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TEMPERATURE AND PRESSURE STUDY OF $\bar{8}$S5

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ABSTRACT

We have studied the liquid crystal phase transitions of 4-*n*-pentylbenzenethio-4'-*n*-octyloxybenzoate ($\bar{8}$S5) as a function of pressure and temperature. There were no pressure induced anomalies. We measured the latent heat at the N-I transition (.5±.1 calories/gram) but were not able to observe any evidence of a latent heat for both the A-N and C-A transitions. We speculate that the continuous nature of these transitions may be linked to the flexibility of the polar part of $\bar{8}$S5.

INTRODUCTION

Recently it was found that the nematic-smectic A (N-A) transitions occurring in the cyanoalkoxy or cyanoalkyl (Schiff base) compounds exhibited the phenomena of re-entrance.(1) That is, as a function of increasing pressure or decreasing temperature, the sequence of phase transitions was nematic-smectic A-nematic. The lower temperature or higher pressure nematic is called re-entrant and appears to be in every way identical to the higher temperature or lower pressure nematic phase.(1-3)

A curious feature of the re-entrant transitions is that the maximum pressure or maximum concentration of a shorter homologue for which the (bilayer) smectic A phase of these compounds(4) is stable was found to be very close to a tricritical point when applying McMillan's criterion(5) (the ratio of the N-A transition temperature (T_{NA}) to the nematic-isotropic transition temperature

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(T_{NI})). At these unusual points in the phase diagram, T_{NA}/T_{NI} was very close to .88 which is the value expected by McMillan for a cross-over from a first order N-A transition ($T_{NA}/T_{NI} > .88$) to a second order ($T_{NA}/T_{NI} < .88$) one. The question that then occurred was: is the N-A transition necessarily of first order since approaching a second order transition in bilayer smectic A's led to re-entrance and the ultimate instability of the A phase. For this reason then, we decided to test whether the compound $\bar{8}$S5 (4-*n*-pentylbenzenethio-4'-*n*-octyloxybenzoate) exhibited re-entrance since specific heat measurement(6,7) of this compound indicated that the N-A transition was very likely to be of second order. As we will show, the answer to the question turns out to be no. $\bar{8}$S5 has no re-entrant nematic phase but it has the interesting new feature of a flexible aromatic part which we speculate may contribute to the continuous character of its transitions - particularly the nematic to smectic A transition.

MOLECULAR STRUCTURE AND TRANSITIONS OF $\bar{8}$S5

The molecular structure of $\bar{8}$S5 and a scale model is shown in Fig. 1. Its transitions as determined by light microscopic observations as a function of temperature were:

$$\begin{tikzcd}
\text{Crystal} \arrow[r, "57.6\text{-}58.0^\circ\text{C}"] & S_A \arrow[r, leftrightarrow, "62.5\text{-}62.6^\circ\text{C}"] \arrow[d, leftrightarrow, "55.3\text{-}55.5^\circ\text{C}"] & N \arrow[r, leftrightarrow, "85.6\text{-}85.9^\circ\text{C}"] & I \\
S_{(\text{mosaic})} \arrow[u, "\sim 21.3^\circ\text{C}"] \arrow[r, leftrightarrow, "30.3\text{-}30.5^\circ\text{C}"] & S_C & &
\end{tikzcd}$$

The material had been recrystallized from absolute ethanol three times.

In Fig. 1(b) we show that the polar part of the molecule is quite flexible due to the presence of a single rather than a double bond between the carbonyl carbon atom and the sulfur atom which makes rotation around the bond possible (although complete rotation is hindered). It is unlikely to occur around the aromatic-carbonyl or the aromatic-sulfur link because of electron overlap with the rings. The flexibility shown in Fig. 1b clearly decreases the smectic A layer spacing should this conformation exist in any appreciable amounts. (b) is much less planar than (a) but conformations between (a) and (b) probably exist.

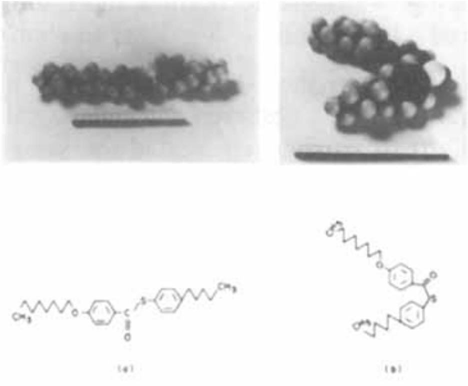

Fig. 1 Scale model of $\bar{8}$S5. In (a) (the left-hand photo) the model is nearly fully elongated whereas in (b) the pentyl-benzene group has been rotated about the sulfur bond to demonstrate that the polar region - the part of the molecule between the two hydrocarbon chains is quite flexible. The scale is 1cm = 1Å. The scale in the foreground is 15cm. long.

We speculate that this flexibility may be a contributing factor to the continuous nature of the liquid crystalline transitions. Recall that in McMillan's original theory(5) second order qualities of the N-A transition are enhanced when the orientational (nematic) order saturates and/or the layer spacing decreases. Reducing the layer spacing by simply tilting the molecules in the layers implies a reduction in orientational order for smectic A's(8) and so would not have any clear consequences on the nature of the nematic-smectic A transition. The flexible polar part of $\bar{8}$S5, however, suggests a new internal degree of freedom whereby layer spacing is decreased without a concomitant reduction in the strength of the nematic ordering. This new mechanism then *could* affect the order of the N-A transition and may be responsible for the minute discontinuity observed at the N-A transition of this compound.

DSC MEASUREMENT

19.1 mg of $\bar{8}$ S5 was used in a Perkin Elmer Differential Scanning Calorimeter (DSC-1B) to determine heats of transition. The calorimeter was calibrated using the melting transition of 1.172 mg Indium.

For $\bar{8}$S5, we found two melting transitions. One at ~53° another at 59° with measured areas under the curves or latent heats ~3.06±.2 and 7.82± 1.4 calories/gm. Due to the closeness in temperature of the two transitions, these are estimated values for the individual peaks. The total area under both peaks was ~ 10.9 calories/gm.

On continued heating, we observed nothing more until ~ 88°C, where the N-I transition produced a latent heat ~ .5 ± .1 calories/gm.

Cooling, we observed again the I-N transition then nothing more until ~ 22° where another transition was observed ~ .97 ± .02 calories/gm. If we only cooled to below 15°C, then immediately heated the sample, this transition was reversible. Cooling below 15°C resulted in another peak at 3°C of ~ 1.42 ± .05 calories/gm and cooling below zero degrees then reheating, we observed again the multiple melting at 53°C and 59°C.

We do not wish to discuss further the complex low temperature transitions. These deserve further study. We only wish to point out that using 19.1 mg and the DSC we were not able to observe any sign of the C-A or A-N transition and conclude that the latent heat associated with these transitions must be smaller than .03 cal/gm and certainly smaller than for example 8OCB (cyano-octyloxybiphenyl) for which we measure a latent heat .1 calories/gm and which has a re-entrant pressure ~ 2.1 kbars.(9)

PRESSURE STUDIES

For these measurements were used the optical microscope pressure bomb(10 and observed the N-I, A-N and (supercooled) C-A transitions. Our data is shown in Fig. 2 and summarized in Table I.

TABLE I: Parameters found from fitting the data of Fig. 2 to the form $T_c = T_0 + (dT/dP)P$ where T is in °C and P in kbars. L is the latent heat taken to be the area under the curves of a DSC measurement at 1 atmosphere only.

Transition	T_0 (°C)	dT/dP (°C/kbar)	L (cal/gm)
A-C	54.7	16.10	<.03
N-A	61.7	20.12	<.03
I-N	85.3	30.14	.5 ± .1

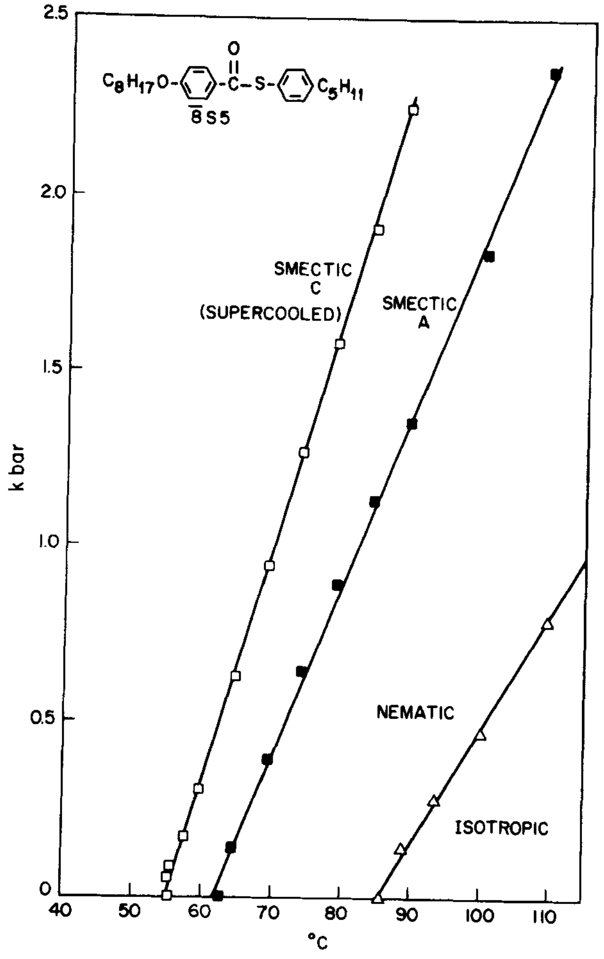

Fig. 2 The N-I, A-N and A-C (supercooled) transition lines as a function of pressure (kbar) and temperature (°C).

The phase lines appear to be unusually straight even for the A-N transition and absolutely no evidence of a tendency toward re-entrance is detected below 2.5 kbar. It may be interesting to pursue this to greater pressures but since the maximum pressure at which the smectic phase is stable is smaller the smaller the latent heat at one atmosphere(9); given that the latent heat at one atmosphere is very small, we would expect a maximum pressure well below 1 kbar. Thus, though the N-A transition is "second-order", $\bar{8}$S5 does not show a re-entrant nematic phase.

X-RAY MEASUREMENTS

We measured the layer spacing of $\bar{8}$S5 in the A phase and found it to be consistent with a monomolecular packing of the layers. Fully extended (see Fig. 1) the molecule measures about 31Å. In Fig. 1(a), it is about 28Å due to the fact that the pentyl-benzene group has been slightly rotated about the sulfur bond. This is in order to show that the measured smectic A spacing of 28Å (see Table II) is compatible with one molecular length.

The results of the x-ray measurements are summarized in Table II. The measurements were made with decreasing temperature from the A phase. At 34°C, the crystal phase observed at 25°C re-appeared.

CONCLUSION

Although the N-A transition of $\bar{8}$S5 is to within existing experimental error a continuous one,(6) we have observed no anomalies in its N-I, A-N and A-C transitions as a function of pressure and temperature. The measured layer spacing of the A phase of $\bar{8}$S5 is consistent with a monomolecular smectic A phase (as opposed to a bilayer smectic A phase). The continuous nature of the A-N transition may be linked to the flexibility of the polar part of this molecule since this additional degree of freedom decreases the layer spacing without necessarily reducing the orientational order.

TABLE II: Summary of X-ray measurements. The lattice parameter measured in the A and C phases are the layer spacings. d_1 and d_2 refer to the first and second order diffraction whenever the second order is observed. It can be seen by a comparison with Fig. 1(a) that the layer spacing of the A phase of $\bar{8}S5$ is smaller than the fully extended length of the molecule.

Phase	Temp (°C)	Lattice parameters Å
crystal	25	$d_1 = 25.8$ $d_2 = 12.07$
A	61	28.29
	59	28.05
C	49	27.29
	44	26.94
	38	$d_1 = 26.70$ $d_2 = 13.39$

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