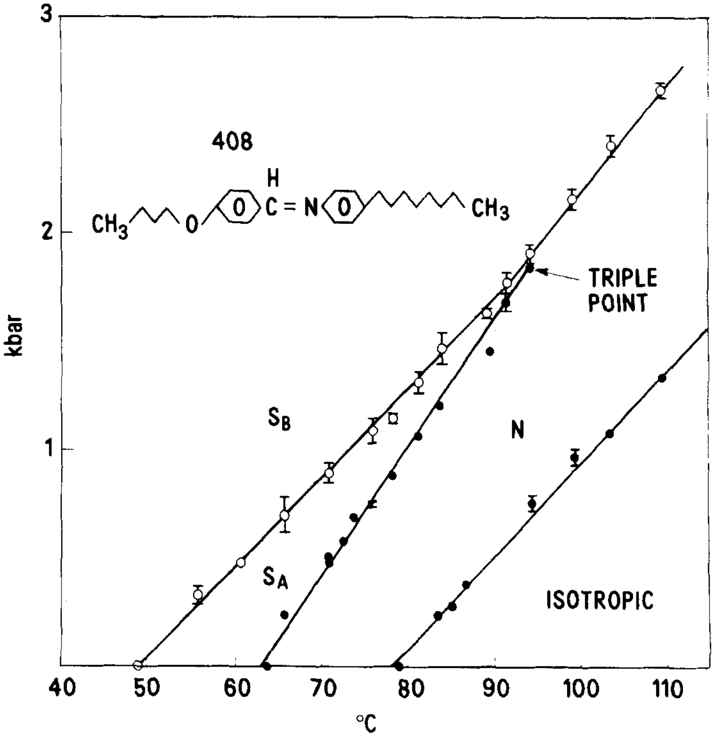

FIGURE 3 The Pressure-Temperature phase diagram for 4O8. Apart from a smectic A-smectic B-nematic triple point at 94°C and 1.89 kbar the phase diagram is unexceptional.

YSI controller. Figure 5b shows the spacings measured in the smectic A phases of the mixtures. Their temperature dependence was also investigated and found to be unimportant for all of the compounds.

The line drawn through the 4O8 points is a guide for the eye and is

$$d(x_M) = 31.49 - 16.58x_M - 7.02x_M^2 + 53.0x_M^3 - 32.9x_M^4. \qquad (4)$$

The standard error in d using this fit is $\Delta d/(\langle d \rangle) = 6 \times 10^{-3}$. Substituting the measured values for d into Eq. (2a), the ratio of the number of pairs (N) to the total number of molecules (T) is deduced and shown in Figure 5a. Interestingly, despite the complicated behavior of $d(x_M)$, for the 4O8 mixtures, $N/T(x_M)$ is a straight line—actually two straight lines, one of slope zero. The non-zero slope of this curve is -1.0 indicating that one 4O8 molecule breaks up one 8OCB pair. At $x_M = 0$, N/T is 0.47 (the maximum value for N/T is 0.5) thus a substantial fraction of the molecules are paired in 8OCB. For $0.47 < x_M < 1$ (which is $51\% \leqslant C \leqslant 100\%$ in Figure 1) there are no pairs.

The maximum temperature at which the smectic A phase is stable occurs

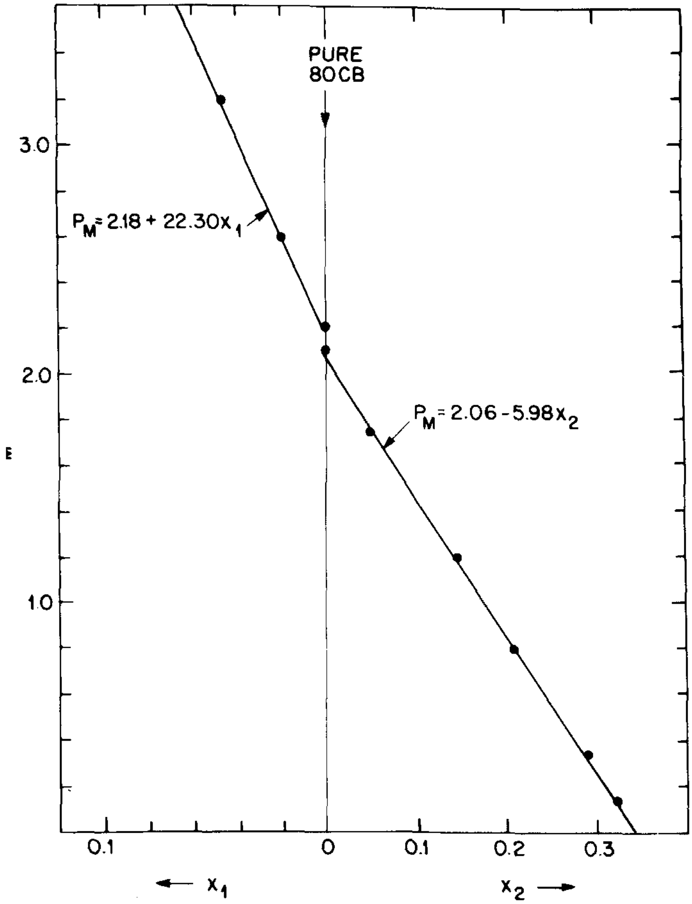

FIGURE 4 Demonstrates the linear dependence between the maximum pressure and the number of unpaired 8OCB molecules (see text).

for a mixture of $\sim 57\%$ 4O8 which is about $x_M = 0.53$, that is the number of single 8OCB molecules is maximum or the mixture is, to within experimental uncertainty at its most polar.

The analysis for the 6OCB–8OCB mixture is similar to the 4O8–6OCB mixtures. Let N^{ij} be the number of (i, j) pairs and M^i the number of single molecules of species i. The species are now 6OCB (6) and 8OCB (8). Then for x mole fraction 6OCB:

$$d = \frac{N^{88}L_p^8 + N^{68}L_p^{68} + N^{66}L_p^6 + M^8 L_s^8 + M^6 L_s^6}{(N^{88} + N^{68} + N^{66} + M^8 + M^6)} \tag{1b}$$

where the Ls are again the legnths of the appropriate units. Let N/T be the

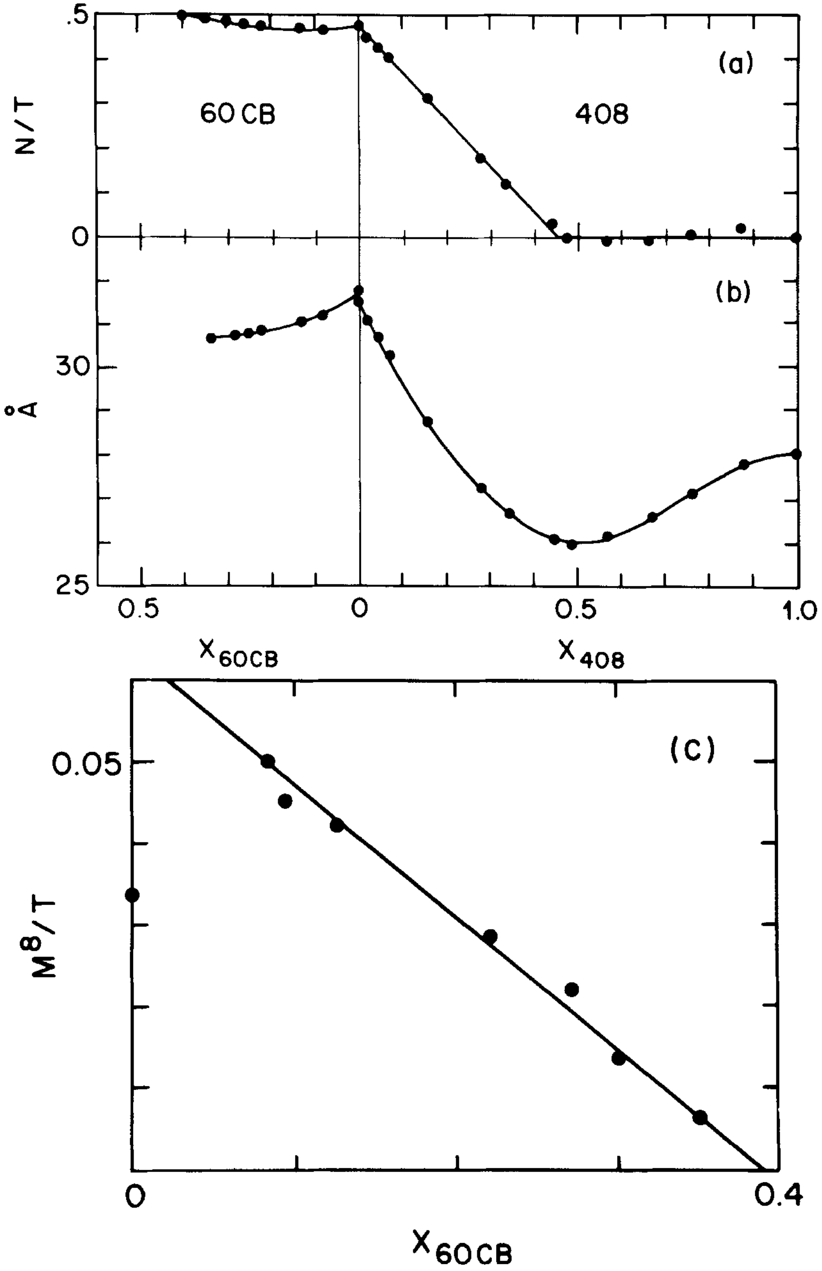

FIGURE 5 a) The ratio of the number of biphenyl pairs to the total number of molecules deduced from b), the measured layer spacing of the smectic A phase as a function of mole fraction 6OCB and 4O8. c) fraction of single 8OCB vs concentration 6OCB.

total number of pairs then:

$$\frac{N}{T} = \frac{N^{88} + N^{68} + N^{66}}{T} \tag{1c}$$

where

$$\frac{N^{88}}{T} = (1 - x)^2 \frac{N}{T}, \quad \frac{N^{68}}{T} = x(1 - x)^2 \frac{N}{T}, \quad \frac{N^{66}}{T} = x^2 \frac{N}{T}$$

and

$$\frac{M^6}{T} = x\left(1 - \frac{2N}{T}\right), \quad \frac{M^8}{T} = (1 - x)\left(1 - \frac{2N}{T}\right).$$

Thus,

$$\frac{N}{T} = \frac{(1 - x)L_s^8 + xL_s^6 - d}{[2[(1 - x)]L_s^8 + xL_s^6] - d - (1 - x)^2 L_p^8 - 2x(1 - x)L_p^{68} - x^2 L_p^6]} \tag{2b}$$

The X-ray pattern of the solid phase of these mixtures gives $L_p^8 = 32.3$ Å, $L_s^8 = 24$ Å, $L_s^6 = 21.9$ Å, $L_p^{68} = 30.3$ Å, $L_p^6 = 28.28$ Å. Figure 5a shows N/T and 5c, M^8/T as a function of $x_{6\text{OCB}}$. In Figure 5c, it is seen that after an initial increase in M^8/T for small $x_{6\text{OCB}}$, M^8/T steadily declines and is zero when $x_{6\text{OCB}} = 0.39$. The smectic A phase ceases to occur when there are fewer than 1 % single 8OCB molecules.

This kind of analysis leads to the consistent interpretation for the increase in layer spacing with pressure observed as the re-entrant transition is approached[18] as being due to the increase in 8OCB pairs.

What is clear from Figure 5 is: 4O8 destroys pairs, 6OCB makes pairs. In the former case the smectic A phase eventually dominates, whereas in the latter, the nematic takes over.

III PHENOMENOLOGICAL DESCRIPTION OF RESULTS

A phenomenological theory would be useful to keep track of, and somehow unify, the large number of results. One possibility is a Landau description of the phase transitions which assumes that the nematic and smectic A order parameters are coupled by means of a temperature dependent coupling constant. A close solid state analogue, for positive coupling, is the polarization of conduction electrons in superconductivity.[19] In our case, the sign of the coupling constant reflects the relative degree of "polarness" of the system.

Let Q be the nematic order and ψ the smectic order parameter. Assume, as is usual, that the free energy does not depend on the phase of Q or ψ. Then, write the free energy functional, $\Delta F = F - F_{\mathrm{I}}$, F_{I} being the free energy of the isotropic liquid:

$$\Delta F = \frac{a}{2}\psi^2 + \frac{b}{4}\psi^4 + \frac{\alpha}{2}Q^2 + \frac{\beta}{4}Q^4 + \frac{\eta}{2}Q^2\psi^2 \tag{5}$$

where $\alpha = \alpha_0(T - T^0_{\mathrm{NI}})$, $a = a_0(T - T^0_{\mathrm{NS}})$, T^0_{NS} and T^0_{NI} refer respectively to the nematic–smectic A and nematic–isotropic transitions in the pure compound, say—in any case, some reference composition. β and b are positive constants so that we assume the uncoupled ($\eta = 0$) transitions to be of second order.[20] A positive value for η favors the nematic over the smectic A phase and would describe mixtures like 8OCB and 6OCB. Negative η's favor the smectic A phase, corresponding to the 4O8–8OCB mixtures. Physically, then η represents the change in the microscopic interactions which stabilize the smectic A phase and, in the example discussed above, this is mediated via the anti-parallel molecular pairs of the biphenyls i.e. the relative polarness of the composition. If the effect of decreasing temperature or increasing concentration is to increase the number of these pairs then $\eta > 0$ describes the observations, whereas the contrary of this is describable by $\eta < 0$.

When $\psi = 0$ (no smectic A phase), then $Q^2 = -\alpha/\beta$ describes the uniform nematic state and $\Delta F = -\alpha^2/4\beta$. If $\psi \neq 0$, but is constant, then,

$$Q^2 = -\frac{[\alpha + \eta\psi^2]}{\beta} \tag{6a}$$

and

$$\Delta F = [-\alpha^2 + 2\psi^2[\beta a - \eta\alpha] + \psi^4[\beta b - \eta^2]]. \tag{6b}$$

The effect of this coupling, like many others,[21] is to drive the nematic–smectic A transition first order. To guarantee that this transition remains second order, we require $\eta^2 < \beta b$. Let $\eta_0 = a_0\beta/\alpha_0$ be an upper limit for the coupling.

We now assume that minimizing Eq. (6b) with respect to ψ will lead to an overall minimum. This is not evident, but the results will be shown to qualitatively (at least) describe the observations. Thus:

$$\psi^2 = -\frac{[\beta a - \alpha\eta]}{(\beta b - \eta^2)} \tag{7a}$$

and

$$\Delta F = -\frac{[\alpha^2 + [\beta a - \eta\alpha]^2]}{(4\beta[\beta b - \eta^2])}. \tag{7b}$$

We now enumerate some results.

A $(T_{NS})_{MAX} = T^0_{NI}$

In Eq. 6a put $\psi^2 = a_0/b\,[T - T_{NS}]$ where T_{NS} is the renormalized transition temperature. Then the nematic phase is stable when

$$T < \frac{T^0_{NI} + (\eta\eta_0/\beta b)T_{NS}}{1 + (\eta\eta_0/\beta b)}, \quad T < T_{NS}. \tag{6c}$$

As T_{NS} increases ($\eta < 0$), T_{NI} increases provided T_{NS} is less than T^0_{NI}. When T_{NS} is greater than T^0_{NI}, T_{NI}, becomes less than T^0_{NI}. Thus, this theory predicts that the smectic A phase will transform directly to the isotropic state for $T_{NS} \geqslant T^0_{NI}$ as is indeed observed. On Figure 1, the nematic phase is pinched off exactly when $T_{NS} = T^0_{NI}$.

This result is a prediction whose validity militates in favor of the existence of this coupling.

B $(T_{NS} - T^0_{NS}) >< 0$ when $\eta <> 0$

T_{NS} is determined from the zeroes of Eq. (7a) or

$$T_{NS} = \frac{[T^0_{NS} - T^0_{NI}(\eta/\eta_0)]}{(1 - \eta/\eta_0)}. \tag{7c}$$

Let N be the number of molecular pairs, and put

$$\eta = \frac{\eta_0 T_0'[N - N_0]}{TN_0} \tag{8}$$

so that the sign of η depends upon whether N increases or decreases with respect to the reference composition. This in turn will control whether T_{NS} increases or decreases relative to T^0_{NS}. As T decreases, the strength of the coupling increases and this is sufficient to qualitatively account for the re-entrant nematic without an additional temperature dependence for N. T_0/T has been chosen *ad hoc* for the temperature dependence of η to illustrate this feature of the theory. Clearly any quantitative theory would require a better idea of the temperature dependence of η.

C Re-entrant Behavior

When the coupling constant, η, grows with temperature faster than the smectic A order parameter, the nematic phase will eventually re-enter. Put $T_0 = T_0'[N - N_0]/N_0$, $M = T^0_{NS}/T^0_{NI}$, and $t = T/T_{NI}$, then Eqs. 7c and

8 lead to:

$$t_{NS} = \frac{t_0 + M \pm \sqrt{(t_0 + M)^2 - 4t_0}}{2}. \tag{9a}$$

The limit of stability of the smectic A phase depends only on the McMillan[22] number, M and is given by the double root of Eq. (9a) or

$$t_0 = 2 - M \pm 2\sqrt{1 - M}. \tag{9b}$$

This result is the same for t'_0 and $t_0 = t'_0(N - N_0/N_0)$. In (9b), the relevant sign for $\eta < 0$ is the negative one. For $M = 0.966$, $t_0 = 0.69$ ($T_0 = -30^\circ\mathrm{C}$) and (9a) gives $T_{NS} = 15^\circ\mathrm{C}$ (much lower than the $38^\circ\mathrm{C}$ that is observed). When $t_0 = 0.5$, $(t_{NS})_{1,2} = 0.938$ (stable) and 0.52 (unstable). These results are graphically represented in Figure 6.

Figure 6 shows that Eq. (9a) qualitatively describes the re-entrant nematic

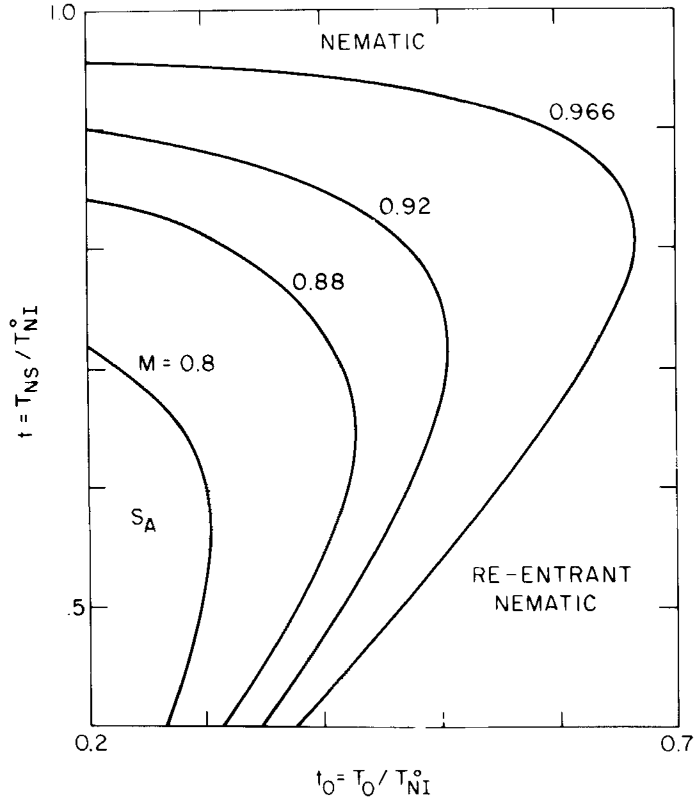

FIGURE 6 Equation (9) vs t_o, the strength of the coupling between the nematic and smectic A order parameters.

phase diagram even when the temperature dependence of the number of pairs is neglected and a simple *ad hoc* temperature dependence is chosen to increase the coupling between the nematic and smectic A order parameters with decreasing temperature. A better understanding of how η varies with T would, no doubt, improve the quantitative aspects of this description. In this regard, if the molecular composition continues to vary even in the re-entrant nematic phase, a nonmonotonic temperature dependence for η would reinstate the smectic A phase below the re-entrant nematic phase—provided it is not pre-empted by another smectic phase or crystallization. The existence of a lower temperature smectic A phase had been predicted to occur[7] and has been subsequently found in another cyano compound.[12]

IV CONCLUSIONS

By studying the 8OCB–4O8 and 8OCB–6OCB mixtures, an estimate of the total number of pairs has been deduced for pure 8OCB. It was found that one 4O8 molecule disrupts one 8OCB pair and 95% of the molecules in pure 8OCB are associated in an antiparallel arrangement. This number seems to depend only weakly on temperature.

A Landau type free energy functional can qualitatively account for both the re-entrant nematic and enhanced smectic A phase if there is a temperature dependent coupling between the nematic and smectic A order parameter. This description correctly predicts the suppression of the nematic phase at large coupling so that the most enhanced value for the nematic–smectic A transition temperature is the nematic–isotropic transition in the pure compound.

Another effect which can be accounted for by this mechanism, but which we have not discussed here, is the pressure induced nematic phases found in some nitro-esters.[24] At one atmosphere, only the smectic A–isotropic transition is observed but a nematic–smectic A transition appears under pressure. This suggests that η becomes less negative with pressure for these compounds. For the biphenyls, η has already a small negative value and pressure drives it positive so inducing the re-entrant nematic phase.

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References

1. P. E. Cladis, *Phys. Rev. Letters*, **35**, 48 (1975).
2. J. W. Park, C. S. Bak, and M. M. Labes, *Journal of the Am. Chem. Soc.*, **97**, 4398 (1975).
3. Apparently this kind of behavior can occur for a variety of reasons other than the single one mentioned here. See for example: John H. MacMillan and M. M. Labes, *Mol. Cryst. Liq. Cryst. Letters* **56**, 7 (1979) and references therein. The polar-non-polar example cited here was proposed by B. Engelen, G. Heppke, R. Hopf, and F. Schneider, *Ann. Phys.*, **3**, 403 (1978).
4. N. V. Madhusudana and S. Chandrasekhar, in *Proc. Inter. Conf. in Liquid Crystals*, Bangalore, *Pramana Suppl.*, **1**, 57 (1973); B. R. Ratna and R. Shashidhar, *Pramana*, **6**, 278 (1976).
5. G. W. Gray, and J. E. Lydon, *Nature* (London) **252**, 221 (1974). J. E. Lydon and C. J. Coakley, *J. Phys.*, **36**, C1-45 (1975).
6. P. E. Cladis, R. K. Bogardus, W. B. Daniels, and G. N. Taylor, *Phys. Rev. Letters*, **39**, 720 (1977).
7. P. E. Cladis, R. K. Bogardus, and D. Aadsen, *Phys. Rev.*, **A18**, 2296 (1978).
8. P. E. Cladis, in *Proceedings of the Second International Bangalore Conference*, Bangalore, Dec. 3–9 (1979).
9. F. Bouchet and P. E. Cladis, *Mol. Cryst. Liq. Crystal. Letters*, **64**, L-81 (1980).
10. Nguyen Huu Tinh and H. Gasparoux, *Mol. Cryst. Liq. Cryst.* (*Letters*), **49**, 287 (1979). J. C. Dubois, H. T. Nguyen, A. Zann, and S. Billard, *Nou. J. Chemie.*, **2**, 647 (1978).
11. N. V. Madhusudana, B. K. Sadashiva, and K. P. L. Moodithaya, *Current Science*, **48**, 287 (1979).
12. F. Hardouin, G. Sigaud, M. F. Achard, and H. Gasparoux, *Phys. Lett.*, **71A**, 347 (1979); *Sol. St. Comm.*, **30**, 265 (1979).
13. F. Hardouin and A. M. Levelut, *Journale de Physique*, **41**, 41 (1980).
14. B. Engelen, G. Heppke, R. Hopf, and F. Schneider, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 193 (1979).
15. P. E. Cladis, D. Guillon, F. Bouchet, and P. Finn, to be published in *Phys. Rev. A*.
16. W. B. Daniels and R. K. Bogardus (unpublished).
17. J. Stamatoff and T. Bilash (unpublished).
18. S. Chadrasekhar, R. Shashidhar, and K. V. Rao, in *Proceedings of the Second International Bangalore Conference*, Bangalore Dec. 3–9 (1979).
19. E. I. Blount and C. M. Varma, *Phys. Rev. Letters*, **42**, 1079 (1979).
20. It seems that simply first or second is too simple to describe these transitions. The transition entropies of the 60CB-80CB mixture and pure 80CB have been measured by Carl W. Garland, Gerald B. Kasting and Kenneth J. Lushington, *Phys. Rev. Letters*, **43**, 1420 (1979), *Phys. Rev. B* (to be published). They find that the nematic-isotropic transitions are of first order with large heat capacity anomalies but the nematic-smectic A transitions are of second order (or immeasurably close) with no transition entropy observed at all for the nematic-smectic A-re-entrant nematic transitions even though they were able to visually observe the transitions.
21. R. B. Meyer and T. Lubensky, *Phys. Rev.*, **B14**, 2307 (1976).
22. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
23. P. E. Cladis, D. Guillon, W. B. Daniels, and A. C. Griffin, *Mol. Cryst. Liq. Cryst. Letters*, **56**, 89 (1979).