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Pressure Studies on $\overline{7}S5$, $\overline{8}S5$ and Their Mixtures†

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Pressure studies have been taken up on heptyloxy-p′-pentylphenylthiobenzoate ($\overline{7}S5$), octyloxy-p′-pentylphenyl thiobenzoate ($\overline{8}S5$) and their mixtures. It is observed that the range of the smectic A phase increases with increasing pressure with an accompanying decrease in the smectic C range. Thus, although two kinds of triple points, *viz.*, crystal-smectic C nematic and smectic (mosaic)–smectic C–smectic A have been observed in the P–T diagrams of $\overline{7}S5$ and $\overline{8}S5$, the NAC point observed in the temperature-concentration diagram of binary mixtures of $\overline{7}S5$ and $\overline{8}S5$ at the 42.5% concentration of $\overline{7}S5$ could not be observed in the P–T diagram of either the pure compounds or the mixtures, whose concentrations were chosen on either side of the critical 42.5% concentration. These studies also show that pressure has the effect of increasing the stability of the monolayer smectic A in contrast to the case of the bilayer smectic A wherein pressure destabilizes the layer causing the nematic phase to reenter.

INTRODUCTION

Based on their differential scanning calorimetric (DSC) and microscopic observations Johnson, *et al.*,[1] reported that the temperature-concentration diagram of binary mixtures of heptyloxy-p′-pentylphenylthiobenzoate ($\overline{7}S5$) and octyloxy-p′-pentylphenylthiobenzoate ($\overline{8}S5$) has a multicritical NAC point at 42.5% concentration of $\overline{7}S5$, this point being the point at which the nematic-smectic A, smectic A–smectic C and nematic–smectic C phase boundaries intersect. Subsequent to this observation, several experimental studies[2–4] have been performed on the $\overline{7}S5/\overline{8}S5$ system to elucidate the nature of this point. We have carried out pressure studies on

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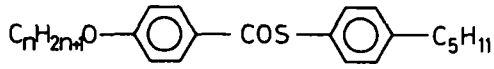
these compounds and their binary mixtures for several reasons: (i) to investigate whether the NAC point observed in the temperature-concentration diagram of these substances can also be observed in the P–T diagram since it is well known that most of the effects like tricritical behavior,[5] reentrant phenomenon[6] observed in binary mixtures by varying concentration can also be observed in a single component system by varying pressure;[7–11] (ii) to study the effect of adding a heavy atom (*viz.*, sulphur) in the linkage group on the stability of various mesophases under pressure; (iii) to see if these compounds which have a practically second order smectic A–nematic transition show the phenomenon of reentrance.

THE COMPOUNDS

The samples of $\bar{7}S5$ and $\bar{8}S5$ used in our pressure studies were kindly given to us by Professor Heppke. These disubstituted phenylthiobenzoates were first synthesized by Reynolds *et al.*,[12] with a view to study the mesomorphic stability when an oxygen atom is replaced by sulphur in the ester linkage of benzyl benzoates. They have the following structural formula:



The transition temperatures as well as the heats of transition (ΔH) for the pure compounds are given in Table I. The transition temperatures of the three mixtures studied are given in Table II (ΔH has not been determined for the mixtures). The concentration of the mixtures (34%, 40% and

TABLE I

Transition temperatures and heats of transition (ΔH) of $\bar{7}S5$ and $\bar{8}S5$

Compound	Transition	Temperature (°C)	ΔH (kJ/mole)	dT/dP (°C/kbar)
$\bar{7}S5$	*K–N*	54.5	29.47	25.9
	N–I	83.0	1.08	42.9
	N–C	(36)	0.26	17.8
$\bar{8}S5$	*K–A*	59.0	34.68	26.7
	A–N	63.0	0.09	23.2
	N–I	86.5	1.30	43.2
	A–C	(55.5)	~0	14.0
	C–S_{mosaic}	(31)	2.89	17.1

( ) Monotropic transition

K–crystal, *N*–nematic, *I*–isotropic, *A*–smectic A, *C*–smectic C, S_{mosaic}–smectic (mosaic).

TABLE II

Transition temperatures of the binary mixtures of $\bar{7}S5$ and $\bar{8}S5$

Molar concentration ($\bar{7}S5$ in $\bar{8}S5$)	Transition	Temperature (°C)
34%	*C–A*	52.0
	A–N	53.0
40%	*C–A*	48.0
	A–N	48.5
45%	*K–C*	46.4
	C–N	49.0

45% $\bar{7}S5$) have been chosen on either side of the critical 42.5% concentration for which the NAC point exists at 1 bar. The transition temperatures as well as the heats of transition are in good agreement with those determined by previous workers.[13–15] $\bar{7}S5$ exhibits a nematic phase in addition to the monotropic smectic C phase. On the other hand, $\bar{8}S5$ exhibits nematic and smectic A phases both of which are enantiotropic and, in addition, it also shows two monotropic smectic phases, *viz.*, smectic C and a hitherto unidentified higher order smectic which exhibits a pronounced mosaic texture.[15] As regards the mixtures, both the 34% and 40% mixtures show smectic C, smectic A and nematic phases while the 45% mixture exhibits only the smectic C and nematic phases.

EXPERIMENTAL

The phase transitions were determined by optical transmission technique. An optical high pressure cell with sapphire windows was used for the experiments. The details regarding the experimental set up have already been published[16,17] and will not be repeated here. Pressures were measured to an accuracy of ±10 bars and temperatures to ±0.025°C.

RESULTS AND DISCUSSION

The P–T diagrams of $\bar{7}S5$, $\bar{8}S5$ and their mixtures are given in Figures 1–5.

$\bar{7}S5$: All the phase boundaries are practically straight. The range of the monotropic smectic C decreases with increasing pressure and finally the smectic C–nematic line joins the crystallization line. Thus the smectic C phase is bounded with a resulting crystal–smectic C–nematic triple point at 1.61 kbar, 62.0°C.

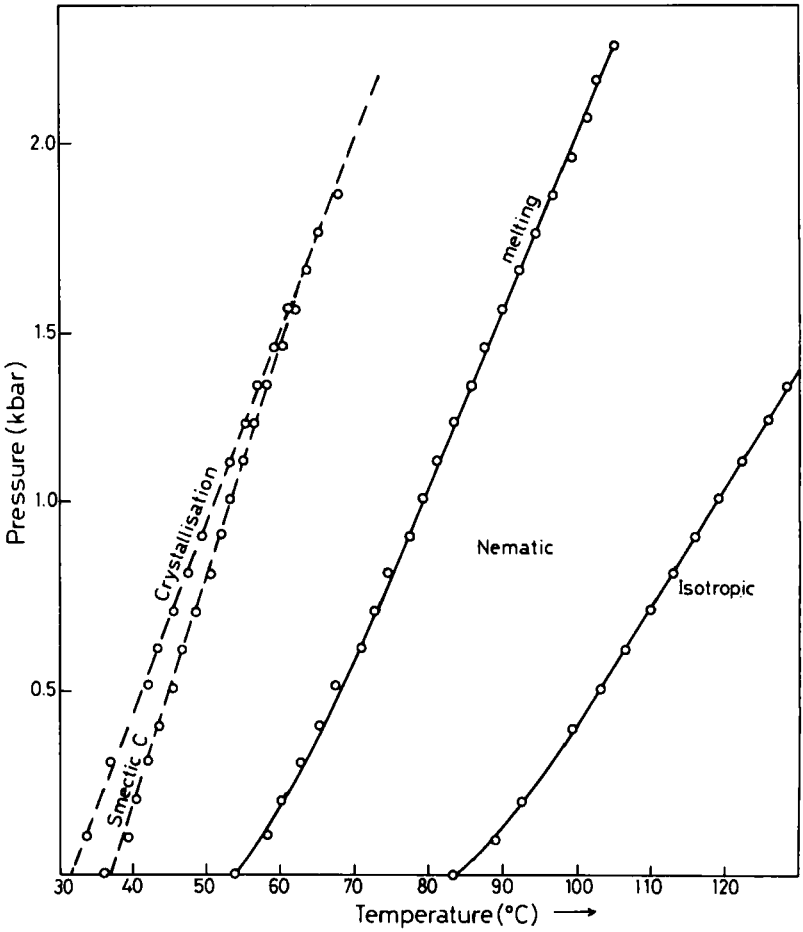


FIGURE 1 P–T diagram of $\bar{7}S5$.

$\bar{8}S5$: The smectic A–smectic C as well as the smectic C–smectic mosaic phase transitions remain monotropic throughout (Figure 2). It is interesting to note that there is a rather steep increase in the smectic A range (in the cooling mode) which is accompanied by a decrease in the range of the

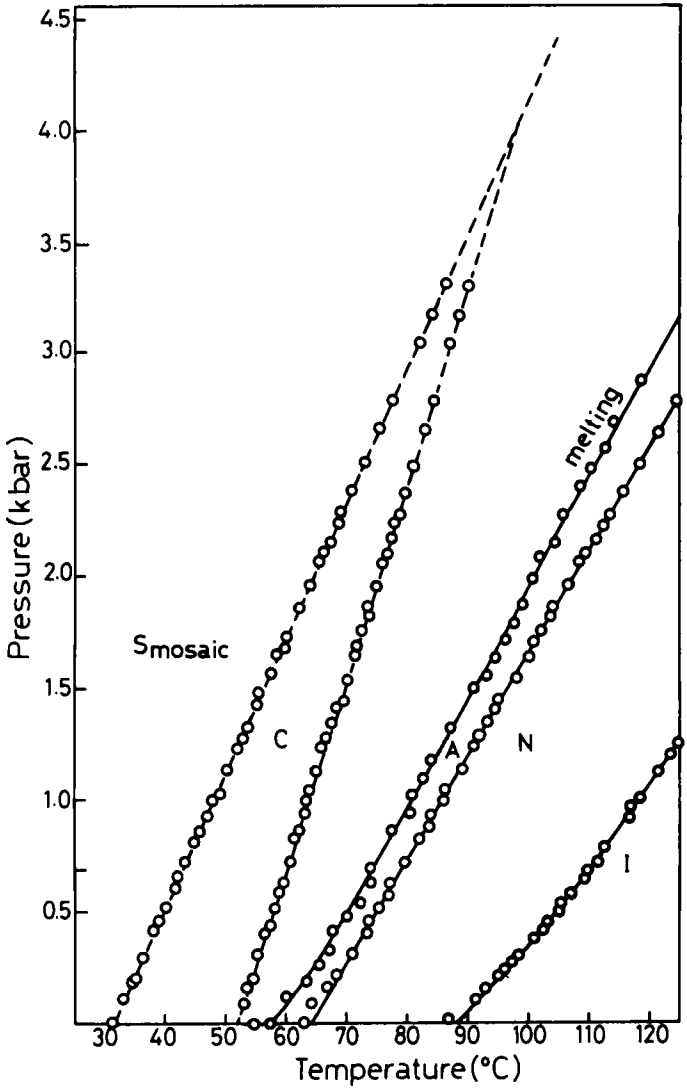


FIGURE 2 P–T diagram of $\bar{8}S5$.

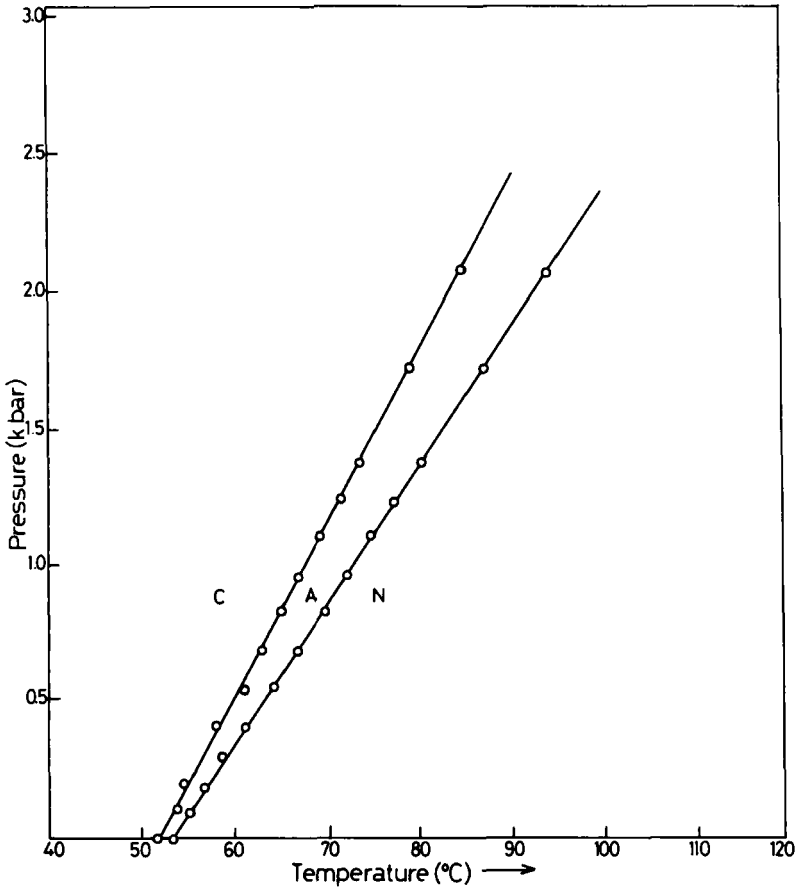


FIGURE 3 P–T diagram of 34% mixture of $\bar{7}S5$ in $\bar{8}S5$.

smectic C. The C phase is ultimately bounded resulting in a $\text{smectic}_{\text{mosaic}}$–smectic C–smectic A triple point at 4.1 kbar and 65.0°C. Thus it was not possible to observe the NAC point in the P–T diagram of $\bar{8}S5$. It must be pointed out that Cladis, *et al.*,[18] have also studied this compound as a function of pressure up to 2 kbar. The latent heat associated with the *A*–*N*

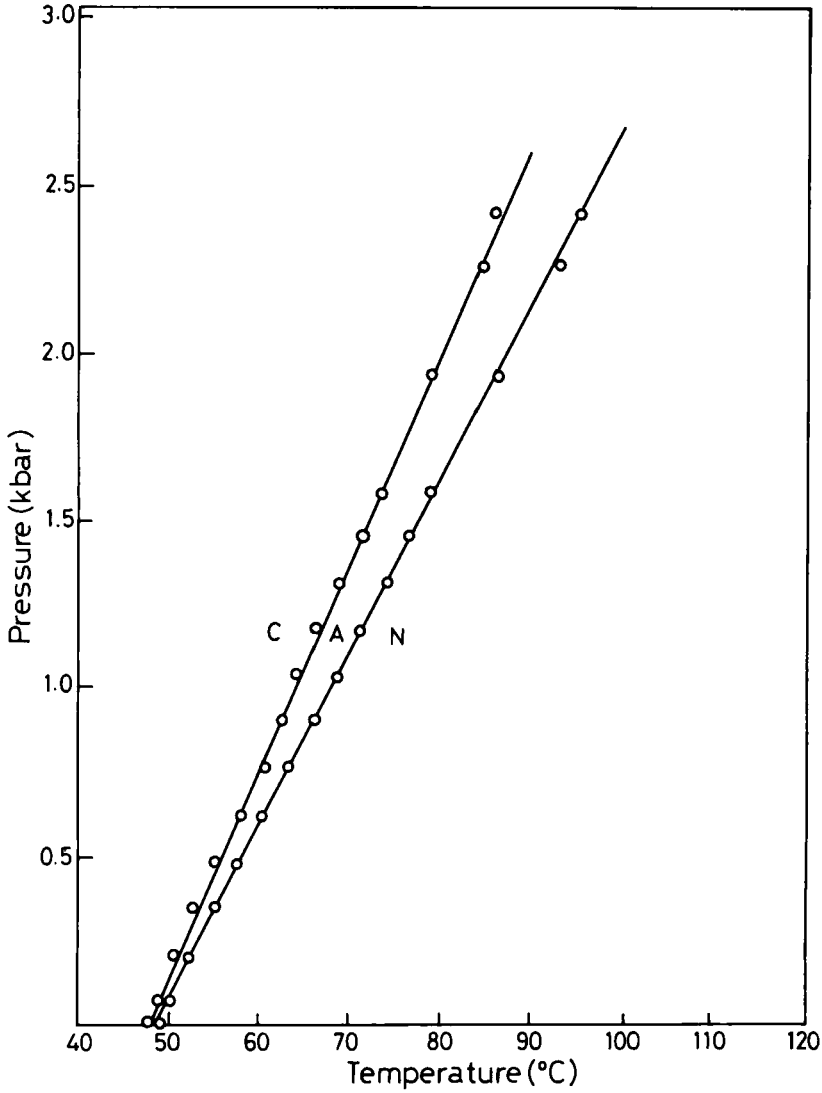


FIGURE 4 P–T diagram of 40% mixture of $\bar{7}S5$ in $\bar{8}S5$.

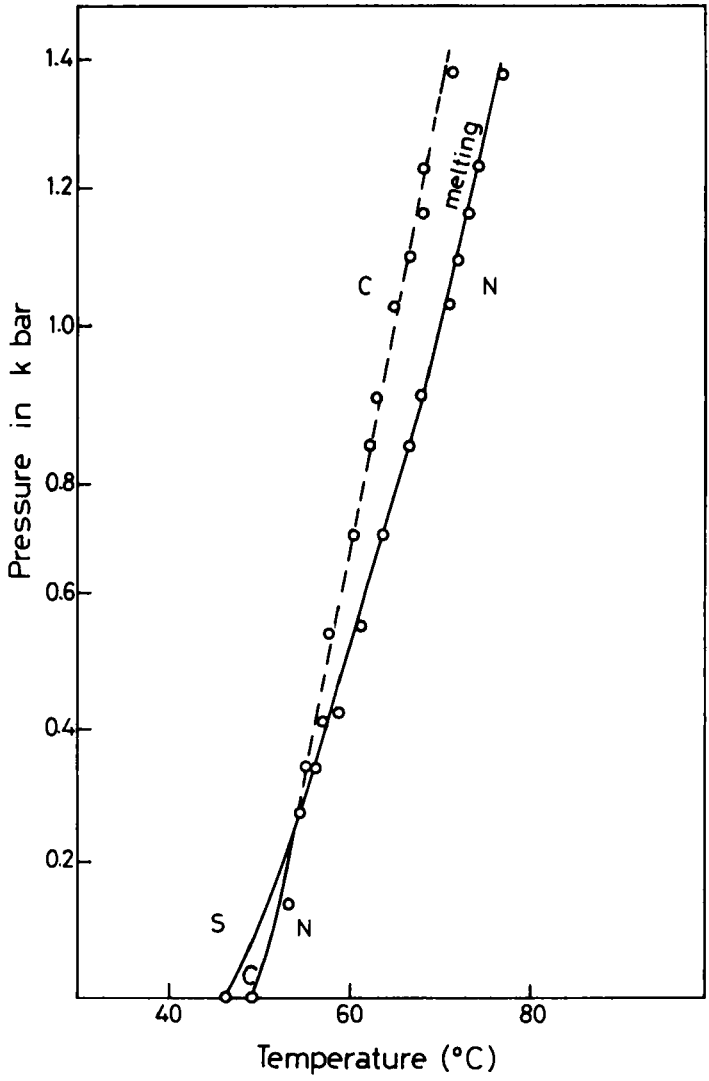


FIGURE 5 P–T diagram of 45% mixture of $\bar{7}S5$ in $\bar{8}S5$.

transition is very small which is attributed to a flexible aromatic part of $\bar{8}S5$. This led Cladis, *et al.*, to carry out pressure studies on this compound in order to see if the compound exhibits reentrant behavior. Our studies have shown that the *A–N* transition does not show any sign of curvature towards the pressure axis. In other words, there is no sign of reentrance even up to 4.2 kbars. Since X-ray studies of Cladis, *et al.*,[18] have shown that the smectic A phase of $\bar{8}S5$ has a monolayer periodicity, we can, therefore, conclude that a bilayer is essential for the reentrant nematic phase to appear.

Binary mixtures of $\bar{7}S5$ and $\bar{8}S5$: As mentioned earlier, pressure studies were undertaken for three binary mixtures whose molar concentrations are close to the critical concentration for which the NAC point is observed in the temperature-concentration diagram. For both the 34% and 40% mixtures, the range or the stability of the smectic A shows a monotonic increase with increasing pressure, thereby precluding the possibility of observing the NAC point. In the case of the 45% mixture there is no smectic A phase at 1 bar nor could it be induced at high pressures. Even the C phase which exists at 1 bar gets bounded in the heating mode and appears beyond 0.22 kbar only as a monotropic phase.

The dT/dP values for the various transitions of $\bar{7}S5$, $\bar{8}S5$ and their mixtures are listed in Table II. As mentioned earlier, $\bar{8}S5$ has also been studied by Cladis, *et al.*[18] It is to be noted that our values of dT/dP for the *C–A* and *A–N* transitions, 14.0°C/kbar and 23.2°C/kbar respectively agree fairly well with those obtained by Cladis, *et al.*, (16.1°C/kbar and 20.1°C/kbar). However, our value of dT/dP for the *N–I* transition which is 43.2°C/kbar differs very much from that of Cladis, *et al.*, (30.1°C/kbar). This rather large difference is perhaps attributable to the discrepancy in the measured heat (ΔH) for this transition at atmospheric pressure. The ΔH value reported by Cladis, *et al.*, is 0.87 kJ/mole while for our sample it is 1.30 kJ/mole although the transition temperatures are practically the same in both the cases.

SUMMARY

The results can therefore be summarized as follows: (i) for both the pure compounds and the mixtures the range of the smectic A phase increases with increasing pressure and hence an NAC point could not be observed;

(ii) the increase in stability of the smectic A phase is accompanied by a decrease in the range of the smectic C phase which is finally bounded at high pressures; (iii) the A–N phase boundary is straight and does not show any curvature towards the pressure axis and hence no reentrant behavior is seen.

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