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STUDY OF AN INCOMMENSURATE SMECTIC A PHASE

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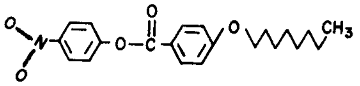
ABSTRACT
The smectic A layer spacing of the 4-nitrophenyl 4'-alkoxybenzoates is incommensurate with the molecular length. We propose a model of the molecular associations which accounts for this observed layer spacing and for the pressure induced nematic phase discovered in 4-nitrophenyl 4'-decyloxybenzoate.

I. INTRODUCTION

Recently, we have studied the liquid crystal transitions of the nitro-esters[1] including



where *n* was 8, 10 and 12. These compounds exhibit smectic A phases for which the measured layer spacing is not commensurate with the molecular length so must be considered of the bilayer sort.[1] For example, in Table I, for $n = 10$, the molecular length is about 28Å as measured from a scaled model (Fig. 1(a)) when the molecule is stretched out. In contrast, the smectic A layer spacing is 32Å.

Overlapping the aromatic section of two molecules in an antiparallel pairing as has been suggested as a model for the smectic A phase of the cyanobiphenyl and cyano-Schiff base compounds[2-5] leads to an associated pair ~ 42.4 Å- or a length 10 Å in excess of what is observed. Despite this fact (as we will point out in the next section, we can think of models which account for the discrepancy between the smectic A layer spacing and the length of overlapped pairs) we note that *inter*molecular association of the aromatic cores has been conjectured to be responsible for the appearance of the re-entrant nematic phases in cyano-compounds.(5) Consequently, observation of re-entrance, would be strong support for this aspect of the model, that is, as a function of decreasing temperature or increasing pressure, the observed sequence of phase transitions is nematic, smectic A then (re-entrant) nematic.(2, 5)

The fact that we have not observed re-entrance has prompted us to consider another model based on *intra*molecular rather than *inter*molecular associations which has the following advantages. It accounts for 1) the observed layer spacing, 2) the non-appearance of a re-entrant rematic phase and 3) the appearance of a pressure induced nematic phase for the $n = 10$ member of this series. Although unusual, *intra*molecular complexing of the sort we propose is not unknown for similar compounds.(6)

In the next section we will discuss the models for this bilayer smectic A phase and in the final section we present our experimental observations.

II. MOLECULAR MODELS

As mentioned in the introduction, overlapping the aromatic cores leads to an associated pair length of 42.4 Å, or a length about 10 Å in excess of what is actually observed for the smectic A layers.

TABLE I The lengths of the molecules and smectic A layer spacings both measured by x-ray diffraction and on a scaled model of a pair of molecules associated as shown in Fig. 1(b).

n	Length of Molecule (Fig. 1(a)) (Å)	Measured Layer Spacing (Å)	Length of Model (Fig. 1(b)) (Å)
8	25-26	29	~ 28
10	27-29	32	~ 32
12	30-31	34	~ 36

This discrepancy can be resolved in at least two ways: first, by assuming the molecular pairs are tilted in the layers with no preferred direction for the azimuthal angle - a kind of disordered smectic C as first conceived by de Vries(7) or second, by assuming that the aromatic portion of the pairs lie parallel to each other but perpendicular to the layers and the hydrocarbon chains are somehow tilted and pushed off to the side.(1) The first model is an adaptation of de Vries' model for first order smectic A to smectic C transitions where the tilt angle is non-zero in both phases. In both models, pretransitional fluctuations in the nematic phase would be manifest in an x-ray scattering experiment by a broad peak centered around the smectic layer spacing with maximum intensity occurring at a mean value not too different from the smectic layer spacing in the vicinity of the transition. Presumably this would change far away from the transition to a length associated with the excluded volume of either a pair or a single molecule. So far, all our attempts to observe this change in lengths have been fruitless and the nematic "excluded volume" length observed by x-rays remains centered about the smectic A layer spacing as listed in Table I.

In Table I, we note that the smectic A layer spacing is only about 5 Å longer than a molecular length. Thus, assuming an overlapped core model implies that the pairs are tilted in the layers about 37 degrees. This large value for the tilt combined with complete azimuthal disorder seems unreasonably loose packing for the layers whereas maintaining the aromatic cores perpendicular to the layers and stuffing the hydrocarbon chains between the layers seems to imply an unreasonably dense view of the smectic A.

In addition, as we will show in the next section, we were not able to observe the phenomenon of re-entrance expected if the association of these molecules is the same as it is for the cyano-compounds. In view of the lack of strongly supporting evidence for the overlapped aromatic core models, we considered exploring other ways in which the smectic layers could be packed.

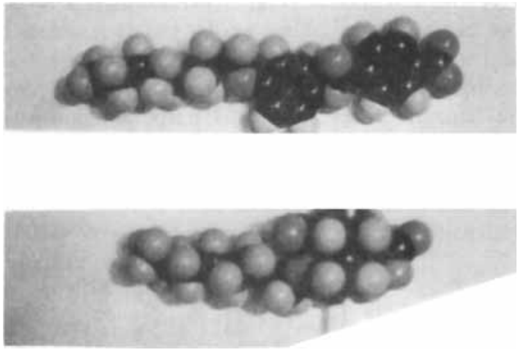


FIG. 1(a) On the top a fully extended molecule, on the bottom the same molecule but with one benzene ring rotated to lie on the other.

Fig. 1(a) shows molecular models for these nitro-esters. On the top of Fig. 1(a) we show the molecule fully extended whereas on the bottom of this same figure, we show that it is possible to completely rotate one of the benzene rings and lay it on top of the other - *intra*molecular associations. The strong *(sigma* and *pi)* electron withdrawing properties (-I and -H, respectively) of the NO_2 group make the aromatic ring to which it is attached partially positive whereas the presence of the *pi* - donating (+M) ether oxygen at the other end of the molecule makes the ring to which it is attached partially negative. Lack of sufficient conjugation between rings effectively insulates them from each other. Furthermore, the presence of a *sigma* bond in the central linkage allows the molecule a considerable amount of flexibility as shown in Fig. 1(a).

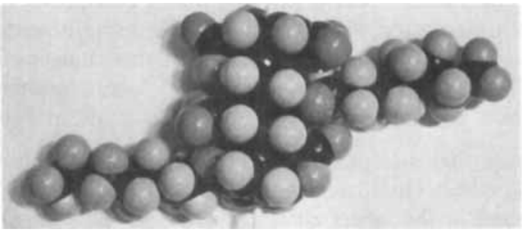


FIG. 1(b) A model of associated pairs which accounts for the measured layer spacing.

Fig. 1(b) shows a pair of such overlapped molecules associated in a stacking consistent both *intra* and *inter*molecular complexing which can be plausibly packed into a smectic A layer. In Table I, we compare the length of the model shown in Fig. 1(b) with the measured values for the layer spacing. For example for $n = 8$, the fully extended molecular length is ~25-26 Å. The measured layer spacing is 29 Å and the model (Fig. 1(b)) predicts a layer spacing of 28 Å! Furthermore, we can estimate the molecular radius from such an associated pair both from the model and from density measurements.(8) Measuring the model (Fig 1b), we find that the diameter of the aromatic core segment is 6 Å in the plane of the benzene rings and 10 Å perpendicular to it, i.e. a mean diameter of 8 Å. For the $n = 8$ compound whose molecular weight is 371.432 grams, the density in the A phase has been measured(8) to be $\rho = 1.113$ *gms/cc* and the layer spacing has been measured to be $d = 29$ Å (Table I). Assuming there is some kind of pairing within the layers and $N_A = 6 \times 10^{23}$ molecules per mole we have,

$$\rho = 1.113\ gms/cc = \frac{371.432\ gms}{(\frac{N_A}{2} \times \pi r^2 d)\,cc} \qquad (1)$$

where r is the radius of the pair. From Eq. (1) we find $2r = 7.0$ Å which agrees very well with the model and is to be compared with typical molecular diameters of 4-5 Å for monolayer smectic A phases as well as the very tight packing of the bilayer smectic A phases of the cyanobiphenyls. Thus, despite its unusual configuration the model shown in Fig. 1(b) also fits the rather large intermolecular spacing estimated for these compounds!

Now that we have listed the points in favor of the model 1(b) -- the most notable being that it fits the measured layer spacing -- we now present points against it. The most difficult objection to overcome is that it seems an energetic conformation. Where does the energy come from? Furthermore, the molecular model shown in Fig. 1(b) *underestimates* slightly the dimension perpendicular to the plane of a benzene ring so that it is not clear that the two rings will lie exactly flat on each other as they do here.

One final point in favour of the model, however, is that in the solid state, the molecules seem to prefer some kind of folded conformation. Evidence for this is provided by x-ray powder patterns of the solid phase which show that the longest spacing is about one benzene ring shorter than the fully extended molecule. For example, diffraction lines associated with the n = 12 solid were 27.1 Å, 13.73 Å, 9.98 Å, 9.01 Å and 7.65 Å. Fully extended, the molecule is ~31 Å.

III. MEASUREMENTS

A. DSC Measurements

Table II shows the results of measurements of the heats of transition at one atmosphere using a differential scanning calorimeter (Perkin-Elmer DSC 1-B) calibrated against the heat of melting 1.172 mg. of indium.

The latent heats shown for the melting transitions are the combined latent heats for the two melting transitions. Like many organic compounds which form liquid crystal phases, there are two melting transitions very close together in temperature. The total area under the double melting curve appears to be constant but the relative strengths of the two peaks can depend upon the rate of melting. For example, for $n = 8$, the two melts occur at 46°C and 51°C. The total area measured under the curves is 11.88 cal/gm. Estimating each melting transition separately we find that on average 3.3 cal/gm is associated with the 46° transition and 8.8 cal/gm with the 51°C one for heating rates of 5°C/minute. At 10°C/minute the 51°C transition seems to have a larger latent heat (10 calories/gm) and the 46° transition a smaller one (~2 cal/gm).

TABLE II The latent heats (L) of the transitions, the slopes and zero pressure intercepts (T_0) as deduced from data shown in Fig. 2.

$n = 8$

Transition	T_0 (°C)	dT/dP (°C/kbar)	L at P = 0 (cal/gm)
Melt - S_A	50.69	21.97	11.88
S_A - N	61.49	12.16	.097 ± .02
N-I	67.63	24.98	.23 ± .02

$n = 10$

Transition	T_0 (°C)	dT/dP (°C/kbar)	L at P = 0 (cal/gm)
Melt-S_A	56.1	20.40	12.7 ± 1.5
N-S_A	77.08	19.0	no transition at P = 0
N-I	74.06	23.37	no transition at p = 0
S_A-I	75.2	20.09	.97 ± .2

$n = 12$

Transition	T_0 (°C)	dT/dP (°C/kbar)	L at P = 0 (cal/gm)
Melt-S_A	62.75	18.09	16.6 ± 1.6
S_A-I	81.09	20.48	1.1 ± .1

Values for the heats of transition of the liquid crystal - isotropic liquid transitions are also shown in Table II where it seems the magnitude of the $S_A - I$

latent heat is about five times that of the N-I transition. Also, we note that the latent heat of the S-N transition is the same order of magnitude as it is for 8OCB (4-cyano 4'-octyloxybiphenyl) i.e. very small - so small that the first order character of this transition may be unimportant. In addition, if there were a re-entrant nematic phase for the $n = 8$ compound, then due to the small value for the latent heat we expect it to occur at a pressure of 2 kilobars or less assuming its smectic A layer is packed the same way as it is in 8OCB.(5)

B. Pressure Studies

Fig. 2 and Table II summarize the results of our pressure studies of the melting (open circles), smectic A-nematic (filled squares), nematic-isotropic (open triangles) and smectic A - isotropic (filled circles) transitions.

As a function of pressure, the phase transition lines are very straight and there is no tendency for the nematic - smectic A transition line to curve towards increasing pressure which results, in extreme cases, in the suppression of the smectic A phase under pressure and the re-entrance of the nematic phase.(2, 5) There is, however, the interesting feature of the induced nematic phase for the $n = 10$ compound. At one atmosphere, $n = 10$ exhibits only the smectic A - isotropic liquid crystal transition. At 0.6 kbar and 85°C there is a triple point where the nematic phase first appears and whose temperature range broadens with increasing pressure indicating that it is *increasing repulsive* forces responsible for this induced nematic phase in contrast to the *decreasing attractive* forces proposed(5) as being responsible for the re-entrant nematic phase. That this is the case is demonstrated by extrapolating the nematic-isotropic transition line back to one atmosphere and noting that the transition temperature at zero pressure is 74.06°C whereas the smectic A - isotropic transition temperature at this same pressure is 75.2°C or about a degree higher.

Shashidhar et al(9) were the first to point out and observe pressure induced mesophases. In their work, they were able to induce nematic then smectic phases by increasing the hydrostatic pressure of several compounds which possessed only the ordinary melting transition at one atmosphere. In their observations, the smectic phases always occurred at higher pressures. Here, we have observed that for $n = 10$, the smectic A phase occurs at lower pressure and it is the nematic phase which is induced to appear at larger hydrostatic pressures.

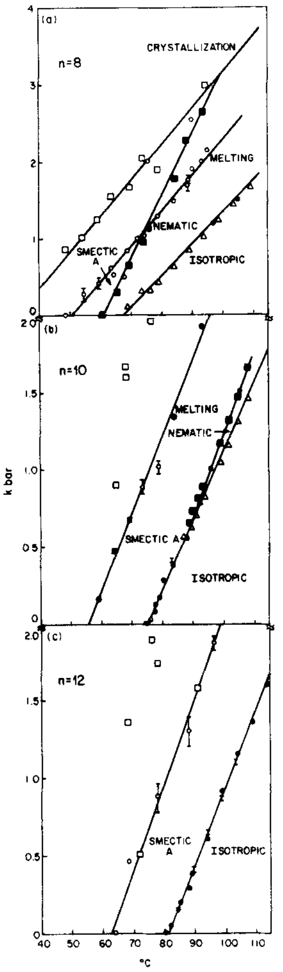


FIGURE 2

The phase transition lines for n = 8, 10 and 12. Open circles delineate the melting transition; filled squares, smectic A-nematic; open triangles, nematic-isotropic and filled circles, smectic A-isotropic. The n = 10 data shows the pressure induced nematic phase.

Table II shows the values for the slopes and zero pressure intercepts of the phase transition lines in Fig. 2 as calculated from the data. An interesting feature is that the magnitude of dT/dP (~ 20°C/kbar) is roughly the same for all transitions except the S_A-N transition of the $n = 8$ nitroester. As has been pointed out by others(10) this value (20°C/kbar) is associated with the melting of the alkanes. For example, dT/dP for the gel transition of phospholipid dispersions is 21°C/kbar whereas for the melting transition of polyethylene dT/dp = 24°C/kbar.

C. X-Ray Measurements

Apart from the values for the layer spacings shown in Table I, we measured the pressure and temperature variation of this parameter for the $n = 10$ compound. We found that the layer spacing decreased ~ 0.1 Å at 70°C when the pressure increased from 0 to 0.6 kbar and it increased ~ .15 Å when the temperature increased from 70°C to 85°C. This kind of behavior is quite typical of smectic A phases.(11)

IV. CONCLUSIONS

We have studied the liquid crystal transitions of 4-nitrophenyl-4'-alkoxy benzoate for $n = 8$, 10 and 12 with a view to understanding how the molecules are packed in the smectic A layers. For the $n = 10$ compound we have discovered a pressure induced nematic phase (Fig. 2). We have argued that this is different from a re-entrant nematic phase and is due to increasing repulsive forces whereas the re-entrant nematic is due to decreasing attractive forces. On this basis then, we expect on a molecular scale that the association of the molecules or the "chemistry" would be different between liquid crystal compounds which exhibit re-entrant behavior in distinction to pressure induced mesophases. We have, therefore, proposed a model (Fig. 1(b)) for the packing of these molecules into smectic A layers which accounts very well for the measured layer spacing and is consistent with estimates of the molecular area as determined from density measurements. Furthermore this model is different from the associated pairs proposed for the cyanoalkoxy compounds which exhibit re-entrant nematic phases.

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