

CHAPTER VI

EFFECTS OF PRESSURE ON SMECTIC C PHASES

6.1 Introduction

It has long been **recognized** that the temperature variation of the **tilt angle** in the **smectic C phase** depends very much on the type of phase that **exists immediately** after it at a higher **temperature**. If the higher temperature phase is smectio A, then the **tilt angle** is rather small and shows a strong temperature **dependence**.^{1,2,3} Further it goes to **zero** at the **smectic C - smectic A (C-A) transition**. On the other hand, when a **smectic C phase** precedes a nematic phase, then the **tilt angle** is comparatively large and is independent of **temperature**.^{3,4} In addition to these two, de Vries,⁵ very recently observed a third kind of smectio C phase in n-pentyl-4-(4'-n-decyloxy benzylidene amino)cinnamate (PDBC) in which the **tilt angle** in **smectic C phase** is about 15° . But the **tilt angle** does not change significantly with the temperature even though **smectic C phase** precedes the **smectic A phase**. Moreover, instead of going to **zero**, the **tilt angle** remains almost constant not only at the **(C-A) transition** but even after it, i.e., even in smectio A phase. Hence it is quite

interesting to carry out pressure studies on the compounds exhibiting these three kinds of smectic C phases with a view to see if the pressure behaviour of smectic C phases is related to the temperature variation of the tilt angle at room pressure.

6.2 Compounds studied

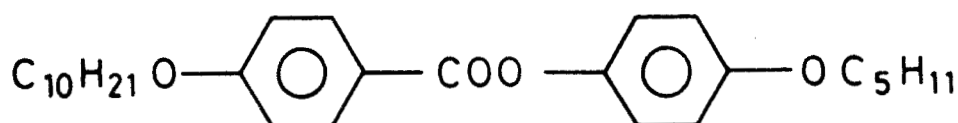
The compounds studied are -

- 1 4-n-pentyloxy-4'-n-decyloxybenzoate (50 PDOB)
- 2 4-n-heptyloxy-4'-n-decyloxybenzoate (70 PDOB)
- 3 p-n-nonyloxybenzoic acid (NOBA)
- 4 n-pentyl-4-(4'-n-decyloxybenzylideneamino)cinnamate (PDBC).

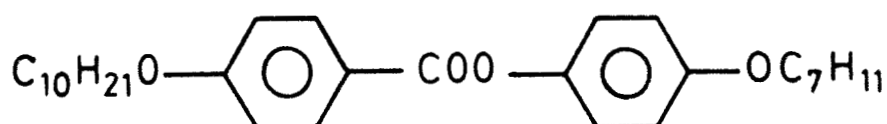
The structural formula of the compounds are given in figure 6.1.

6.2.1. 50 PDOB and 70 PDOB: They are the 5th and 7th member of the homologous series 4-n-alkyloxy phenyl-4'-n-alkyloxybenzoates. These compounds have been synthesised by Schroter⁶ and also by Deutscher et al and Steinstrasser.^{7,8} They are quite stable substances with relatively low transition temperatures, and hence are particularly suitable for high pressure studies. They were kindly given to us by Dr. Demus. Both these

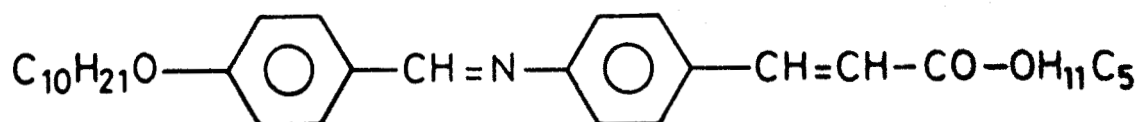
4 - n - Pentyloxyphenyl - 4' - n decyloxy Benzoate (50 PDOB)



4 - n - heptyloxy - 4' - n decyloxy Benzoate (70 PDOB)



n Pentyl- 4 (4' - n - decyloxy Benzylidene amino) cinnamate (PDBC)



Nonyloxy Benzoic acid (NOBA)

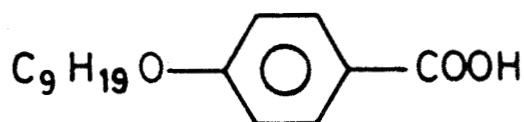


FIGURE 6.1: Structural formula of the compounds studied

compounds exhibit smectic C, smectic A and nematic phases. The calorimetric investigations revealed that A-H transition is of first order characterised by sharp peaks in the DSC runs. But the nature of the C-A transition does not seem so clear since we could not detect any clear peak which could be analysed in terms of normal transition enthalpy, thereby indicating the second order nature of the (A-C) transition. Further by observing the textures, Demus et al⁹ found qualitatively that the tilt angle in the smectic C phase of the compounds are temperature dependent and tends to zero near the A-C phase transition. Therefore smectic C phase in these compounds belongs to the first type,

6.2.2. NOBA: This belongs to a well known homologous series p-n-alkoxybenzoic acids, the general discussion of which was given by Gray.¹⁰ The transition temperatures have been reported by Gray and Jones¹¹ and by Herbert,¹² who also measured the transition enthalpies. NOBA exhibits smectic C and nematic phases. All the phase transitions in this case are of first order involving significant transition enthalpies. Further the tilt angle in the smectic C phase has been measured by Chistyakov et al¹³ employing X-ray diffraction technique and also by Taylor

et al¹⁴ by optical methods. From these investigations, it has been shown that the tilt angle is somewhat large (about 45°) and does not depend on the temperature. Further, there is no A phase, hence smectic C phase in this case can be classified as belonging to the second type. The sample used in our study was synthesised in our chemistry laboratory.

6.2.3: PDBC: n-Pentyl-4(4'-n-decyloxybenzylidene amino)cinnamate is also a well known compound which has been synthesised according to the standard procedure.¹⁵

The compound was given to us by Dr. Mary Neubert. Besides smectic C, there are smectic B and smectic A phases. All the phase transitions except (C-A) involve significant transition enthalpies and hence are first order, while (C-A) transition is either second order or very weakly first order in character since we could not get any sharp peak corresponding to (C-A) transition in the DSC runs. Further, de Vries measured the layer thickness not only in smectic C phase but also in smectic A phase of the compound. Figure 6.2 shows the plot of the tilt angle as a function of temperature both in smectic C and A phases, which are estimated from de Vries' data on layer thickness of the compound.⁵ It is seen that the tilt

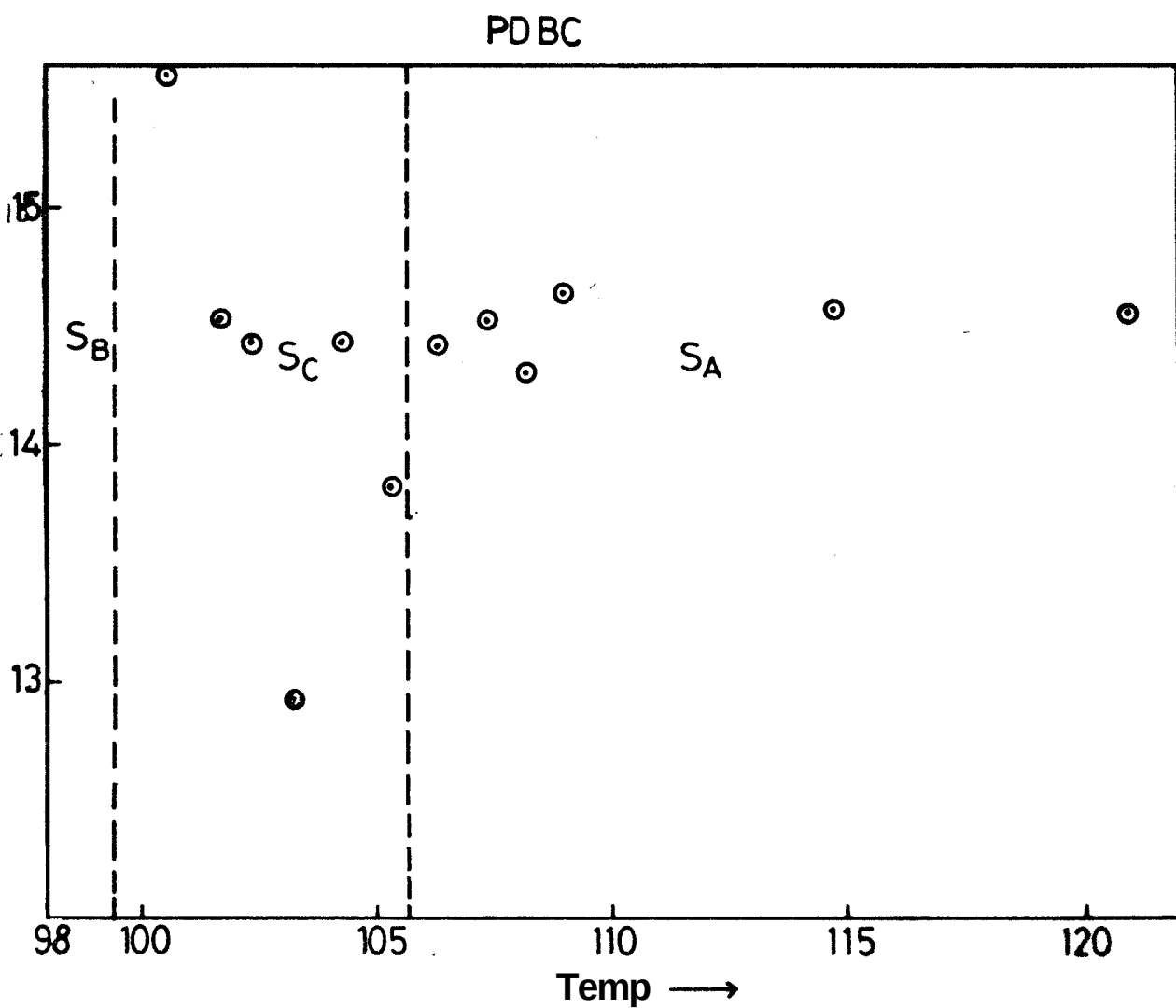


Figure 6.2: Variation of tilt angle of PDBC with temperature (after de Vries⁵).

angle being about 15° is much smaller than that in the case of NOBA. Further, the tilt angle does not change significantly at the O-A transition. It is quite evident that the tilt angle in the A phase is not zero as is generally assumed for A phase, but is approximately equal to 15° . Hence as per the classification of de Vries, smectic C, in this case, belongs to the third type.

6.3 Experimental

The transition temperatures and the heats of transition have been determined by differential scanning calorimeter (Perkin Elmer DSC-II). The transition temperatures and enthalpies were determined from two or more DSC runs. The transition temperatures were confirmed by thermal microscopy. The values, which are in good agreement with the literature data^{9,11,15} are tabulated in table 6.1.

The transition temperatures at high pressure were determined using different types of cells depending on the substances investigated and the range of pressure. Further all the transition temperatures were measured in the heating mode only. The experiments on 50 PDOB and 70 PDOB were conducted using the opposed diamond anvil

cell described in chapter II, since the experiments have been conducted up to pressures of 7 kbar. The diamond anvil cell data were brought to an absolute scale by conducting a separate calibration experiment using the DTA cell described in chapter II, on the same compound. The solid-smectic C (or smectic A) phase boundary determined with the DTA cell were used to bring the diamond anvil cell data to the absolute scale. To check the reliability of the calibration, the data points (on an absolute scale) for smectic A - nematic and nematic - isotropic phase boundaries as determined by two cells were compared in the phase diagram (refer figures 6.2 and 6.3) for these two compounds. It is seen from the phase diagram of the compounds that there is a very good correlation between the data obtained with the two cells. Further, it is also found that the independent set of measurements (not shown as such in the figures) using the diamond anvil cell agree well with each other.

On the other hand experiments were conducted on NOBP using a DTA cell since all the transitions are of first order involving significant transition enthalpies. But in the case of PDBC, transition temperatures were measured as a function of pressure using high pressure

optical cell by light **transmission technique** as described in **chapter II**.

6.4 Results and discussion

6.4.1. 50 PDOB and 70 PDOB: The P-T data for 50 PDOB and 70 PDOB are given in tables 6.2 and 6.3 and the corresponding phase diagrams are shown in figures 6.3 and 6.4 respectively. The features of the phase diagrams are (1) the range of nematic phase or its stability increases with the increase of pressure, (2) amectic A stability also increases with pressure, (3) smectic C phase is bounded in both the cases.

In the case of 50 PDOB, the range of smectic C phase is 4.3°C . With the increase of pressure the range reduces rapidly and beyond a pressure of 1.32 kbar, the smectic C phase ceases to exist and the solid directly transforms into smectic A phase. The resulting solid - smectic C - smectic A triple point is at 1.32 ± 0.05 kbar, $76.8 \pm 0.7^{\circ}\text{C}$. The same behaviour of smectic C phase can be seen in 70 PDOB also, but it gets 'bounded' at a much higher pressure, the triple point in this case being at 3.40 ± 0.05 kbar and $103 \pm 0.7^{\circ}\text{C}$. It is evidently because of the greater stability of smectic C

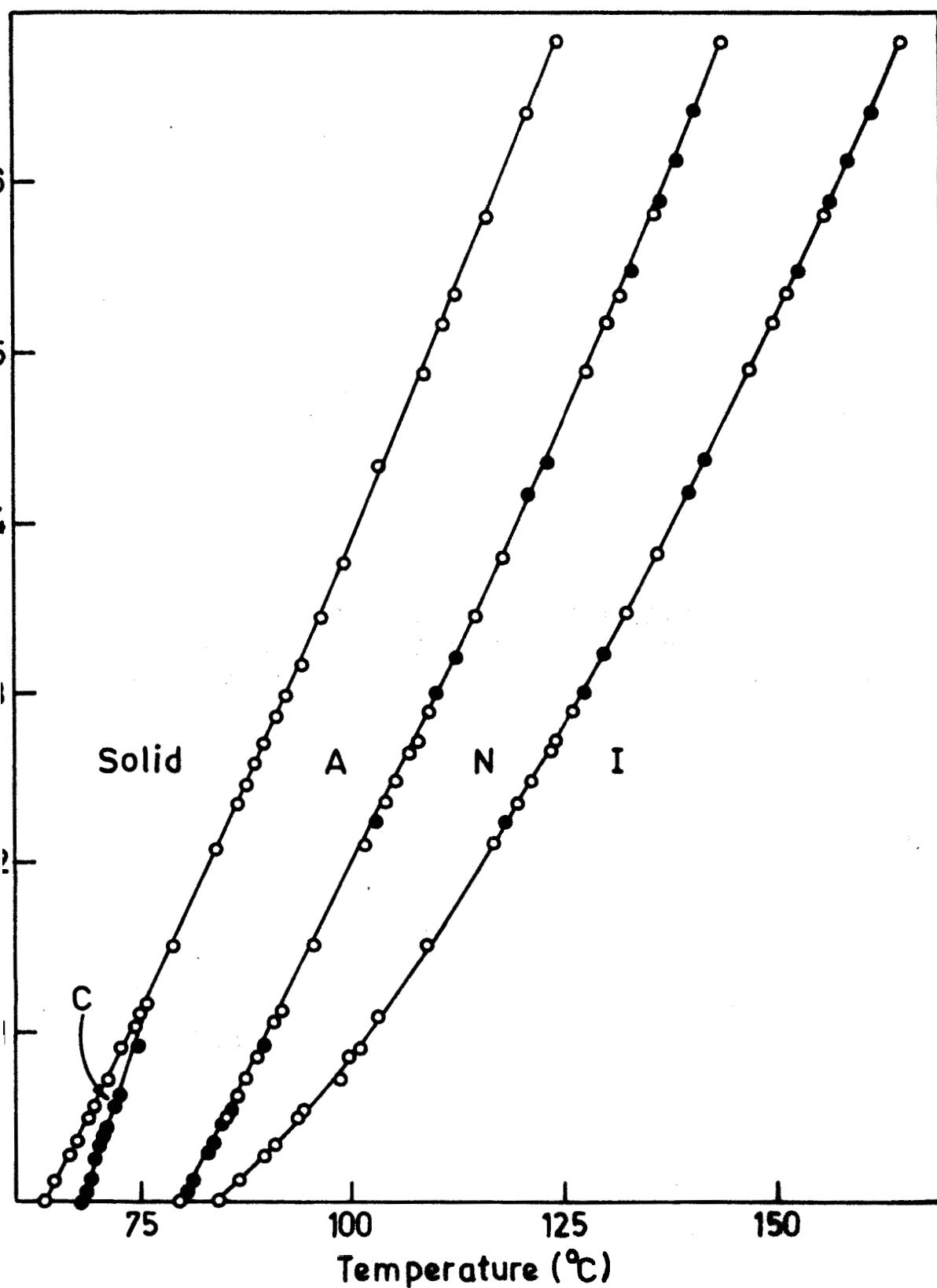


Figure 6.3: Phase diagram of 50 PDOB. O, ● represent data points obtained using DTA cell and diamond anvil cell respectively

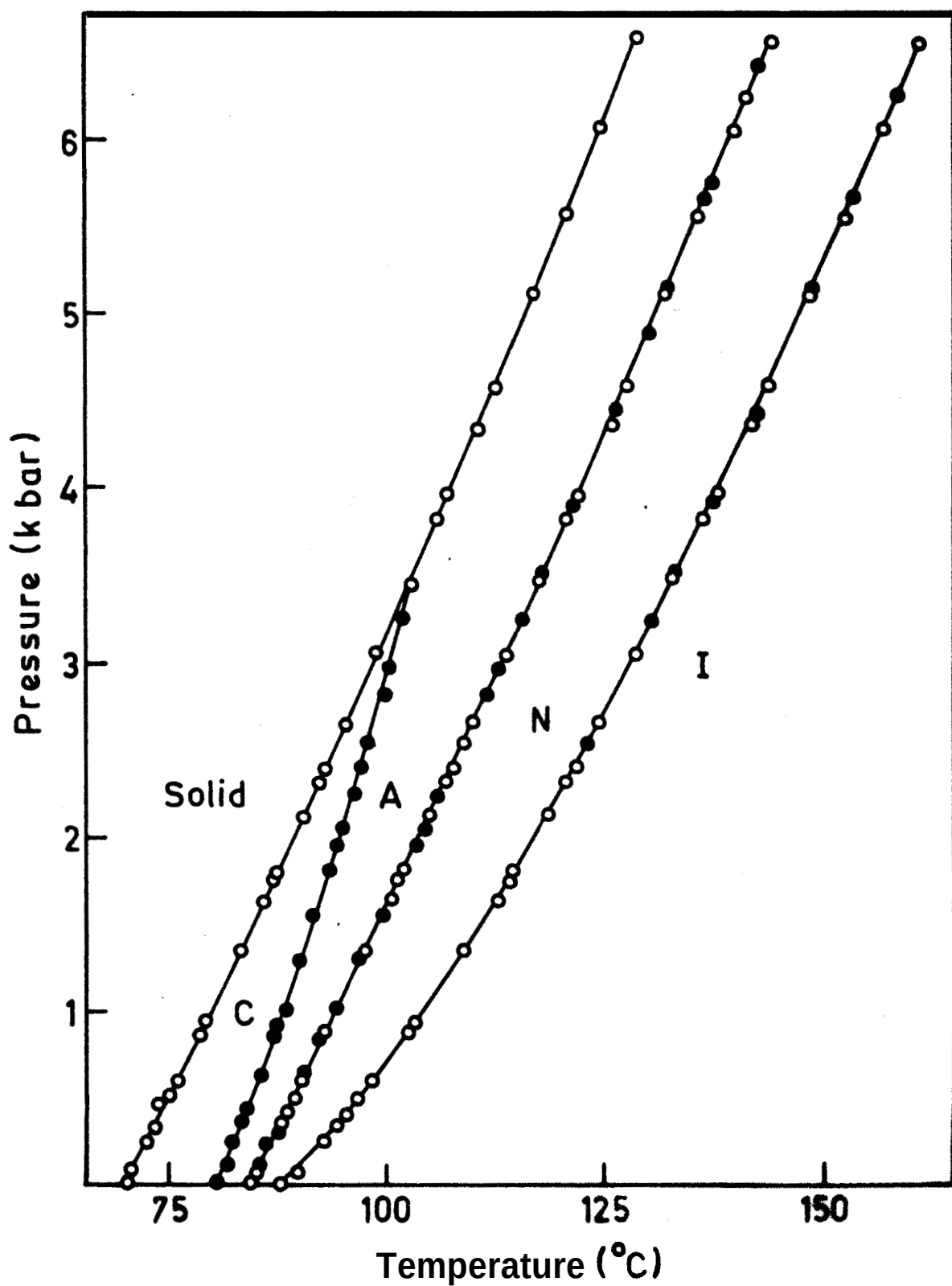


Figure 6.4: Phase diagram of 70 PDOB. O, ● represent data points obtained with DTA and diamond anvil cell respectively.

phase in 70 PDOB (as seen by the large range of smectic C phase compared to 50 PDOB) at room pressure. It may be recalled that a similar case of bounded smectic C was observed earlier.¹⁶

6.4.2. NOBA: The P-T data of this compound are given in table 6.4 while the figure 6.5 represents the phase diagram. As described already, this compound has no smectic A phase but only smectic C and a nematic. The tilt angle of the C phase is independent of the temperature. Jones observed for this compound only a single melting transition at a temperature of 93.3°C. On the other hand, we have found that there are two solid phases K_{II} and K_I . These transitions are clearly seen at room pressure both by DSC as well as by thermal microscopy at a temperature 92.3°C and 93.6°C. We have followed all the transitions, viz., $K_{II} - K_I$, $K_I - O$, $C - N$ and $N - I$ as a function of pressure. The feature of the P-T diagram is again the suppression of C phase at high pressures. The triple point solid II - S_C - N occurs at 1.92 kbar and 164.0°C. It may be mentioned that the C - N boundary is practically straight up to the triple point while in 50 PDOB and 70 PDOB, the C-A boundary has a tendency to show a slight curvature as the triple point

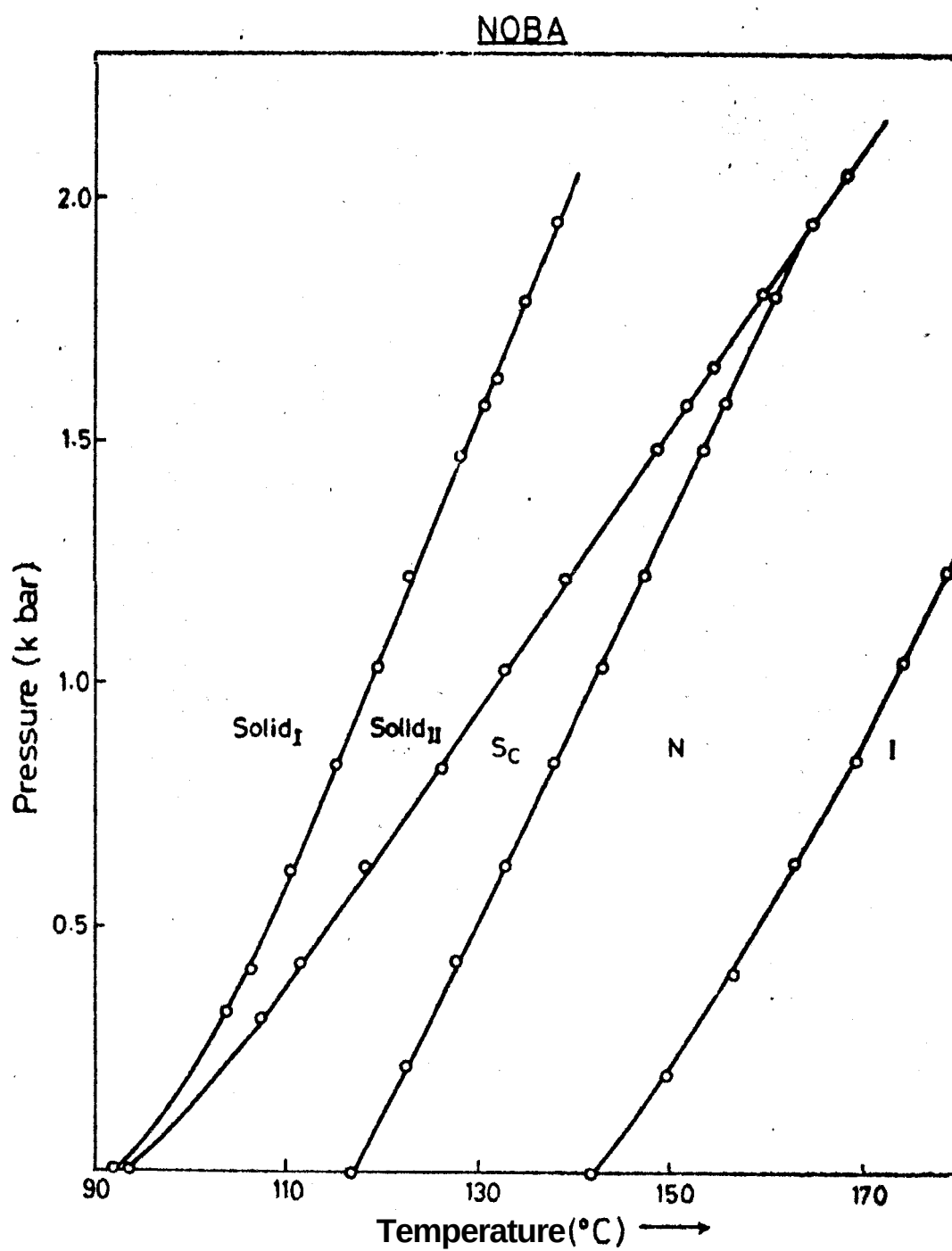


Figure 6.5: Phase diagram of NOBA

is approached. The range of solid I phase rapidly increases with pressure being 1.3°C at 1 bar and 28°C at 2 kbar. The range of the nematic phase also increases but the rate of increase is considerably slower than that in 70 PDOB or 50 PDOB.

6.4.3. PDBC: As mentioned earlier the compound PDBC is unique for the following reasons: (1) the tilt angle in S_C phase seems to be more or less constant in the entire smectic C phase and (2) there is no appreciable change in the tilt angle at the (C - A) transition and moreover, even the A phase also retains the same tilt-angle.

The P-T data for this compound are given in table 6.5 and the figure 6.6 represents the corresponding phase diagram. The smectic C phase is again suppressed, and the resulting smectic A - smectic C and smectic B triple point occurs at 1.57 kbar and 157.0°C . But the phase boundaries in this case show much greater curvature than in NOBA. Further, the rate at which the range of S_C phase decreases with the increase of pressure is much less here than in any of the three earlier cases. The S_C phase has a range of about 4.7°C at 1 bar which changes very slowly with the increase of pressure, and at a pressure

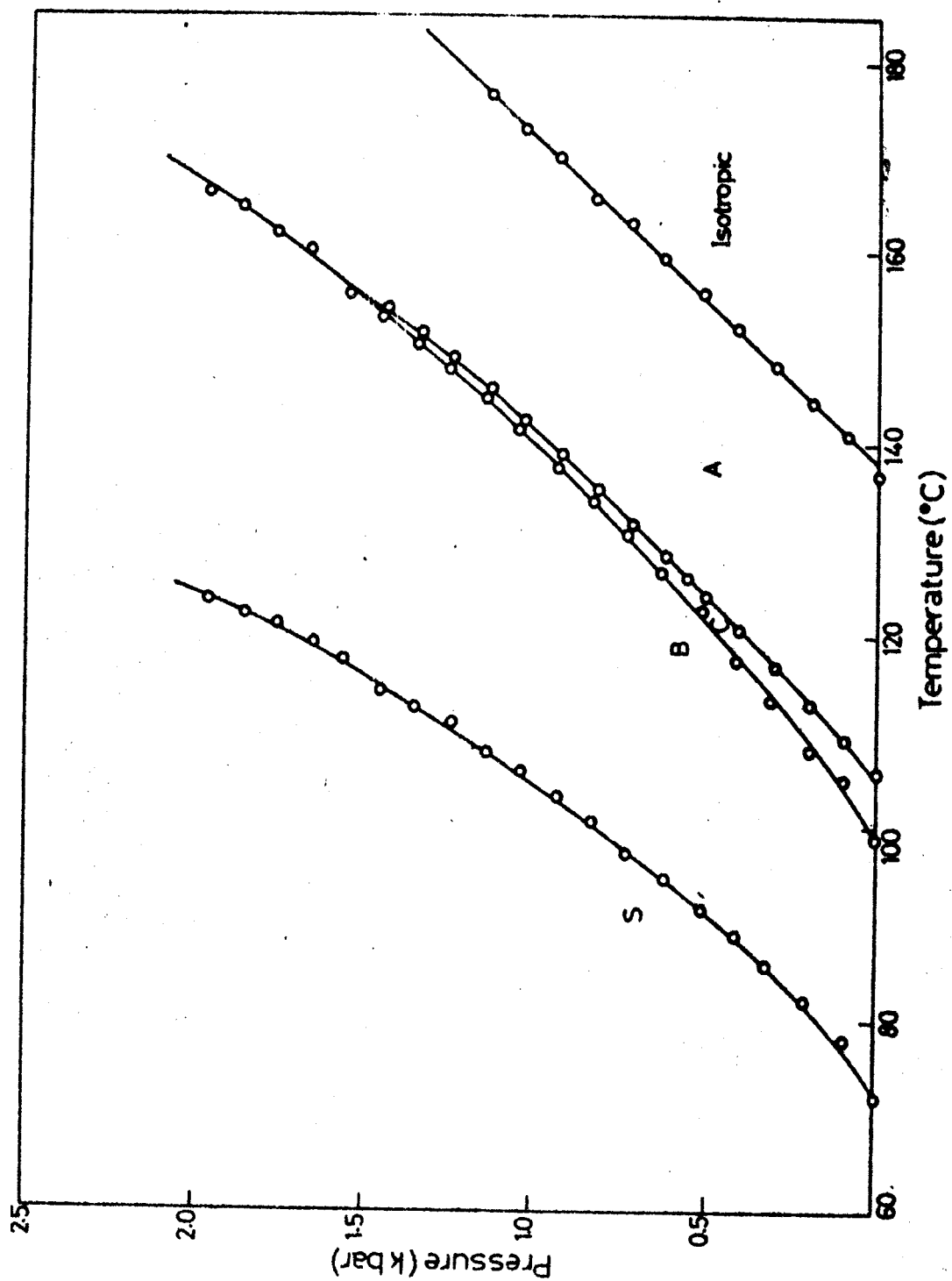


Figure 6.6: Phase diagram of PDBO

of 1 kbar, the range is still approximately 15°. The range of the smectic A phase shows an interesting behaviour as a function of pressure. It is 35.5° at 1 bar, but decreases to about 30° at 0.7 kbar, beyond which it starts increasing. This is evident due to the curving of C-A phase boundary towards the pressure axis which becomes more prominent beyond this pressure. But the smectic A - isotropic phase boundary is almost straight at all pressures and the range of smectic B phase on the other hand shows continuous increase with the pressure.

It looks as though the smectic C phase definitely gets unstable at high pressures and finally ceases to exist. This suppression of the smectic C phase at high pressure seems to occur regardless of the type of the smectic C phase. The exact correlation between the tilt angle variation and the maximum pressure of the smectic C stability would therefore be very interesting to study. This of course requires a careful high pressure X-ray studies of the variation of the layer spacing of the smectic C phase as a function of pressure.

6.5 Calculation of dT/dP at one bar and the estimation of the volume change at the transition using Clausius-Clapeyron equation

For all the compounds studied by us, the data points

were fitted to the polynomial equation suggested by Born,¹⁷ viz., $T_P = T_0 + AP - BP^2$, by the method of least square fit. From the initial linear portion of the phase boundaries, dT/dP values at one bar have been evaluated and are found to be equal to the value of the constant A of the polynomial equation. The values of A & B are listed in Table 6.6 along with the R.M.S. error. Using the dT/dP values at 1 bar the volume change ΔV associated with the various transition have been evaluated using Clausius-Clapeyron equation, and the results are tabulated in table 6.7 along with the dT/dP values at room pressure.

It is seen from the table 6.7 that dT/dP is very small for all the transitions in 50 PDOB and 70 PDOB. The C-A boundary particularly has extremely small dT/dP values (about 6.78°C/kbar) when compared to that for PDBC. The suppression of smectic C phase in these two compounds can be predicted by the dT/dP values for smectic C - smectic A transition which is much lower than that for solid - smectic C transition. In the case of both NOBA and PDBC, dT/dP values are much higher for all the transitions. The variation of the transition temperature with pressure is unusually large for K_1 -C

transition of NOBA when compared to C-N transition thereby indicating that the C phase will be bounded at a higher pressure. The same trend can be observed in the case of PDBC, but it is quite interesting to note that solid - smectic B (melting) and smectic A - isotropic phase boundary have the same value of dT/dP at 1 bar.

TABLE 61

Transition temperatures and heats of transitions of
the compounds

S.No.	Compound	Transition	Transition temperatures °C	Heat of transition in kJ/mole
1	500PDOB	K - C	64.0	46.03
		C - A	68.3*	0
		A - N	79.9	1.13
		N - I	84.6	1.80
2	70 PDOB	K - C	70.3	50.56
		C - A	80.5*	0
		A - N	84.5	1.06
		N - I	87.8	2062
3	NOBA	K _{II} - K _I	92.3	23.51
		- C	93.6	2042
		C - N	117.0	1.55
		N - I	140.0	2.15
4	PDBAC	K - B	72.3	24.62
		B - C	99.8	4.92
		C - A	104.5*	0
		A - I	140.0	8.34

*determined from optical microscopy

K - crystal , A - smectic A, B - smectic B,
C - smectic C, N - nematic, I - isotropic.

Table 6.2

Transition temperatures of 5 OPDOB as a function of pressure

Solid-smectic C (or S _A)		Smectic C-smectic A		Nematic-isotropic	
Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C
room pr.	64.0	room pr.	68.3	room pr.	84.6
0.11	65.0	0.05	68.7	0.12	86.7
0.27	66.6	0.12	69.2	0.27	89.6 [±]
0.34	67.5	0.22	69.8	0.34	90.7
0.48	68.7	0.29	70.3	0.51	93.5 [±]
0.56	69.5	0.33	70.5	0.55	94.2
0.72	71.1	0.35	70.7	0.72	97.0 [±]
0.89	72.0	0.38	71.0	0.87	99.5
0.91	72.5	0.45	71.4	0.95	100.7 [±]
1.03	74.2	0.52	71.8	1.10	103.3 [±]
1.12	75.0	0.53	72.0	1.14	103.9
1.49	78.6	0.57	72.2	1.51	108.7 [±]
2.07	84.0	0.62	72.6	1.52	109.0
2.45	87.6	1.16	75.5	2.1	116.6 [±]
2.57	88.6			2.22	118.0
2.68	89.6			2.35	119.5
2.84	91.2			2.65	123.4 [±]
2.97	92.2			2.7	124.0
3.16	94.0			2.88	126.2 [±]
3.43	96.5				
3.76	99.2				
3.77	99.5				
4.32	104.2				
4.33	104.3				
4.85	108.3				
5.29	112.4				
5.77	116.2				
6.37	120.8				
6.8	124.5				

Table 6.2 continued

Smectic A - Nematic		smectic A - nematic		smectic A - nematic	
Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C
room pr.	80.0	1.12	91.5	3.78	117.8
0.05	80.3	1.16	92.1	3.8	118.2
0.12	81.0	1.45	95.0	4.15	121.4
0.22	82.3	1.55	95.5*	4.3	123.0*
0.27	82.7*	1.51	95.6	4.33	123.1
0.29	83.0	1.7	97.6	4.63	125.7
0.33	83.4	1.88	99.4	4.86	127.9*
0.35	83.6	2.08	101.5*	5.15	133.0
0.38	83.9	2.18	102.5	5.31	131.7*
0.45	84.7	2.22	102.8	5.45	133.2
0.51	85.2*	2.34	104.0	5.78	136.0*
0.52	85.4	2.45	105.2*	5.85	136.6
0.54	85.6	2.51	105.7	6.10	138.6
0.55	85.7	2.62	106.8	6.38	140.6*
0.62	86.5	2.7	107.8	6.60	142.6
0.72	87.0*	2.86	109.2*	6.8	144.0*
0.87	89.0	2.98	110.1	6.82	144.1
0.92	89.6*	3.18	112.3*	6.86	144.4
1.06	90.8*	3.45	114.7		

*transition temperature determined by DTA experiment.

Table 6.3

Transition temperatures of 7 OPDOB as a function of pressure

Solid - S_C (or S_A)		$S_C - S_A$		N - I	
Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C
room pr.	70.3	room pr.	80.7	room pr.	88
0.08	70.8	0.12	81.7	0.08	89.8
0.25	72.6	0.16	82.0	0.27	92.5*
0.34	73.5	0.21	82.4	0.42	95.2
0.45	74.1	0.23	82.6	0.5	96.7
0.50	75.0	0.36	83.5	0.6	98.2*
0.85	78.5	0.41	83.7	0.89	102.7
0.94	79.3	0.63	85.5	0.94	103.5
1.35	83.2	0.87	87.3	1.35	109.2*
1.62	85.7	1.01	88.3	1.64	113.0
1.74	87.0	1.28	90.1	1.77	114.3*
1.78	87.2	1.33	90.5	2.14	118.8
2.12	90.5	1.78	93.4	2.32	120.8*
2.31	92.4	1.96	94.5	2.4	122.0*
2.38	93.0	2.04	95.1	2.52	123.3
2.63	95.4	2.2	96.1	2.66	124.7
3.04	99.1	2.23	96.3	3.05	129.0
3.46	103.0	2.41	97.4	3.23	131.0
3.81	106.1	2.8	99.6	3.48	133.6*
3.95	107.2	2.96	100.5	3.82	136.7
4.33	110.7	3.23	102.0	3.92	138.0
4.57	112.7			3.97	138.5*
5.09	117.2			4.35	142.2
5.56	120.8			4.43	142.9
6.06	125.0			4.58	144.2*
6.58	129			5.11	149.4
				5.55	153.0

...contd.

Table 6.3 continued

$S_A - N$		$S_A - N$		$S_A - N$	
Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C
room pr.	94.5	1.35	97.7 [‡]	3.47	118.0
0.08	85.4	1.53	99.6	3.5	118.7 [‡]
0.12	85.6 [‡]	1.64	100.6	3.82	121.0
0.16	85.9	1.76	101.6 [‡]	3.93	121.2
0.21	86.5	1.78	101.9	3.98	121.9
0.23	86.6 [‡]	1.81	102.0	4.34	126.2
0.26	87.0	1.96	103.7	4.43	126.6
0.27	87.2 [‡]	2.04	104.5 [‡]	4.58	127.8 [‡]
0.36	88.0	2.13	105.3	5.1	132.2
0.42	88.5 [‡]	2.2	106.1	5.15	132.6
0.5	89.5	2.23	106.3	5.55	136.0 [‡]
0.6	90.2	2.32	107.0 [‡]	5.65	136.8
0.63	90.7 [‡]	2.39	107.6	5.73	137.5
0.82	92.5	2.41	108.0	6.06	140.1 [‡]
0.87	93.0 [‡]	2.52	109.0 [‡]	6.23	141.3 [‡]
0.89	93.2	2.65	110.2 [‡]	6.4	142.8
0.94	93.7 [‡]	2.8	111.7	6.55	144.0 [‡]
1.01	94.3	2.96	113.0 [‡]		
1.28	97.0 [‡]	3.05	114.0 [‡]		
1.33	97.4	3.23	115.7		

[‡]Transition temperature determined by DTA experiment

Table 6.4

Transition temperatures of NOBA as a function of pressure

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		SOLID II--- SOLID I	SOLID I - SMECTIC C	SMECTIC C- NEMATIC	NEMATIC- ISOTROPIC
1	1	92.3	93.6	117.5	142.5
2	208	103.25	-	-	150.0
3	210	-	-	122.8	-
4	313	104.25	107.25	-	-
5	420	106.5	117.8	-	156.5
6	423	-	-	127.8	-
7	425	-	-	128.8	157.3
8	625	110.5	-	133.0	-
9	630	-	118.0	-	-
10	635	-	-	-	162.8
11	833	115	126.25	-	-
12	842	-	-	138.0	-
13	850	-	-	-	169.0
14	1027	119.25	133	-	-
15	1037	-	-	143.0	-
16	1050	-	-	-	174.5
17	1210	123.25	139.5	-	-
18	1215	-	-	147.8	-
19	1235	-	-	-	179.0
20	1470	128.5	-	-	-
21	1480	-	149.25	154.3	-
22	1500	-	-	-	184.75
23	1567	130.8	-	-	-
24	1582	-	152	156.6	-
25	1630	132	-	-	-
26	1650	-	155	-	-
27	1785	135	-	-	-
28	1800	-	160.5	161.0	-
29	1850	138.1	165	-	-

Table 6.5**Transition temperatures of PDBC as a function of pressure****SET I**

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		K - B	B - C	C - A	A - I
1	room pr.	72.3	99.4	105.7	136.6
2	0010	78.37	104.96	109.13	141.18
3	0.21	82.40	108.36	111.53	144.50
4	0.31	86.16	113.03	116.51	148.17
5	0.41	89.18	117.25	120.55	152.03
6	0.52	91.44	122.33	123.84	155.60
7	0.62	95.00	126.56	128.31	159.47
8	0.72	97.21	130.12	131.56	163.22
9	0.83	100.48	134.14	135.34	165.49
10	0.93	103.25	137.56	138.86	170.26
11	1.04	106.00	141.58	142.43	173.26
12	1.14	107.76	145.20	146.0	177.70
13	1.24	110.78	148.20	148.96	
14	1.35	112.54	150.97	151.72	
15	1.45	114.54	153.48	153.73	
16	1.55	117.55	155.74		
17	1.66	119.32	160.52		
18	1.76	121.08	162.27		
19	1.86	122.58	164.78		
20	1.97	123.59	166.04		

Table 6.5

Transition temperatures of PDBC as a function of pressure

Set 11

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Solid - smectic B	smectic B - smectic C	smectic C - smectic A	smectic A - isotropic
1	room pressure	72.3	99.4	105.7	136.6
2	0.10	78.51	104.1	109.23	
3	0.21	82.60	107.96	112.74	
4	0.31	86.43	113.13	117.29	
5	0.41	89.38	117.33	120.30	
6	0.52	91.64	122.33	124.70	
7	0.62	95.31	126.71	128.21	
8	0.72	97.17	130.59	131.84	
9	0.83	100.56	134.14	135.14	
10	0.93	103.45	137.66	138.57	
11	1.04	106.53	141.75	142.36	
12	1.24	110.92	148.35	148.96	
13	1.35	112.54	150.87	151.45	
14	1.45	114.73	153.48	153.78	
15	1.55	117.65	156.25		
16	1.66	119.52	160.25		
17	1.76	121.18	162.52		

Table 6.6

Constants A & B of the polynomial equation

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

Sl. No.	Compound	Transition	A (kbar)	B (kbar ²)	R.M.S. error
1	50 PDOB	K - C	10.00	0.17	± 0.14
		C - A	7.20	0.87	± 0.16
		A - N	10.70	0.19	± 0.29
		N - I	16.40	0.07	± 0.49
2	70. PDOB	K - C	9.90	0.14	± 0.21
		C - A	7.90	0.40	± 0.07
		A - N	10.10	0.15	± 0.19
		N - I	15.70	0.73	± 0.44
3	NOBA	K _{II} - K _I	32.08	4.55	± 0.40
		K _I - C	40.98	2.34	± 0.48
		C - N	27.54	1.54	± 0.44
		N - I	35.68	5.01	± 0.26
4	PDBAC	K - C	41.22	7.78	± 0.51
		B - C	47.43	6.65	± 0.48
		C - A	38.25	3.16	± 0.39
		A - I	40.01	5.14	± 0.49

Table 6.7

 $(dT/dP)_1$ bar and volume change ΔV at transition

Sl. No.	Compound	Transition	$(dT/dP)_1$ bar $^{\circ}\text{C}/\text{kbar}$	ΔV in $\text{cc}/\text{gm} \times 10^{-14}$
1	50 PDOB	K - C	10.06	312.3
		C - A	6.78	~ 0
		A - N	10.50	7.6
		N - I	18.48	21.1
2	70 PDOB	K - C	10.15	319.4
		C - A	8.42	~ 0
		A - N	9.84	6.2
		N - I	18.42	28.6
3	NOBA	$K_{II} - K_I$	32.1	782.5
		$K_I - C$	41.0	102.5
		$C - N$	27.5	41.4
		N - I	35.7	70.40
4	PDBAC	K - B	41.22	617.84
		B - C	47.44	131.25
		C - A	38.25	~ 0
		A - I	40.00	170.95

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