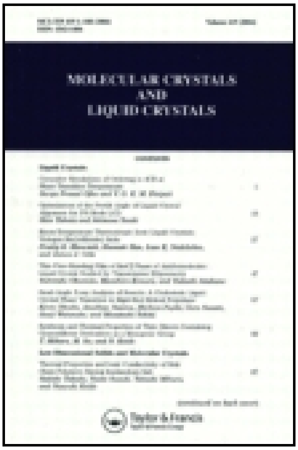

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Incommensurate and Commensurate Smectic a Phases with Pressure Induced Nematic Phases

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INCOMMENSURATE AND COMMENSURATE SMECTIC A PHASES WITH PRESSURE INDUCED NEMATIC PHASES

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ABSTRACT
Our previous resolution of the discrepancy between the molecular length, L_s, and the observed smectic A lattice parameter, d (incommensurate smectic A phase, $d \neq L_s$) of some nitro esters now seems unnecessary. A new interpretation is presented. It turns on the appreciation that an x-ray diffraction experiment on intercalated smectic A layers, composed of different sorts of molecules: N molecules of length L_p and M, of length, L_s, would sense an average spacing:

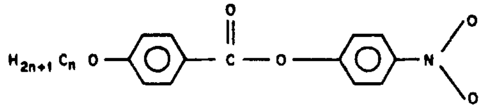
$$d = (NL_p + ML_s)/(N + M) .$$

For the nitro esters, L_p is the length of an anti-parallel associated pair (similar to the one proposed for the cyanobiphenyls) and L_s, the (unassociated) molecular length. N is estimated for the previously studied nitro-esters.

In contrast, the weaker dipole of fluorinated Schiff bases cannot stabilize such pairwise associations at one atmosphere resulting in a commensurate smectic A phases: $d \sim L_s$; $N \sim 0$. A pressure induced nematic phase is observed in the decyloxy member of this series, as it was for the nitro-esters, and indicates that pressure stimulates pair production (N>0) and thus incommensurability which in turn stabilizes the nematic phase but at the expense of the smectic A phase. This is consistent with the recent Landau theory of the nematic smectic A transition in which the nematic and smectic A order parameters are coupled.

INCOMMENSURATE SMECTIC A PHASE

Recently we studied(1) the liquid crystal transitions of the nitro-esters(2)



where n was 8, 10 and 12. In particular, these compounds exhibited smectic A phases for which the layer spacing, d, is not commensurate with the molecular length, L_s.(2,3) For example, for $n = 10$, the molecular length measured from a scaled model is, $L_s \sim 28\text{Å}$. In contrast $d \sim 32\text{Å}$ and an anti-parallel associated pair(2–4) as shown in Fig. 1c measures $L_p \sim 42.4\text{Å}$ or 10Å in excess of d. The large discrepancy between L_p and d was used as an argument against the occurrence of the kind of associations represented in Fig. 1(b) and a more complicated one was proposed which gave a length on the order of the observed d. Here we show that such complicated associations are unnecessary since an x-ray diffraction experiment on *intercalated smectic A layers* composed of molecules of different lengths(5,6) observes (unless exceptional circumstances pertain) the average length, d, which for N anti-parallel pairs and M single molecules is

$$d = (N\ L_p + M\ L_s)/(N + M)\ . \tag{1}$$

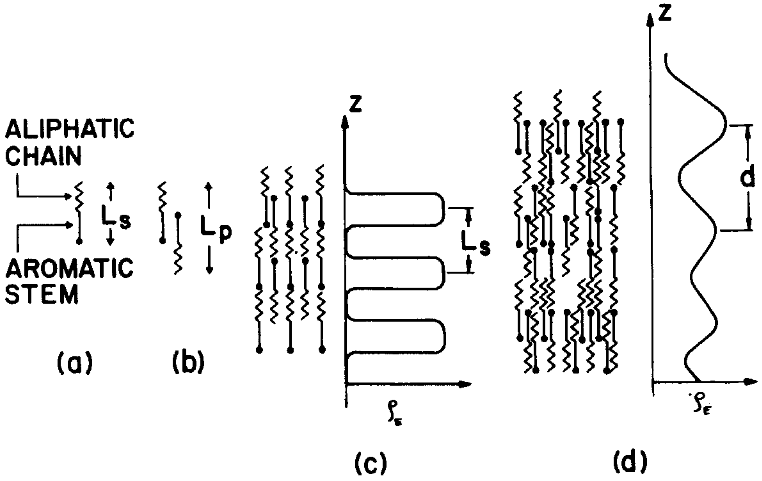


Fig. 1. Schematic for (a) single nitro-esters, (b) overlapped pair, (c) completely intercalated smectic A layers and (d) intercalated layers composed of some single (a) and some overlapped (b) pairs. The zero temperature electron densities for schemes (c) and (d) show that the amplitude (i.e. modulus of the S_A order parameter) is smaller for (d) than (c).

If T is the total number of molecules, $T = 2N + M$, then

$$N/T = (d - L_s)/(L_p - 2L_s + d) \ . \tag{2}$$

Measuring d and estimating L_s, L_p from molecular models or from the solid phase diffraction, leads to an estimate for N/T.

In Table I, we do this for the previously studied nitro-esters.⁽¹⁾

Table I. Re-interpretation of the nitro-ester data. T is the total number of molecules. The maximum value for N/T = .5

n	d(Å)	L_s(Å)	L_p(Å)	∴ N/T
8	29	25.5	36.8	.24
10	32	28.5	42.5	.20
12	34	30.5	45.5	.19

Table I shows that a small decrease in N/T from .24 for $n = 8$ to 0.20 for $n = 10$, correlates with the eclipse of the nematic phase at one atmosphere in the $n = 10$ member. In the next section we argue that increasing pressure stimulates pair production and incommensurability thus stabilizing the nematic phase at elevated pressures at the expense of the smectic A phase.

A comparison of the data shown in Table I with that found in the 408 (butyloxybenzilidene-octylaniline) and 80CB (octyloxybiphenyl) mixtures,⁽⁵⁾ shows that at one atmosphere, the pure nitro-esters have about half the number of pairs as pure 80CB. In the mixtures, the nematic phase disappeared when $N/T \sim 0.22$ which is compatible with the results in Table I.

Conclusion: Pairs stabilize the nematic phase, non-pairs the smectic A phase.

COMMENSURATE SMECTIC A PHASE

Why should a commensurate layering in compounds composed of a very polar aromatic stem and a single methylene chain favor the smectic A phase?

In Fig. 1c, a commensurate smectic A phase is shown for just such molecules. Here we immerse the aliphatic chains from one layer into the aliphatic chains of neighboring layers while simultaneously overlapping the aromatic cores in the antiparallel arrangement. The difference in this layering compared to one formed exclusively from overlapped pairs is that alkyl chains fill space better than benzene rings so that the in-plane packing for the aromatic stems is looser for Fig. 1c than it is for the pairwise associated unit in Fig. 1b. Consequently, the electrostatic fields associated with the dipoles do not cancel as completely as in the closer packed arrangement. The molecular ensemble is quite polar, however, its ultimate stability depends upon the strength of the attractive forces between the aromatic segments: when strong, as it would be for the nitro esters, a small fluctuation in the in-plane packing enhances pairwise associations and the onset of incommensurability (1d); when weak, as it is for the fluorine compounds shown in Fig. 2, then a commensurate smectic A phase like 1c has a greater possibility of being stable to these fluctuations. However, applying pressure to configuration 1c forces a closer packing of the aromatic cores thereby stimulating pair formation (1b) and an incommensurate smectic A phase (1d) where there are both pairs and single molecules. In this scheme (1d), there is a loss in the distinction between the aromatic part of the layers and the aliphatic part, noted in 1c, which is physically equivalent to weakening the smectic A order parameter even though the orientational order is enhanced. This ends in the induction of the nematic phase under pressure at the expense of the smectic A phase. These ideas have been phrased in terms of a Landau theory in which the nematic and smectic A order parameters are coupled.$^{(5)}$

Fig. 2 shows the pressure temperature phase diagram for the $n = 10$ and $n = 6$ members of the fluorinated alkoxy Schiff base. Table II summarizes the relevant parameters.

Table II. Slopes and zero pressure intercepts from Fig. 2.

$n = 10$

Transition	dT/dP (°C/kbar)	T_0(°C)
N-I	19.4	65.8
A-N	15.4	65.4
Cryst	19.0	55.5
Melt	22.7	70.3

$n = 6$

Transition	dT/dP (°C/kbar)	T_0(°C)
N-I	25.6	62.9
A-N	19.6	62.3
A-B	22.9	57.9
B-N	18.1	65.2

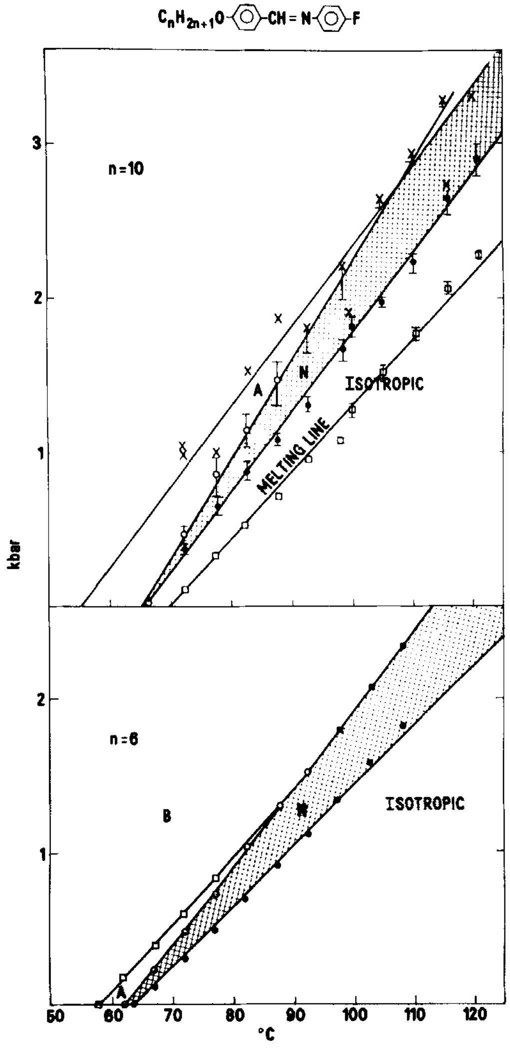


Fig. 2 Pressure-temperature phase diagram for the fluorinated alkoxy Schiff base. The cross-hatched area is the nematic phase, N. The smectic phases are smectic A(A) and smectic B(B). The X's in the top diagram indicate crystallization.

For the $n = 10$ member, at one atmosphere, the sequence of transitions is:

$$\begin{tikzcd}
K \arrow[rr, "68.7^\circ C"] & & I \, . \\
 & S_A \arrow[ul] \arrow[ur, "66.3^\circ C"'] &
\end{tikzcd}$$

Under pressure, a smectic A-nematic-isotropic triple point is observed at $p = 0.34\text{—}0.44$ kbar and $t = 72.3\ ^\circ C$. The extrapolated zero pressure nematic-isotropic transition temperature (Table II) is less than the one atm. smectic A-isotropic transition temperature - as it was also observed to be for the nitro-esters. This is predicted by the previously mentioned Landau theory.$^{(5)}$

A measurement of the layer spacing gave 23Å for the solid phase and 27Å for the monotropic smectic A phase which is about the length of the fully extended molecule. At one atmosphere the smectic A phase is commensurate (Fig. 1c). Stimulating the onset of incommensurability by forcing a closer packing of the aromatic stems with increasing pressure thereby increasing pair production, weakens the smectic A order parameter, enhances the nematic order and sets the stage for the observed pressure induced nematic phase (Fig. 2).

The pressure-induced nematic-smectic A transition is accompanied by exceptional turbulence. Once one of the phases is established, the extreme chaos observed in the transition region clears. A reasonable interpretation is demixing between the commensurate and incommensurate regions; the commensurate S_A is not miscible with the incommensurate one. When the pressure exceeds 2.6 kbar and the temperature, 105°C, the solid phase is more stable and the mesophases are difficult to nucleate.

For the $n = 6$ member of this series, the nematic-smectic A-smectic B triple point is 1.5 kbar and 92°C. The reduced pairing of these compounds, compared to the cyanobiphenyls, is consistent$^{(5)}$ with the existence of the smectic A phase for $n = 6$ of these compounds whereas only the nematic is observed in the equivalent cyanobiphenyl, 60CB, cyanohexyloxy biphenyl.

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