

CHAPTER IV

HIGH PRESSURE STUDIES ON 4 '-n-ALKYL-4-CYANOBIPHENYLS

1. Introduction:

The importance of liquid crystals with strong positive dielectric anisotropy was brought to focus by the observation of the twisted nematic effect by Schadt and Helfrich (1) which resulted in the development of a new type of electro-optic device. (2-3) Liquid crystals with large positive dielectric anisotropy are obtained by incorporating a strong dipole moment along the long molecular axis; for example, the presence of a C = N end group contributes 4.05 debye (4) to the parallel component of the dipole moment of the molecule. 4 '-n-alkyl-4-cyanobiphenyls (nCB) synthesized by Gray et al (5) suit these requirements. Ever Since their synthesis and the realization of their synthesis and the realization of their suitability for display device, these compounds have been the subject of a variety of experimental investigations like orientational order and birefringence measurements, (6) dielectric studies X-ray studies, (8-9) etc. A study of nCB under pressure is therefore of considerable interest. We have undertaken a systematic study of the effect of pressure on the phase transitions in four successive members ($n = 5, \dots, 8$) of this series.

2. Experimental

The transition temperatures (at atmospheric pressure) of the compounds used, as determined from Mettler FP-52 hot stage, and FP-5 temperature control, are given in table I. Their structural formulae are given in figure 1. 5CB, 6CB and 7CB used in our chemistry laboratory, and 8CB was obtained from BDH England. The transition temperatures given in table I agree very well with those reported by Gray et al. (5)

The cell used for these experiments has already been described in chapter II. It must be mentioned here, however, that these compounds are extremely stable chemically; nevertheless after the completion of each experiment it was ascertained that the transition temperatures were the same as those determined before the commencement of the experiment. The transition temperatures at any pressure could be reproduced to an accuracy of 1.5C for the nematic-isotropic (N-I) and smectic A-

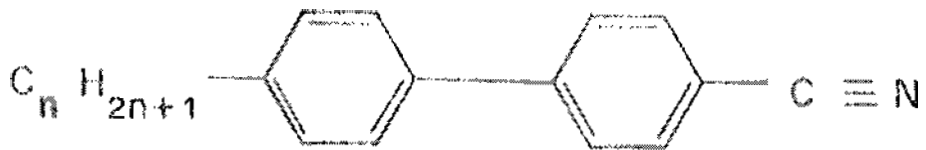
nematic (A-N) transitions, but the error was found to be somewhat greater for the solid – mesophase transition, probably because of the broader nature of the transition. All the transition temperatures were recorded in the heating mode only.

For 5CB, experiments were carried out using three different cells and the data from the three independent set of measurements were self consistent confirming the reproducibility of the measurements. It was therefore thought sufficient to carry out only one set of experiments each for both 6CB and 7CB. For 8CB, however, since our interest was to investigate the possibility of it's A-N transition showing tricritical behaviour, the experiments were done in a more elaborate manner. From two initial experiments, its was ascertained that the A-N transition does become weak beyond about 2.5 kbar, while a third experiment in which the pressure was varied by very small intervals, pin pointed the tricritical point.

STRUCTURAL FORMULA

OF

4'-n-alkyl-4-cyanobiphenyls.



(n = 5, -----8).

Figure 1

3. Results and Discussions

A. Phase Diagrams

a) **4'-n-Pentyl-4-cyanobiphenyl (5CB)** : The transition temperatures were determined at different pressures going up to a maximum of 3.3 kbar. The data are given in table II and the phase diagram in figure 2. This phase diagram represents the simplest type of liquid crystal phase diagram with general features which are common to a number of compounds studied so far, i.e., the phase diagram tends to curve towards about 12^o.5 C at atmospheric pressure, becomes about 50^oC at 3.5 kbar, an almost four fold increase. Such a large increase of nematic range with increase of pressure indicates a much higher stability of the nematic phase at higher pressures. A similar four to five fold increase in the range of the nematic phase was observed for another cyano compound, viz., p-cyanobenzylidene (CBNA) by McKee and Mc Coll. ⁽¹⁰⁾. In the case of compounds like PAA ^(11,12) and 4-methoxybenzylidene-4'-butylaniline (MBBA), ^(12,13) the rate of increase of the nematic range with pressure is very less. This is perhaps due to the difference in the molecular associations between compounds like PAA and the cyano compounds, the latter being known to process a bilayer structure. The dT/dP for the S-N and N-I transitions are 25^o.65 C/kbar and 37^o.48 C/kbar respectively, which agree well with those of horn ⁽¹⁴⁾ who obtained 28^o.4 C/kbar and 37^o.2 C/kbar from the refractive index measurements.

b) **4'-n-Hexyl-4-cyanobiphenyl (6CB)**: The data for this compound are presented in table III and the phase diagram in figure 3. The addition of an extra CH₂ end group to 5CB, has a marked effect on the transition temperature of this compound at atmospheric pressure. Both S-N and N-I transition temperatures are appreciably lower than 5CB. The range of the nematic phase (15^o C) in 6CB, however, is still comparable to the nematic range of 5 CB (12^o.5 C) at atmospheric pressure. On the other hand, at higher pressures, the increase of the nematic range is much less pronounced for 6CB. Also the phase boundaries appear to be almost exactly straight right up to 1.7 kbar. The dT/dP of the S-N and N-I transitions are 25^o.4 C/kbar and 31^o.75 C/kbar respectively.

c) **4'-n-Heptyl-4-cyanobiphenyl (7CB)**: The table IV gives the transition temperatures determined at different pressures for this compound and the data are plotted in the figure 4. Here again the increase of the nematic range with pressure is more pronounced and the phase diagram resembles that of 5CB rather than that of 6CB. The dT/dP for the S-N and N-I transitions are respectively $24^{\circ}.7 \text{ C/kbar}$ and $47^{\circ}.43 \text{ C/kbar}$. Considering that the higher homologue, viz., 8CB, has a smectic A phase, the possibility of inducing a smectic A phase in 7CB was probed by using different sensitivities, but did not prove to be successful.

d) 4'-n-Octyl-4-cyanobiphenyl (8CB): As discussed earlier, this compound has a smectic A phase at atmospheric pressure. The data at different pressures are given in table V. and the phase diagram in figure 5. The smectic A phase is seen to reduce at higher pressures, whilst the range of the nematic phase increases. Also; the A-N phase boundary has a positive slope throughout in contrast with the behaviour of other cyano compounds studied earlier. We shall make a detailed comparison at the end of this section. After the completion of these experiments we learnt that Liebert and Daniels⁽¹⁵⁾ and also Cladis et al.⁽¹⁶⁾ have studied this compound. Liebert and Daniels have found that smectic A phase disappears with a solid-smectic A-nematic triple point at 3 kbars and 94° C , while Cladis did not observe any such triple point even up to 4 kbars. Cladis has attributed this difference in behavior to the rather impure sample used by Liebert and Daniels. We could not either confirm or contradict the observation of Liebert and Daniels, since it was not possible to detect the A-N transition at pressures beyond 2.78 kbar, the transition having become second order. We shall discuss this aspect of our experiment later. The dT/dP evaluated from the experimental P-T diagram (figure 5) are $24^{\circ}.11 \text{ C/kbar}$ for the S-Sm_A transition, $30^{\circ}.4 \text{ C/kbar}$ for the A-N transition and $36^{\circ}.0 \text{ C/kbar}$ for the N-I transition. Since data on both volume change at transition (ΔV) and heat of transition (ΔH) are available for 8CB, we shall compare the experimental dT/dP values with those evaluated from the Clausius-Clapeyron equation. So far there have been three measurements of ΔH for 8CB. These are due to Karat,⁽¹⁸⁾ Leadbetter et al.⁽¹⁹⁾ and Liebert and Daniels.⁽¹⁵⁾ Their values agree with one another fairly well. Taking the average of these three measurements and the ΔV values of

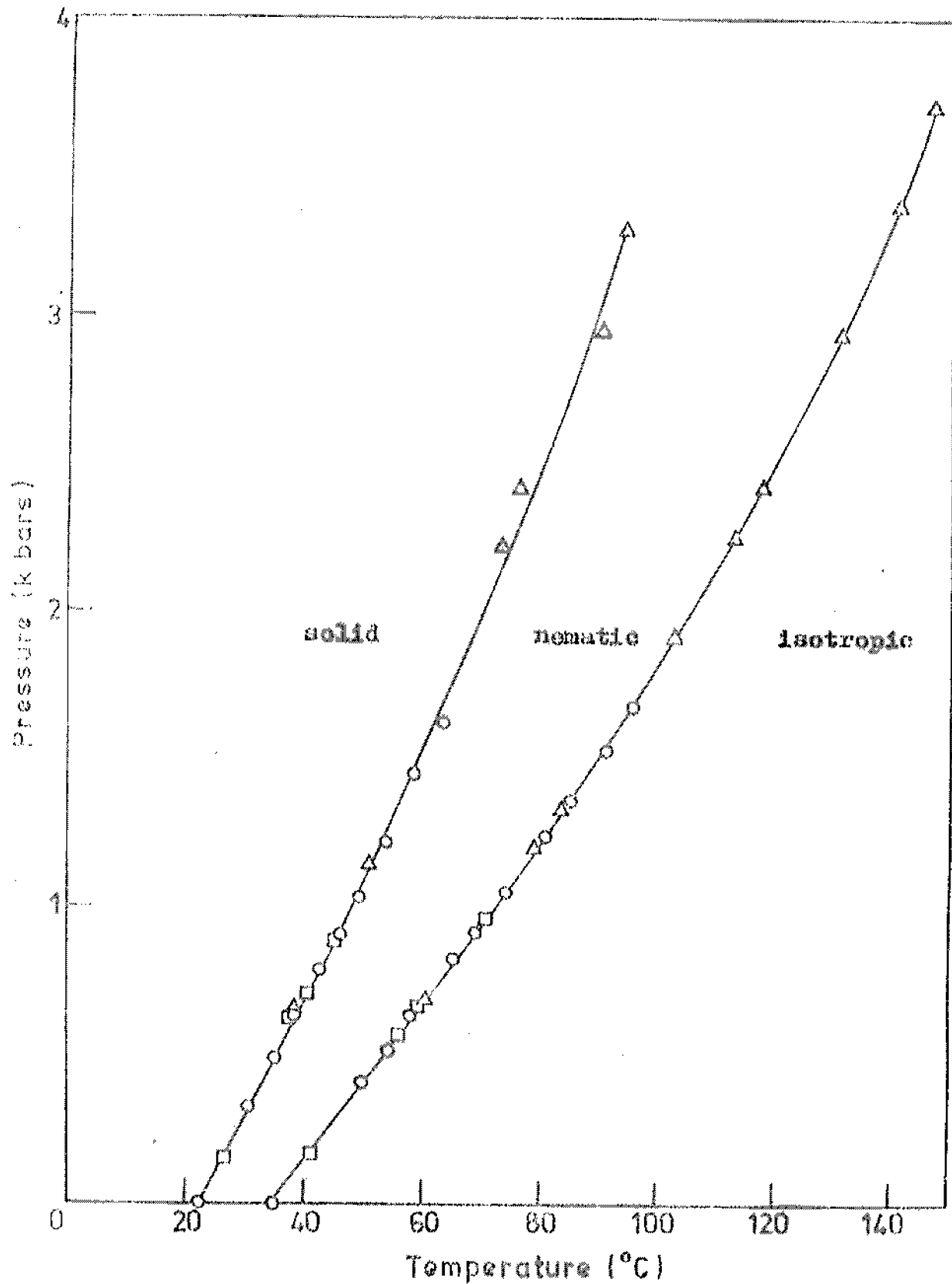


Figure 2: Phase diagram of 4'-n-pentyl-4-cyanobiphenyl
 Δ , \circ and \square represent three independent sets of measurements.

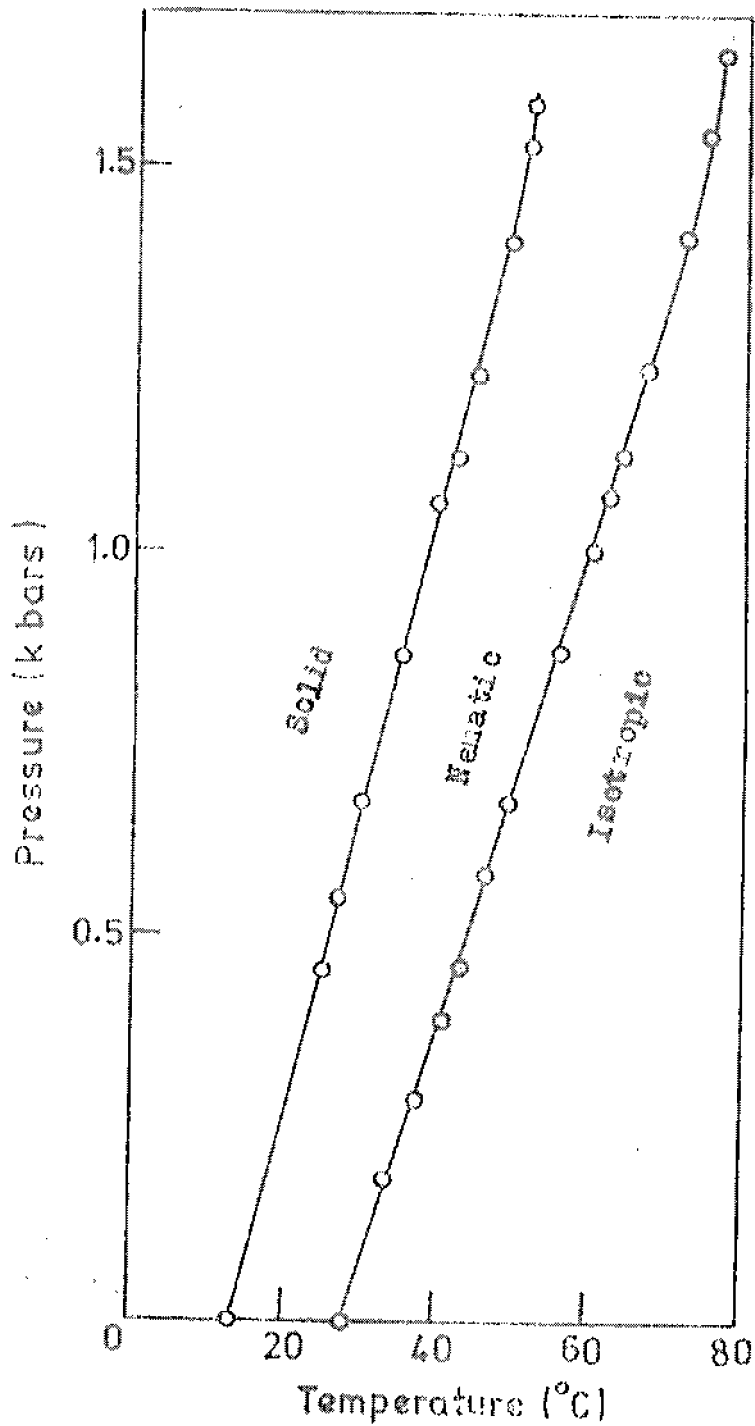


Figure 3: Phase diagram of 4'-n-hexyl-4-cyanobiphenyl

Leadbetter et al, we get slopes to be $28^{0.1}$ C/kbar and $38^{0.2}$ C/kbar (No calculation could be made for solid-smectic A transition owing to the non-availability of V data for this transition). These values compare very well with experimental values of dT/dP showing the validity of the Clausius-Clapeyron equation for both A-N and N-I transitions.

B. Comparison of the phase diagrams of **nCB** with those of other cyano compounds

There have been some high pressure studies on similar cyano compounds. They are the early work on CBOOA by Lin et al, ⁽¹⁹⁾ NMR study of cyanobenzylidene nonylaniline (CBNA) by McKee and McColl, ⁽¹⁰⁾ and more recently on 8 OCB by Cladis et al. ⁽²⁰⁾ The molecular formulae of these compounds are given in figure 6 along with the molecular formulae of **nCB** for comparison. It is seen that all these compounds have only subtle difference in their molecular structure. However this subtle alteration appears to have an enormous influence on the nature of their phase diagrams [see figures 7 (a), (b) and (c)]. The difference between CBOOA and CBNA is the extra oxygen in the end chain of the former in addition to an extra CH₂ group. The phase diagrams however look completely different. The A-N phase boundary in CBOOA has a negative slope throughout indicating that the nematic phase, along this portion of the phase boundary must be denser than the smectic A phase. The phase diagram of CBNA (figure 7b), however, shows a positive slope throughout the pressure range studied for both the A-N

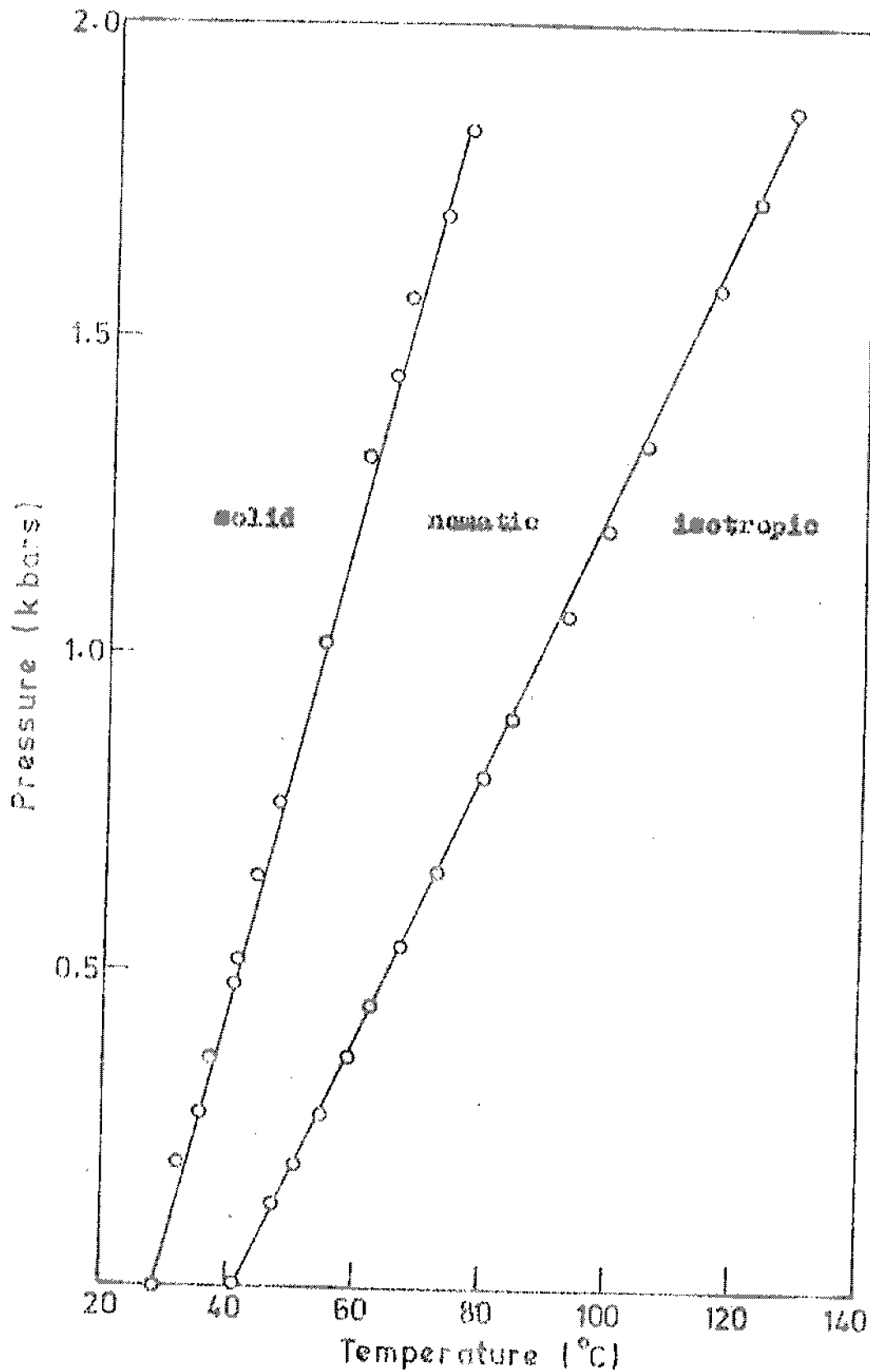


Figure 4: Phase diagram of 4'-n-heptyl-4-cyanobiphenyl

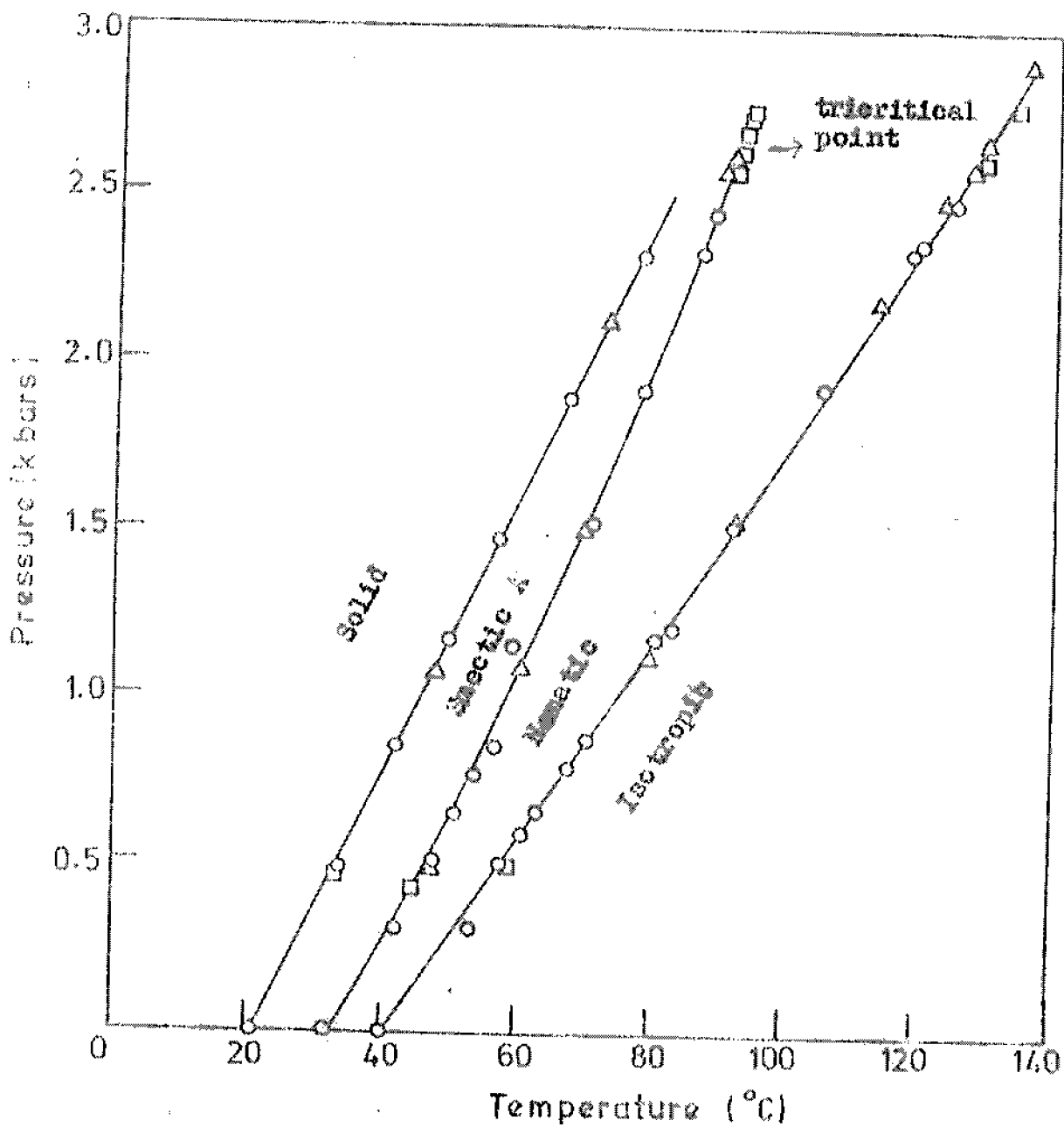
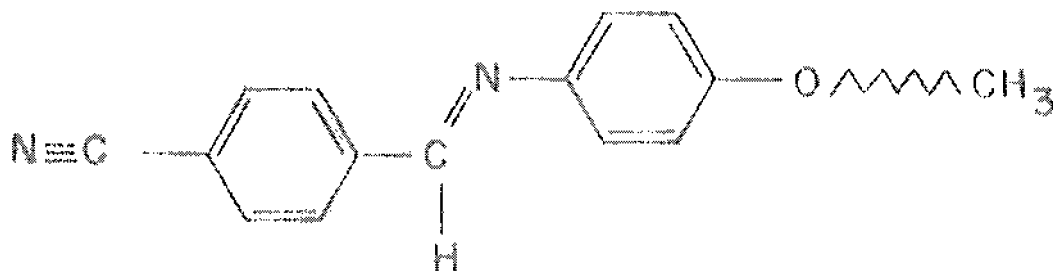
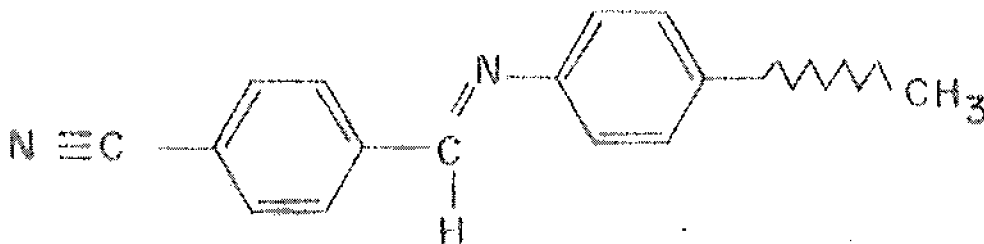


Figure 5: Phase diagram of 4'-n-octyl-4-cyanobiphenyl
 Δ, ○ and ◻ represent three independent sets of measurements.

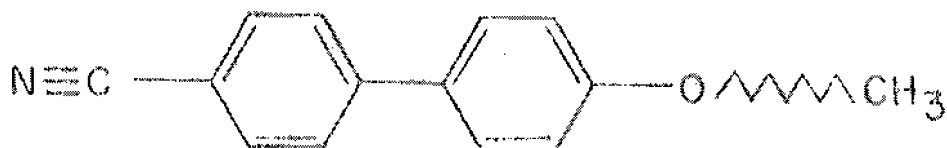
N-P-Cyanobenzylidene - p'- Octyloxyaniline. (CBOOA)



N-P-Cyanobenzylidene - p'- Nonylaniline. (CBNA)



4 - Cyano - 4' - Octyloxy biphenyl (BOCB)



4 Cyano - 4'-Octylbiphenyl (BCB)



Figure 6: Molecular formulae of compounds having cyano end groups

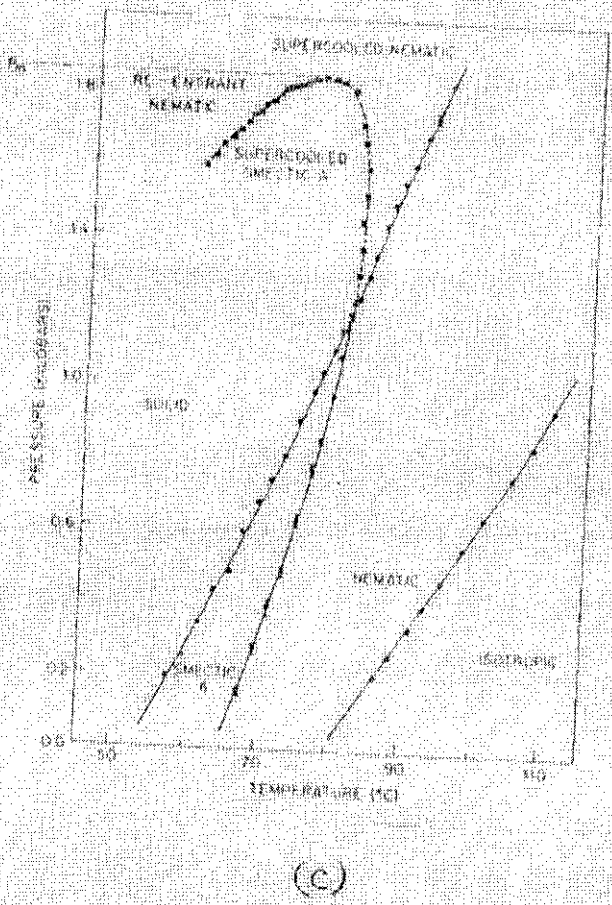
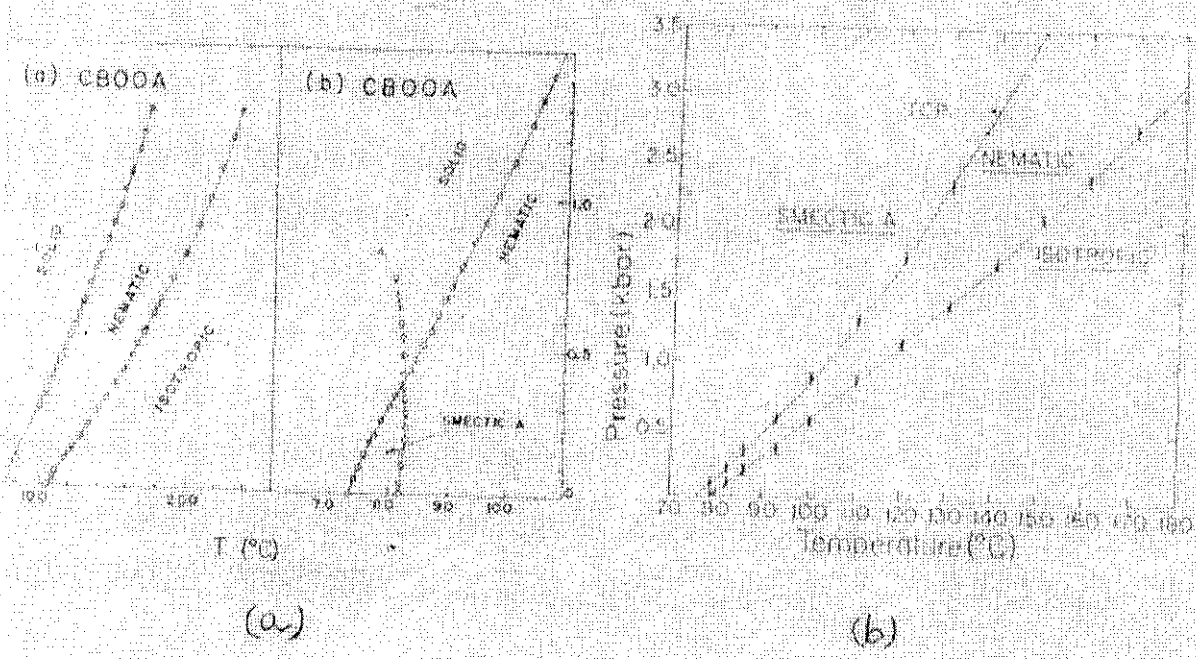


Figure 7: Phase diagrams of (a) CBOOA, (b) CBNA and (c) 8 OCB

and N-I transitions. Perhaps, it is of interest to mention here another related compound, viz. , n-p-cyanobenzylidene-p-octylaniline (CBOA) which is the lower homologue of CBNA does not even have a stable smectic phase, although, there is a monotropic nematic-smectic transition at atmospheric pressure. The same situation regarding the A-N transition continues to be monotropic at all pressures. ⁽¹⁶⁾

Comparing 8 OCB and 8CB, where the difference in the molecular structure is even more subtle (just an extra oxygen atom in the end chain of 8 OCB), the phase diagrams are again quite different [see figures 7c and 5], 8 OCB shows a re-entrant behaviour in the pressure range of 1.6 to 1.78 kbars ⁽²⁰⁾ while 8 OCB does not show any such behaviour. The recent work of Cladis et al ⁽²⁰⁾ on 8CB up to 7 kbars also has failed to show any re-entrant behaviour of this compound. Thus, although all the compounds discussed above have a common feature, namely, a bilayer structure, they behave differently under pressure.

C. Behaviour of dT/dP for the successive homologues

We shall now discuss the effect of increasing alkyl chain length on dT/dP. The slopes dT/dP for the S-N and N-I transitions for the four successive homologues studied are given in table VI for comparison. The dT/dP for the N-I transition show a pronounced odd-even effect (see fig. 8) similar to that exhibited by T_{NI} at atmospheric pressure. This is similar to the results obtained by Feyz and Kuss ⁽²¹⁾ for other homologous series. On the other hand dT/dP of the solid-mesophase transition is roughly the same around 25 °C/kbar for all the compounds, although the transition temperatures themselves show an alternation at atmospheric pressure. It is interesting to note that Feyz and Kuss, and also Cladis et al ⁽¹⁶⁾ have found that the magnitude of dT/dP for the S-N transition is the same (approximately 20-24 ° C Ikbar) for all the members of the homologous series studied by them. This is perhaps because, as suggested by Centerick et al , ⁽²²⁾ this value of 20 ° C/kbar is associated with the melting of the end chains or alkanes. For instance, dT/dP of the melting transition for most of the n-alkanes studied is about 23-25 ° C/kbar. ⁽²³⁾ The pressure studies of Stamatoff et al ⁽²⁴⁾ on the gel transition of phospholipids dispersions also give dT/dP of 21 ° C Ikbar.

D. Variation of transition temperature with pressure

The variation of transition temperature with pressure may be expressed by the relation,

$$T_p = T_0 + AP - BP^2$$

Where T_p and T_0 are the transition temperatures measured at pressures P and at atmospheric pressure respectively, A and B are empirical constants.⁽¹⁴⁾ For each compound and for each transition a least squares fit to the set of measured data points was carried out using a Hewlett-Packard 9821 A programmable calculator and the constants A and B determined. The values of A and B obtained in this manner are given in table VII. It is seen from this table that the constant A for the two transitions also reflect the behavior of dT/dP .

The constants of the Simon equation were evaluated for each compound as described in chapter III. The constants for each compound and for each transition are given in table VIII.

F. Tricritical behavior in 8CB

Of late there has been much interest in tricritical phase transitions⁽²⁵⁾ in which a variation of a field not directly coupled to the order parameter can change the character of the transition from first to second order. Examples of such transitions are the transition in He^3 - He^4 mixtures⁽²⁶⁾ and the metamagnetic-antiferromagnetic transition in $FeCl_2$.⁽²⁷⁾ The possibility of observing a tricritical point in Liquid crystals was first pointed out by McMillan.⁽²⁸⁾ Based on the mean field calculations, he showed that the smectic A-nematic (or cholesteric) transition can become second order when $T_R = T_{AN} / T_{NI} 0.87$. The simplest way of testing this, as McMillan himself observed, is by studying a homologous series wherein the variation in T_R is achieved by changing the alkyl chain length. This has been verified by Doane et al⁽²⁹⁾ from their NMR measurements of the order parameter of the 4-n-alkoxybenzylidene-4'-phenylazoaniline series. They found that the discontinuity at the A-N transition decreases as the chain length is reduced and is practically zero for the second homologue. However, this type has a limitation in that T_R is not continuously variable.

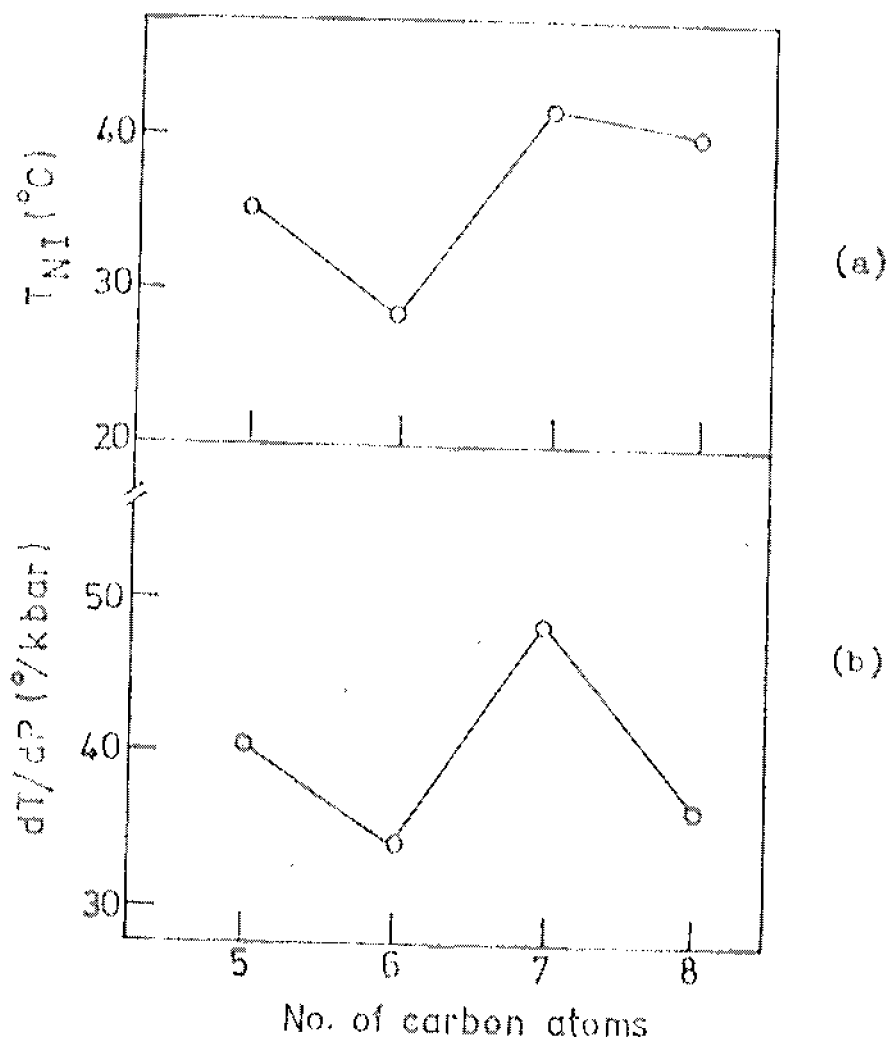


Figure 8: Variation of (a) the nematic-isotropic transition temperature (T_{NI}) at atmospheric pressure, and (b) dT/dP for the nematic-isotropic transition as functions of the number of carbon atoms in the alkyl chain length.

Alben ⁽³⁰⁾ suggested that tricritical behavior can also be observed by varying the concentration of mixtures in compounds with first and second order transitions. This has been verified for several mixtures by calorimetric studies.⁽³¹⁻³³⁾

The first observation of a tricritical point in liquid crystals using high pressure techniques was by Keyes et al ⁽³⁴⁾ who investigated smectic A- cholesteric transition in cholesteryl oleyl carbonate using an optical transmission technique. By a least squares fit to the two straight line portions of the curves relating the transmitted intensity versus pressure they concluded that there is a tricritical point at 2.66 ± 0.12 kbar, 60.3 ± 1 .

The first observation of a tricritical behaviour of an A-N transition was by McKee and McColl ¹⁰ on the basis of their careful proton NMR dipolar splitting measurements.

Considering that McKee et al observed the tricritical behaviour in a strongly polar compound, viz., CBNA, it was thought that 8CB, with its low A-N transition temperature at atmospheric pressure could be a good compound for such an investigation.

As mentioned earlier, a few initial experiments gave the clue that the tricritical point might exist beyond about 2.5 kbar. To exactly locate this point very careful experiments were carried out by taking DTA runs under identical rates of heating at very small intervals of pressure starting from 2.56 kbar. Figure 9 shows raw DTA records taken at 5 different pressures. It is seen that the strength of the DTA signal, which is about $2.5 \mu V$ at 2.56 kbar progressively decreases increase of pressure until at 2.68 kbar it is less than $0.25 \mu V$, the resolution of our experimental set up. Thus we can ascribe a tricritical point at 2.68 ± 0.08 kbar and $92.5 \pm 1.5^{\circ} C$. The ratio of the A-N to the N-I transition temperature at the tricritical point is 0.9, which is in good agreement with McMillan's theory.⁽²⁸⁾

A question may be asked whether it is possible to unequivocally claim that the transition is truly second order or not at 2.68 kbars from DTA runs. We can only say that within the limits of resolution of our experimental set up we are unable to detect any kink associated with the transition, which appears only as a change of slope in the DTA run. Accurate high pressure measurements of a first derivative property like isothermal compressibility would be required to ascertain the exact nature of this transition

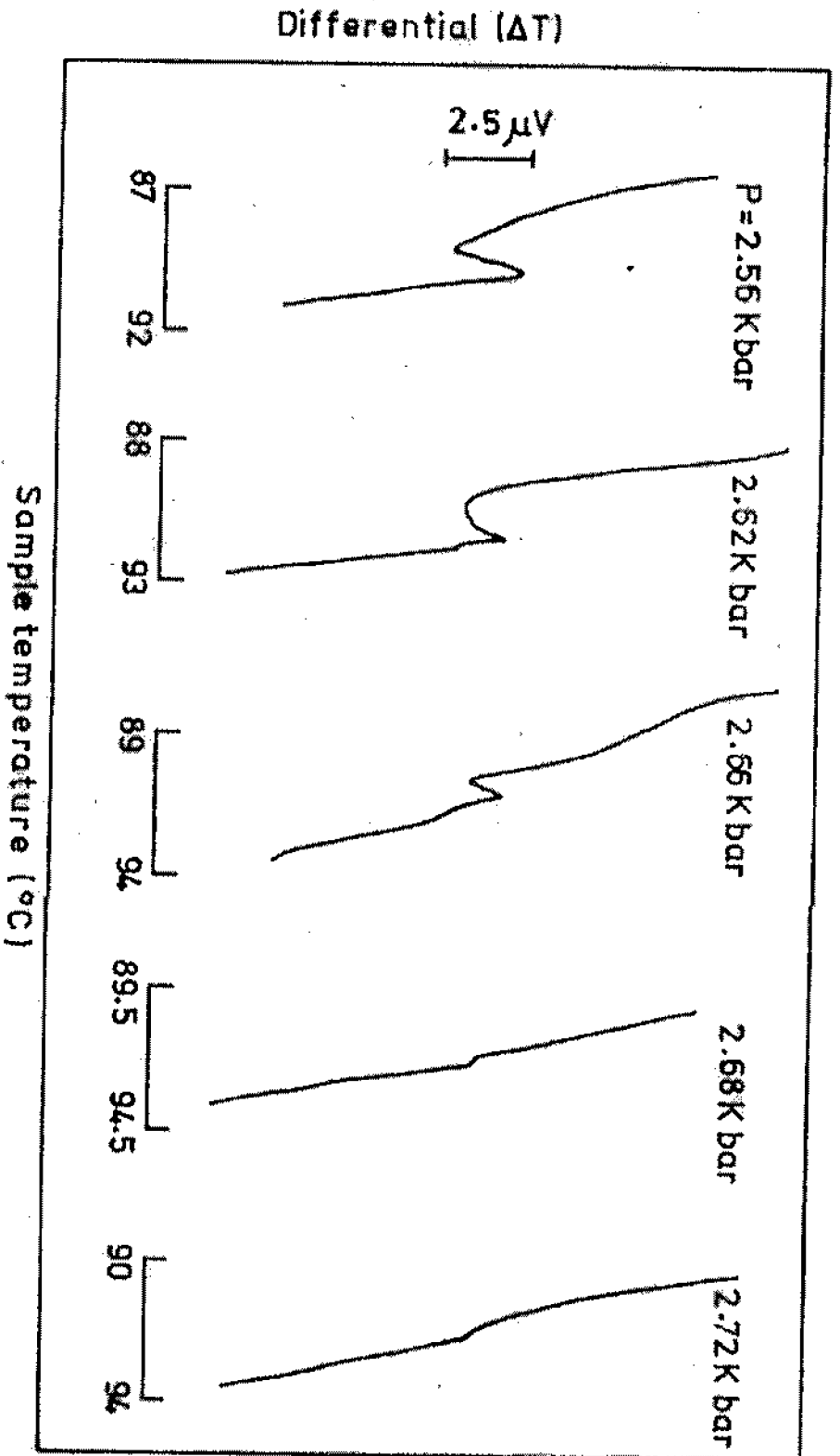


Figure 9: Raw DTA traces obtained for the smectic A-nematic transition in 8 OB at 5 different pressures (heating rate 4 $^{\circ}C/min$)

Table I

Transition temperatures of nCB (at atmospheric pressure) in °C

Compound	Solid-nematic (or smectic)	Smectic-nematic	Nematic-isotropic
5 CB	22.5	-	35.0
6 CB	123.0	-	28.0
7 CB	28.5	-	41.5
8 CB	21.0	32.5	40.0

Table II

Transition Temperatures of 5CB as a function of pressure

Solid – nematic		Nematic - isotropic	
Pressure in kbars	Temperature in °C	Pressure in kbars	Temperature in °C
0.140	27.0	0.143	41.75
0.320	30.5	0.409	49.6
0.491	35.0	0.514	54.0
0.603	37.75	0.560	56.75
0.630	38.25	0.641	58.5
0.657	39.0	0.657	59.25
0.703	40.25	0.676	60.1
0.908	45.5	0.831	65.5
1.036	49.0	0.927	69.75
1.152	51.5	0.955	70.8
1.210	53.25	1.066	74.6
1.457	58.75	1.196	79.75
1.635	62.0	1.241	81.0
1.642	62.5	1.321	83.5
2.214	73.2	1.361	85.2
2.411	76.0	1.542	91.0
2.933	92.0	1.685	96.0
3.289	94.4	1.913	103.0
		2.242	113.0
		2.423	118.1
		2.933	131.5
		3.363	141.0
		3.710	146.5

Table III

Transition temperatures of 6CB as a function of pressure

Solid - nematic		Nematic - isotropic	
Pressure in kbars	Temperature in °C	Pressure in kbars	Temperature in °C
0.458	24.75	0.186	33.5
0.550	27.0	0.286	37.75
0.673	30.1	0.379	40.75
0.866	35.0	0.464	43.0
1.055	39.75	0.574	46.0
1.125	42.0	0.673	49.0
1.233	44.75	0.866	55.5
1.401	48.75	1.001	60.0
1.531	51.0	1.071	62.0
1.572	51.75	1.129	64.0
		1.237	67.0
		1.409	71.8
		1.544	75.1
		1.645	77.0

Table IV

Transition temperatures of 7CB as a function of pressure

Solid - nematic		Nematic - isotropic	
Pressure in kbars	Temperature in °C	Pressure in kbars	Temperature in °C
0.197	32.7	0.128	47.4
0.271	35.1	0.197	50.4
0.475	40.5	0.278	54.75
0.519	41.0	0.367	59.0
0.653	44.0	0.448	62.5
0.769	47.5	0.460	63.25
1.020	54.5	0.526	66.0
1.314	60.5	0.533	66.75
1.442	64.5	0.653	72.5
1.569	67.0	0.807	79.5
1.697	72.0	0.896	84.0
1.836	75.5	1.066	92.25
		1.202	99.0
		1.333	105.25
		1.581	116.5
		1.727	122.5
		1.863	128.0

Table V

Transition Temperatures of 7CB as a function of pressure

Table V**Transition Temperatures of 7CB as a function of pressure**

Solid – Smectic A		Smectic A - Nematic		Nematic - isotropic	
0.463	32.75	0.309	42.25	0.340	53.5
0.483	33.25	0.425	44.75	0.497	57.8
0.850	41.5	0.479	46.75	0.580	60.75
1.061	47.25	0.502	47.5	0.657	63.0
1.171	49.0	0.649	50.4	0.788	67.5
1.472	56.5	0.777	53.5	0.866	70.25
1.890	66.8	0.850	56.25	1.109	79.5
2.130	72.25	1.155	59.0	1.175	80.0
2.325	77.25	1.500	69.75	1.210	83.0
		1.909	78.2	1.520	93.0
		2.235	86.0	1.932	105.0
		2.456	88.25	2.182	113.25
		2.576	90.0	2.304	118.25
		2.586	90.75	2.361	119.75
		2.620	91.5	2.493	123.25
		2.679	92.2	2.576	127.25
		2.721	93.0	2.624	129.0
		2.750	93.75	2.771	133.75
				2.887	135.75

Table VI**The dT/dP for nCB for the S-N (S-S_A) and N-I transitions in °C/kbar**

Compound	Solid – nematic (or smectic A)	Smectic – A Nematic	Nematic – isotropic
5CB	26.65	--	37.48
6CB	25.4	--	31.75
7CB	24.7	--	47.43
8CB	24.11	30.4	36.0

Table VII

Constants A and B for nCB

Compound	Solid – Nematic (or smectic)			Smectic-Nematic			Nematic – Isotropic		
	A	B	RMS Error	A	B	RMS Error	A	B	RMS Error
5CB	26.4	1.29	1.06	-	-	-	40.3	2.64	0.82
6CB	26.4	0.37	0.37	-	-	-	33.7	2.10	0.49
7CB	24.6	0.52	0.52	-	-	-	47.9	0.54	0.46
8CB	24.4	0.38	0.38	30.4	3.04	1.38	36.0	0.94	0.67

Table VIII

Constants of the Simon equation for nCB

Compound	Transition	Constants		
		A	C	RMS Error
5CB	S-N	4924.2	2.3	- 0.0034
	N-I	2826.2	2.64	0.0186
6CB	S-N	6800.4	1.61	- 0.0126
	N-I	4263.1	2.12	0.0193
7CB	S-N			
	N-I	6421.7	1.04	0.007
8CB	S-SA	8569.6	1.38	0.018
	SA-N	2425.6	4016	- 0.0178
	N-I	5228.3	1.64	0.00084

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