

CHAPTER V

THE SEARCH FOR AN NAC POINT IN A SINGLE COMPONENT LIQUID CRYSTALLINE SYSTEM

5.1 Introduction

Of late, there has been a considerable interest in the NAC multicritical point. When such a point was first suggested, the two proposed theoretical explanations of it were quite different. Chu and McMillan¹ proposed a model in which the smectic C has the dipolar order parameter of McMillan's theory² while the order parameter corresponding to smectic A was the one dimensional density wave described in theories of Kobayashi,³ McMillan⁴ and de Gennes.⁵ The tilt of the director away from the layer normal entered the model somewhat incidentally through a gradient term coupling the two order parameters. Chen and Lubensky,⁶ on the other hand, found an NAC point in a model wherein the only order parameter considered was the one dimensional density wave. The tilt of the director relative to the layer normal is a central feature of this model and occurs when the coefficient of the transverse gradient term becomes negative. From the experimental point of

view the differences between the two models are essentially two fold. Firstly, in the Chen and Lubensky model (CL model) NAC point is a type of Lifshitz point⁷ which leads to the prediction that Xray scattering in the nematic phase in the vicinity of NAC point falls off in the transverse direction as $k_{\perp}^{-4}$, rather than the usual $k_{\perp}^{-2}$ predicted by Chu-McMillan model (CM model). Secondly, the nematic-amectic C (N-C) transition entropy is zero in the CM model while it is finite in the CL model.

The first observation of the NAC point was by Johnson et al⁸ who on the basis of differential scanning calorimetry measurements and thermal microscopy studies reported that the temperature-concentration diagram of binary mixtures of heptyl and octyloxy-p'-pentylphenyl thiobenzoate (7S5 and 8S5) shows a NAC polycritical point. Of the two compounds, 7S5 shows smectic C and nematic phases while 8S5 exhibits smectic C, smectic A and nematic phases. When the mole fraction of 7S5 in 8S5 is increased, the range of the smectic A phase decreases and finally at a concentration of about 42%, the smectic A phase is bounded, resulting in a NAC point (figure 5.1). The important features observed by Johnson et al from the differential scanning calorimetric studies

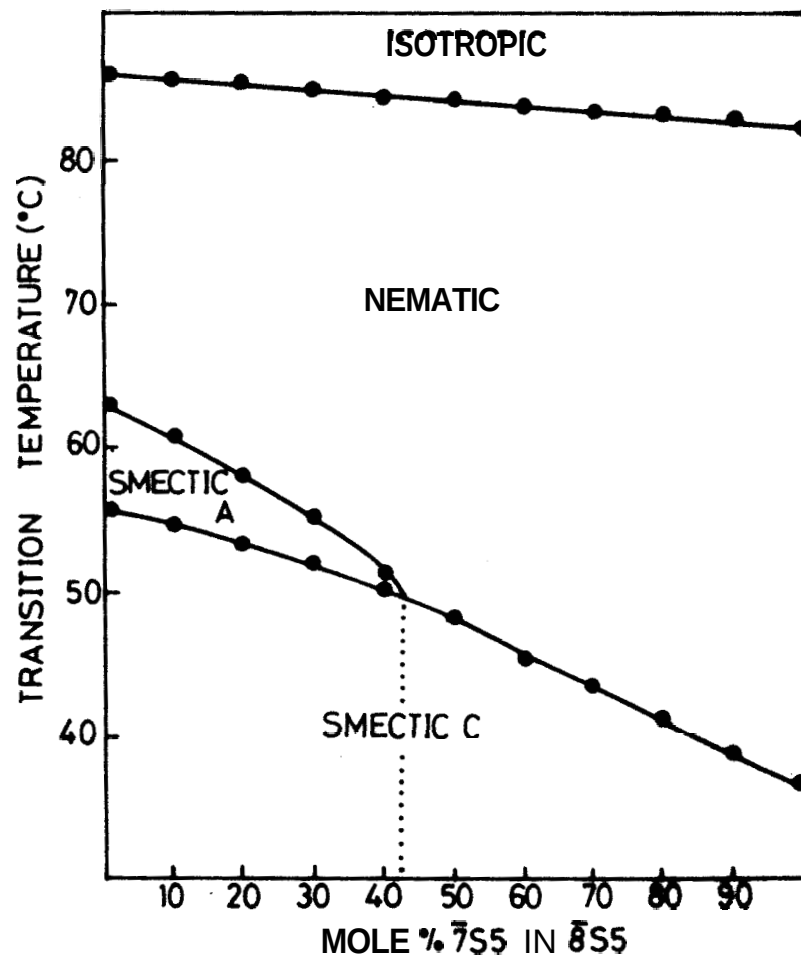


Figure 5.1: Isobaric concentration-temperature diagram of binary mixtures of 7S5 and 8S5 (after Johnson et al⁸)

are (1) **smectic A - smectic C (AC) transitions** are continuous and show little or no **pretransitional effects**, (2) the **smectic A - nematic (AN) transitions** are continuous and show rather strong **pretransitional effects** which **vanish as** the NAC point **is** approached, (3) the **smectic C - nematic (CN) transitions** are very weakly first order and **show** very weak **pretransitional effect**, (4) the point where the second order **AN** and **CA boundaries** and the first order **CN** boundary intersect **is** a multicritical point. They have **also** presented a phenomenological Landau type theory which qualitatively **describes the observed** phase diagram. Sigaud et al⁹ have also discovered a binary liquid crystalline system which exhibits the NAC point with a slightly different topology.

As mentioned earlier, Chen and Lubensky termed the **NAC** point as **Lifshitz** point. However, Safinya et al,¹⁰ on the basis of **high** resolution **Xray** studies and De Hoff et al,¹¹ on the basis of precise **ac calorimetry** measurements have concluded that the **NAC** point is **definitely &** a **Lifshitz** point as proposed by Chen and Lubensky, but **is, instead** a multicritical point. **An** **NAC** point has never been observed in a single component system and hence we have undertaken pressure **studies** on a number of **compounds with**

a view to **observe** such a point in the P-T diagram of a **single component liquid crystalline system**. We present here, the **results** of two compounds (kindly given to us by Dr. D. Demus), viz., N-(4-n-pentyloxybenzylidene)-4'-n-hexyl aniline (50.6) and 4-(4-n-decyloxybenzoyloxy) benzylidene-4'-cyanoaniline (10 BBM).

5.2 Pressure studies of 50.6

5.2.1 Compound: The structural formula of N-(4-n-pentyloxybenzylidene)-4'-n-hexylaniline (50.6) is shown in figure 5.2. This compound belongs to the well known **nO.m** series which was **synthesised** by Smith et al.¹² It must also be mentioned that the **compound** exhibits 5 **smectic** phases at **atmospheric pressure**, But, since our **interest is essentially restricted** to the **transitions** involving nematic, **smectic A** and **smectic C** **phases** only, we **have** not studied the **higher order smectics** in the **present** investigations. The **temperatures** and the **heats** of transition at atmospheric pressure, as **determined** by Perkin-Elmer DSC-2 differential scanning **calorimeter** are given in Table 5.1.

5.2.2 Experimental: The **P-T** diagram was obtained by using the **opposed** diamond anvil cell described in

N - (4 - n - Pentyloxy benzylidene) - 4 - n - hexyl aniline (50.6)

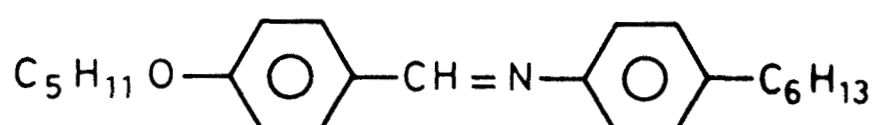


Figure 5.2: Structural formula of N-(4-n-pentyloxy)-4-n-hexyl aniline (50.6)

chapter 11. All the transitions could easily be detected by optical transmission technique. The data obtained using the diamond anvil cell were brought to an absolute scale by conducting a calibration experiment using a differential thermal analysis (DTA) cell which is also described in chapter II. The transition temperatures could be measured to a relative accuracy of $\pm 0.1^\circ\text{C}$ and the pressure to ± 15 bars; the absolute accuracies are reckoned to be about $\pm 1^\circ\text{C}$ and $\pm 2\%$ respectively.

5.2.3 Results and discussion: In all, five different sets of measurements were carried out (each time using a fresh sample), one set with the DTA cell and the rest with the diamond anvil cell. First, the DTA cell was used to obtain the BC and AN phase boundaries up to 8 kbar. Then the diamond cell was used to record all the transitions BC, CA, AN and NI. The BC phase boundary determined with the DTA cell was used to bring the diamond anvil cell data to an absolute scale. To check the reliability of the calibration, the data points (on an absolute scale) for the A-N phase boundary as determined by the two cells were compared; these are shown in figure 5.3. It can be seen from the figure that

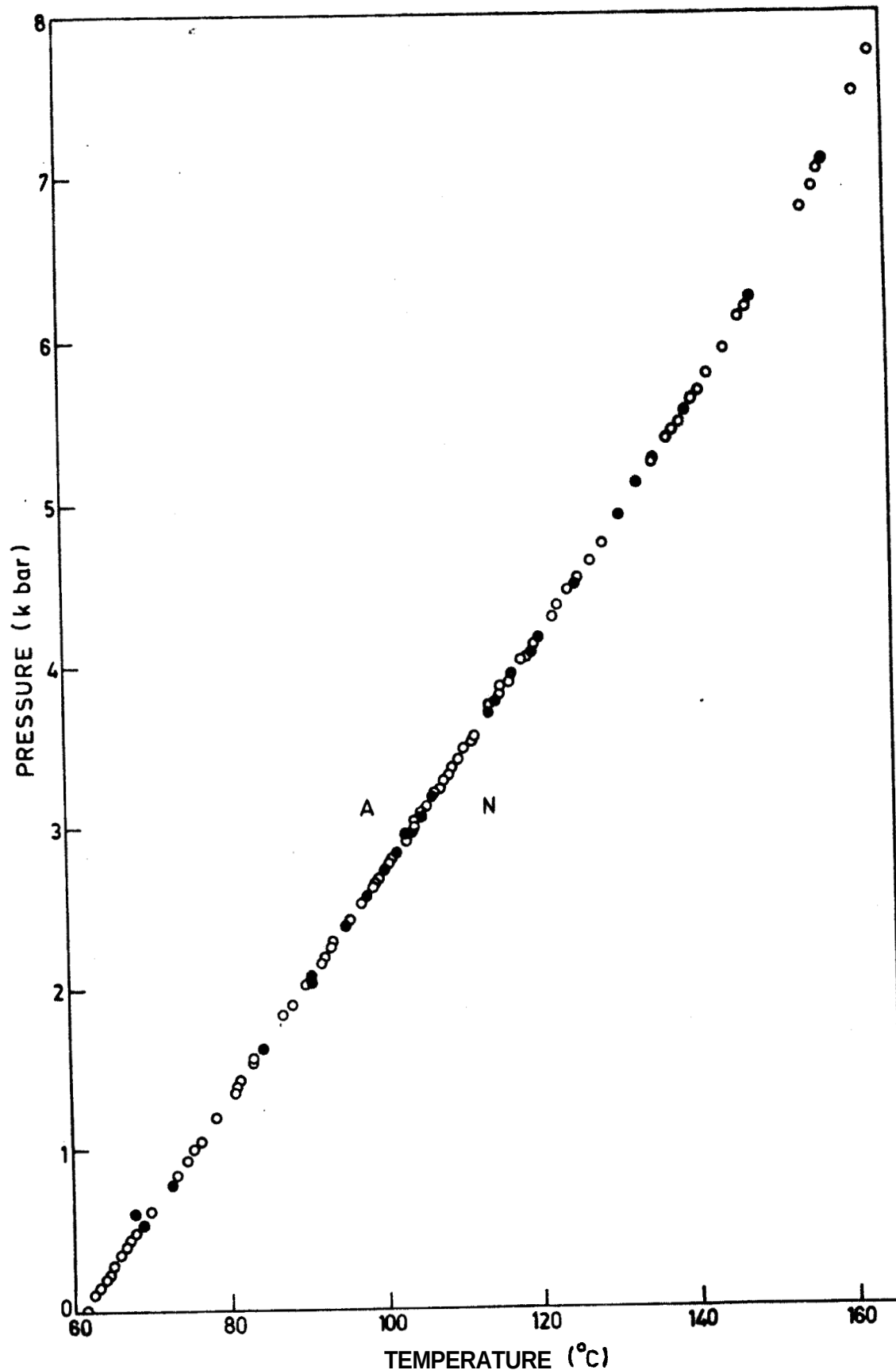


Figure 5.3: The AN phase boundary of 50.6. ● data points using DTA cell, ○ data points (representing 4 independent sets of measurements) using the diamond anvil cell.

there **is** excellent **accord between** the data **obtained** with the two cells, and further that the five independent **set of measurements** using the **diamond anvil cell** agree well with each other. After the completion ^{of} **each** set of measurements, the sample in the **gasket** was **removed** and its **transition** temperatures (at **atmospheric pressure**) were determined. They were found to be **exactly the same** as before the commencement of the experiment, thus **confirming** that the material did not suffer any **decomposition**.

The **P-T** data of this compound **are** given in Table 5.2 and 5.3. The complete phase diagram **is** shown in **two** parts, for **convenience** of presentation of the data; the measurements up to 4 kbar are shown in figure 5.3 **while** **those** for **pressures** between 4 kbar and 8 kbar are shown on an **enlarged** temperature scale in figure 5.4. It is **seen** that the temperature range of **smectic A** phase **diminishes** with **increasing** pressure. This range which is 8.9°C at 1 bar, becoming **as** small as about 0.7°C at 4 kbar (figure 5.4). At higher pressures the range **of** the A phase decreases even further **but** the rate of decrease is very **slow**. At 8 kbar, the **maximum pressure** up to which we have studied this compound, the range of **smectic A** is about 0.4°C (figure 5.5). **Had** the resolution of our experimental

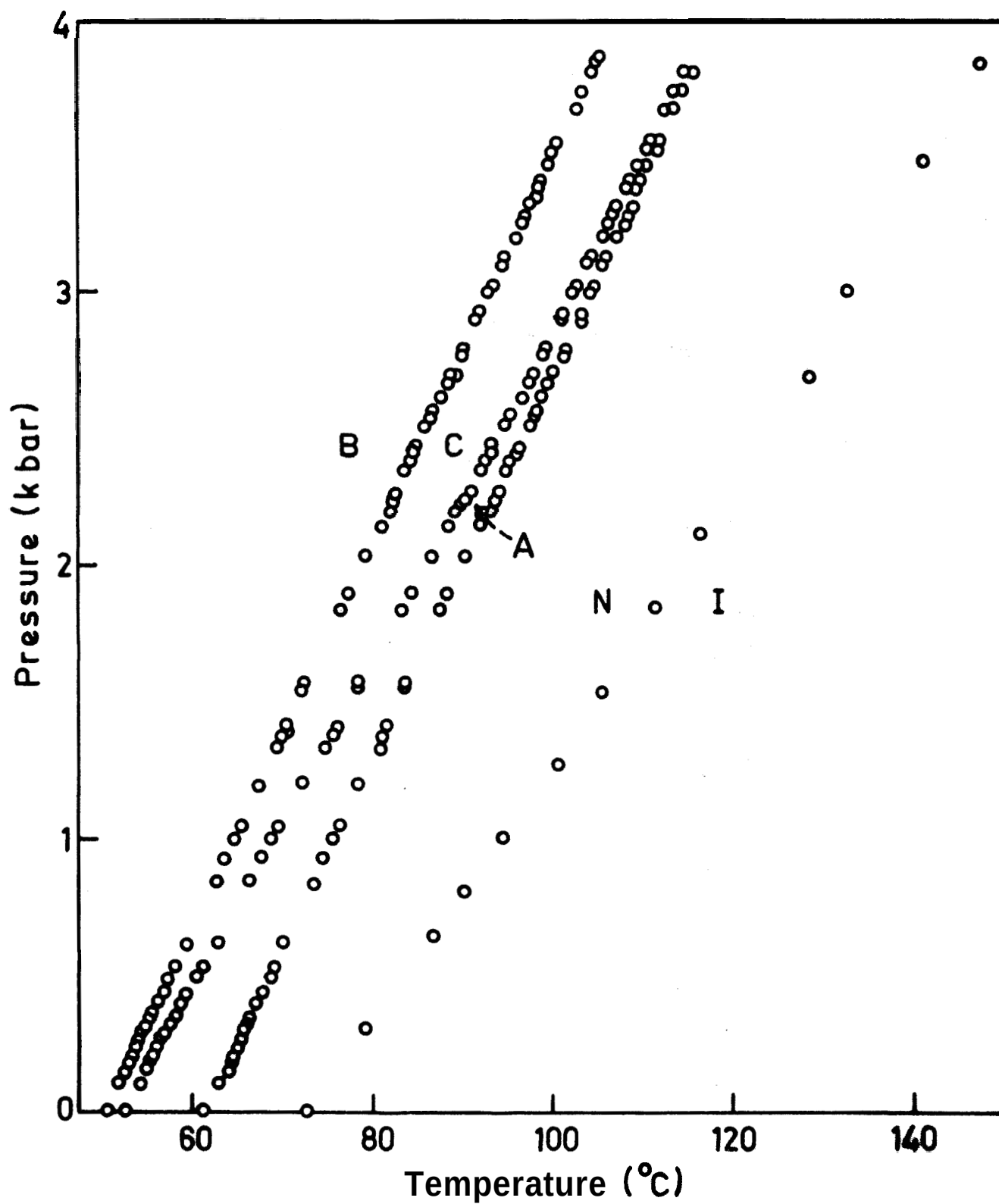


Figure 5.4: P-T diagram of 50.6 up to 4 kbar.

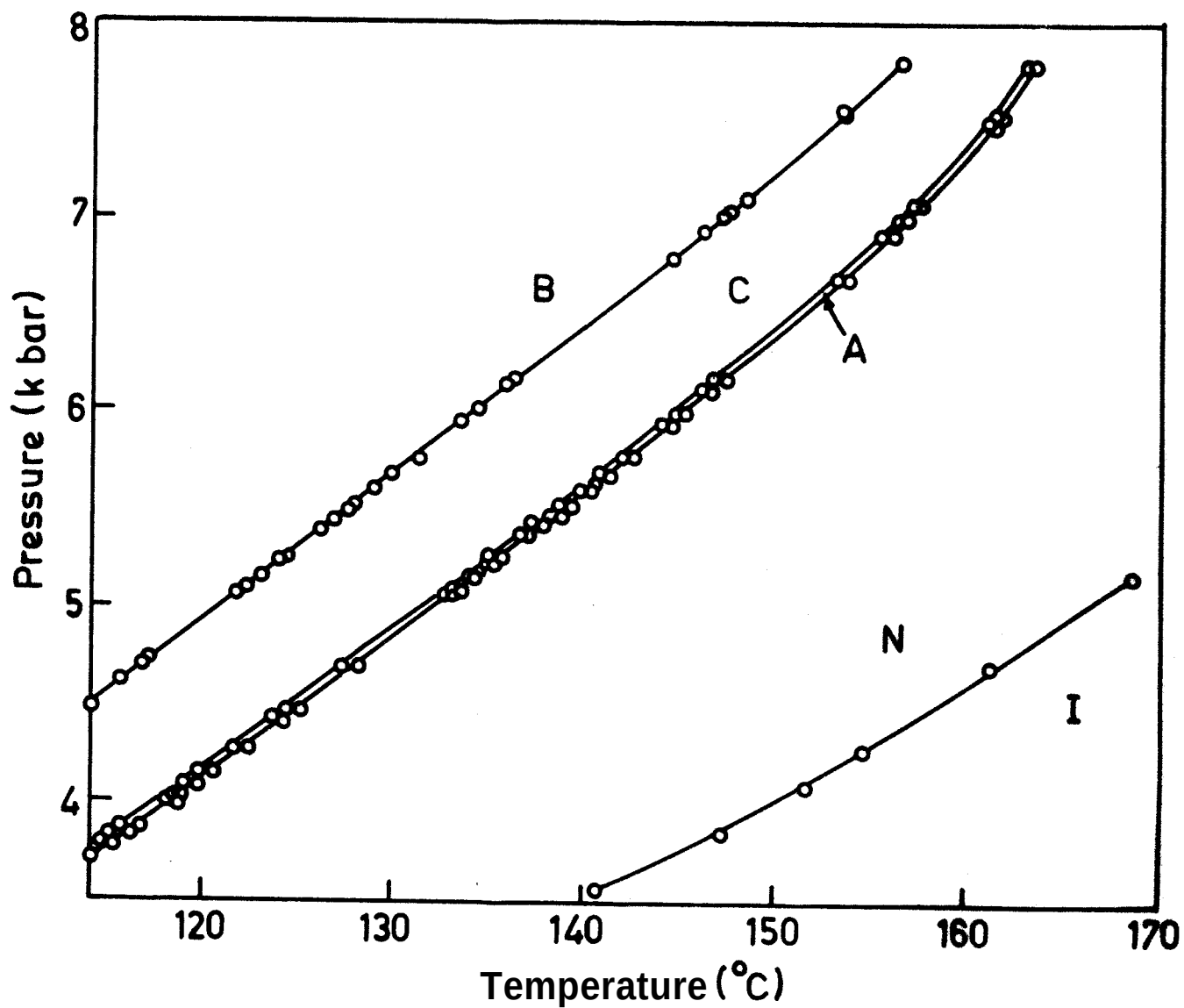


Figure 5.5: P-T diagram of 50.6 from 4 to 8 kbar.

set up been less than what it is at present, we might have concluded that C-A and A-N phase boundaries intersect at about 4 kbar. However, the precision of our data shows that this is not in fact the case. We can therefore only infer that the NAO point for this compound will probably occur at a pressure higher than 8 kbar.

It may also be mentioned that it has been theoretically predicted by Benguigui¹³ that a tricritical point should precede the NAO point which was previously referred to as Lifshitz point. Special care was therefore taken to see from the DTA experiment of the AN transition line shows a tricritical point.^{14,15} It was observed that the first order character of this transition diminishes with increasing pressure up to about 4 kbar (figure 5.6). But beyond this pressure, the change is hardly detectable. The AN transition remains first order though weakly so, right up to 8 kbar (figure 5.7). This perhaps is partly the reason why the NAO point is not observed in 50.6.

5.3 Pressure studies of 4-(4-n-decyloxybenzoyloxy)benzylidene-4'-cyanoaniline (10 BBOA)

5.3.1 Compound: It was recently reported¹⁶ that 4[4-n-octyloxybenzoyloxy]benzylidene-4'-cyanoaniline exhibits a reentrant nematic phase at atmospheric pressure.

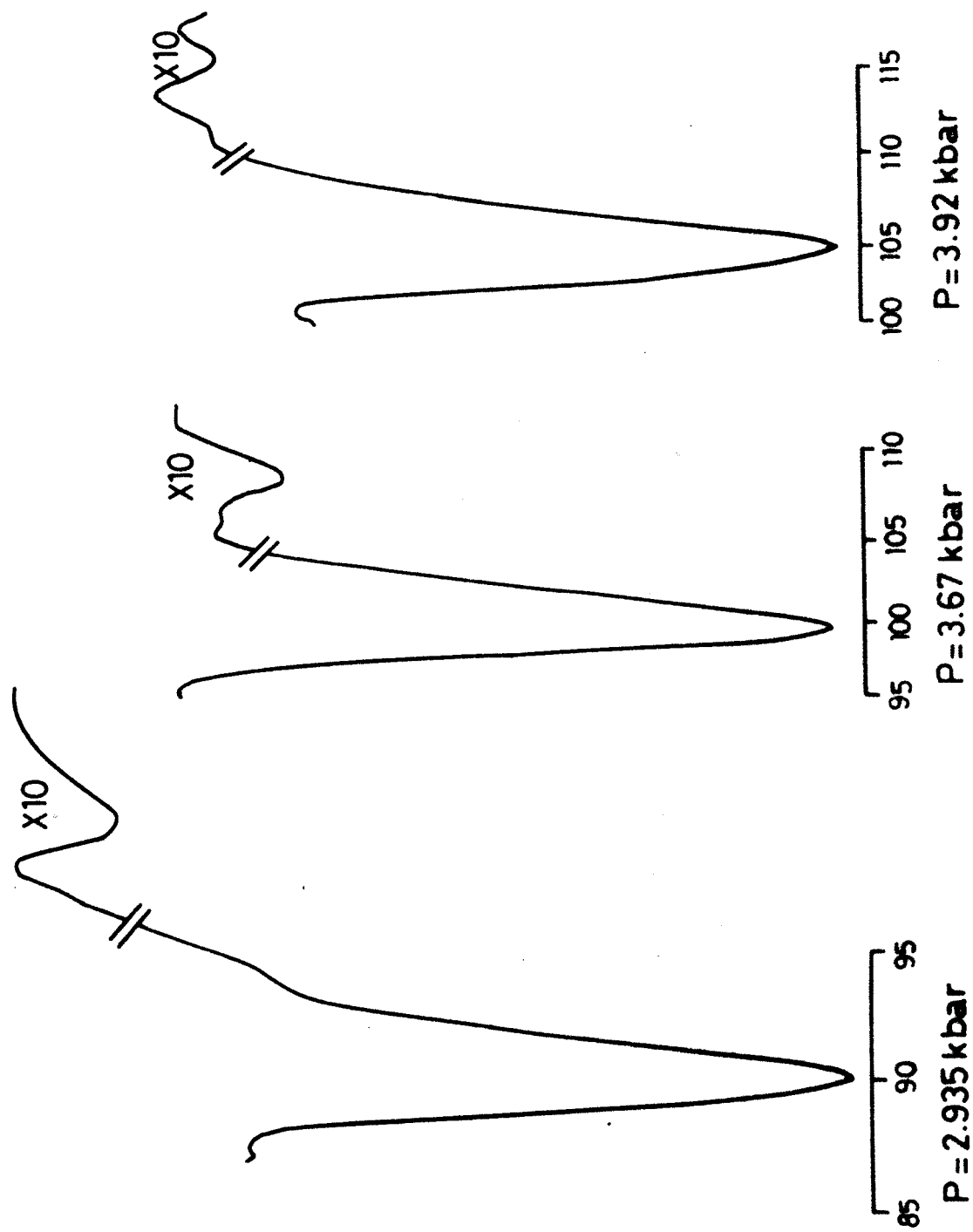


Figure 5.6: Raw DTA traces of B-O and A-M transitions in 50.6 up to 4kbar.

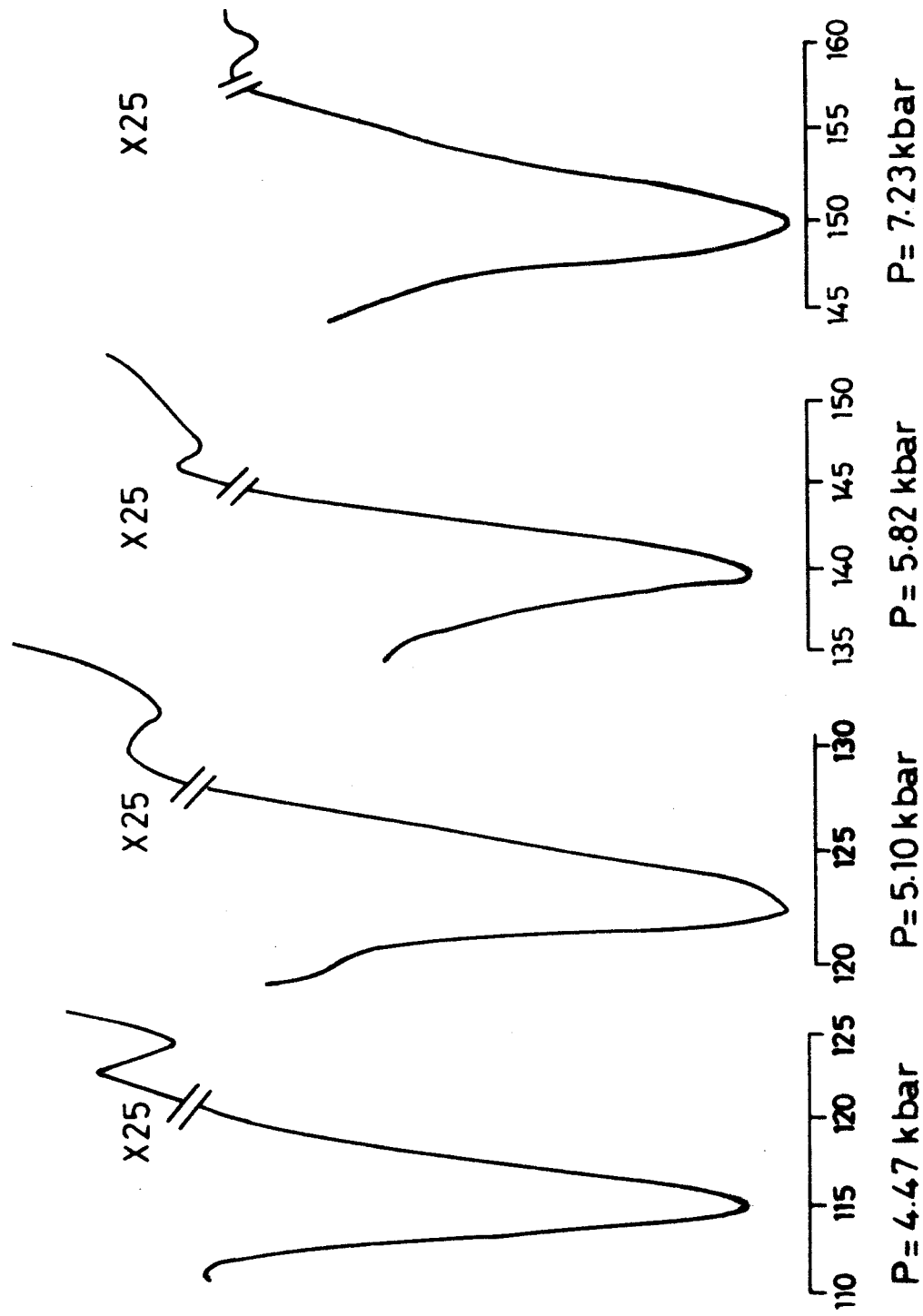
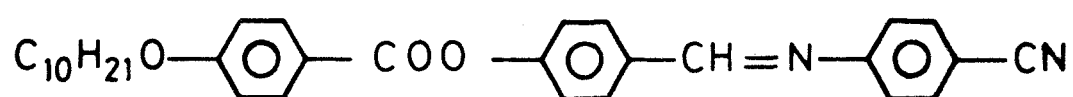


Figure 5.7: Raw IMA traces of B-O and A-N transitions in 30.6 from 4 to 8 kbar

Subsequently, Weissflog et al¹⁷ synthesised several members of this homologous series which show a remarkable sequence of transitions. The transition temperatures of these compounds as observed with a polarising microscope are given in Table 5.4. As seen from the table, the first four homologues show only normal nematic phases with a large temperature range and also metastable smectic A phases. The octyloxy compound shows an additional stable phase, viz., reentrant nematic. But in the higher homologues, the reentrant nematic phase is metastable in character. Most surprisingly, in the decyloxy derivative whose structural formula is shown in figure 5.8, the smectic C phase exists besides reentrant nematic and smectic A phase. This was the first observation of smectic C liquid crystal compound possessing a strong longitudinal dipole moment. We have conducted a high pressure study on this compound, viz., 4(4-n-decyloxy benzoyloxy)benzylidene-4'-cyanoaniline (10 BBCA) with a view to see if NAC point can be obtained at high pressures.

5.3.2 Experimental: Experiments were conducted using a high pressure optical cell described in chapter II with light transmission technique as the probe since we had gone up to a pressure of about 3.2 kbar only. All the



4 (4 - *n* - decyloxy - benzoyloxy) benzylidene - 4' cyanoanilines

Figure 5.8: Structural formula of 4-(4-*n*-decyloxybenzoyloxy) benzylidene-4'-cyanoaniline 10 BBCA

transitions were easily detected by this technique. In **all**, two independent **sets** of measurements were conducted and the data from **these** two independent sets of **measurements** were self consistent thereby **confirming** the reproducibility of **the** measurements.

5.3.3. Results and discussion: Table 5.5 **gives** the transition temperatures and the transition **enthalpies** **as measured** by a Perkin Elmer DSC-2 differential scanning calorimeter.

Since the **N-I** transition temperature is rather **high** (242°C) at one bar, this transition has not been studied as a function of pressure, essentially because **the seals** used in the pressure cell become soft and **unusable** for temperatures higher than about 245°C . For the ~~same~~ reason, the **A-N** transition has been followed only up to **about** 100 bars. On the other **hand**, the melting transition and the monotropic smectic A - **smectic C** (A - C) and smectic **C**--reentrant nematic (**C-RN**) **transitions** all occur at relatively lower temperatures and therefore can easily ~~be~~ followed. **Figure** 5.9 shows the complete phase diagram while the **P-T** data are ~~given~~ in Table 5.6. The interesting result emerges that the **range** of smectic C **which** is initially 13°C at 1 **bar** decreases quite rapidly with the increase of

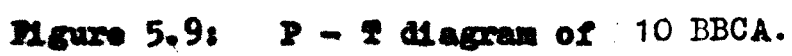


Figure 5.9: P - T diagram of 10 BBCA.

pressure and the C phase is **completely** bounded at 520 bars, thus resulting in a RN - C - A point at 0.52 kbar and 86.0°C. **The** region of the phase diagram surrounding this point is shown on an **enlarged scale** in figure 5.10. Experiments have also been conducted using the DTA **cell** to determine the nature of the **transitions** **close** to the RN - C - A point. It ~~was~~ observed that **RN - C and C - A** transitions are more or less **continuous** in nature, but the RN - A transition is definitely first order in character. In other words, it appears that **the** two second order phase boundaries, **vie.**, **RN - C and C - A** culminate and continue as a first order RN - A **phase** boundary. **We** have **thus** obtained a new kind of **multicritical** point namely RN - C - A point at 0.52 kbar and 86.0°C in **this compound**.

As regards to **the** topology of the P-T **diagram**, the following features **may** be seen from the enlarged **phase** diagram shown in figure 5.10. The RN - C **and** RN - A lines are not continuous through the RN - C - A point. **The** C - A line is straight till **very** close to **the** RN - C - A point and approaches it **slightly** obliquely. **The** RN - A boundary **appears** to have a curvature right from the RN - C - A point. It is to be mentioned that on **the** basis of **the** topo-

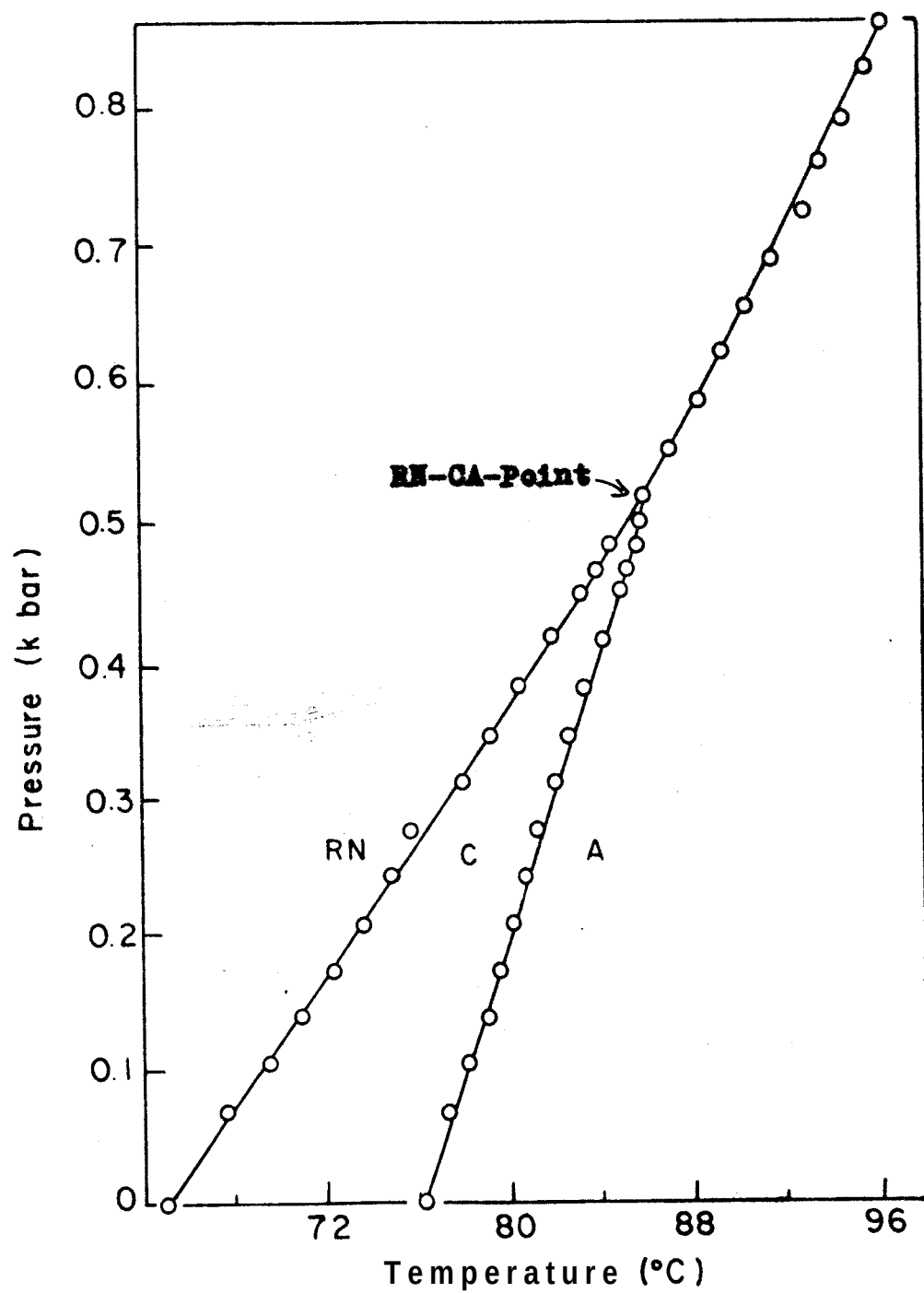


Figure 5.10: P-T diagram of 10 BBGA on an enlarged scale near RN-C-A point.

logy alone, it is hard to make any definitive conclusion regarding the nature of this point. Experiments like measurements of elastic constants, high resolution X-ray studies, etc. are required to be conducted at high pressures in order to provide more information concerning the nature of this point.

It is to be noted that the rest of the phase diagram (figure 5.9) is also quite interesting. Beyond a pressure of 1.7 kbar, the RN - A phase boundary starts curving towards the temperature axis as it is indeed expected since it should form a part of the elliptical phase boundary which should join the AN phase boundary. Owing to the problem of going to high temperatures in the high pressure optical cell (as described earlier) we have not been able to follow the complete elliptical AN phase boundary. It may also be noted that the smectic A phase is bounded on heating at 2.90 kbar, 171.0°C, but it, of course, continues to exist beyond this pressure on cooling.

Summarising these results for these two compounds, although the NAC point has proved to be elusive in the case of 50.6, we have been able to find a new multicritical point, viz., RN - C - A point in the case of 4-(4-n-decyloxy-benzoyloxy)-benzylidene-4'-cyanoaniline.

Table 5.1

**Transition temperatures and heats of transition
of 50.6**

Transition	Temperature °C	Heats of transition ΔH in kJ/mole
smectic B-smectic C	51.5	2.45
smectic C-smectic A	52.7 [‡]	~0
amectic A-nematic	61.6	0.80
nematic-isotropic	72.6	1.05

[‡]determined by thermal microscopy

Table 5.2

Temperatures of $S_B - S_C$, $S_A - N$ and $N - I$ transitions of
50.6 as a function of pressure using DTA cell

$S_B - S_C$		$S_A - N$		$N - I$	
Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C	Pressure in kbar	Temp. in °C
room pr.	51.3	room pr.	61.4	room pr.	72.6
0.52	58.0	0.53	67.5	0.3	79.2
0.59	59.0	0.59	68.0	0.66	86.8
0.78	61.3	0.6	68.1	0.81	90.0
1.4	70.2	0.78	72.4	1.01	94.2
1.63	73.3	1.40	81.4	1.29	100.3
1.88	75.3	1.63	84.4	1.54	105.2
2.04	78.9	1.86	86.8	1.85	111.0
2.07	79.3	2.07	90.9	2.12	116.2
2.41	84.2	2.41	95.2		
2.72	89.0	2.72	100.1		
2.82	90.3	2.82	101.7		
2.97	92.4	2.94	103.0		
2.98	92.6	3.06	105.0		
3.06	93.7	3.18	106.2		
3.17	95.0	3.68	113.7		
3.68	102.7	3.74	114.8		
3.74	103.2	3.92	117.0		
3.92	105.5	4.06	119.2		
4.06	107.5	4.15	120.3		
4.25	110.2	4.47	125.1		
4.46	113.8	4.89	130.6		
4.86	119.0	5.11	132.9		
5.1	122.5	5.57	139.4		
5.56	128.5	6.23	147.1		
6.23	137.2				
6.7	144.2				
7.25	150.2				
7.86	157.7				

Table 5.3

**Transition temperatures of 50.6 as a function of pressure
using diamond anvil cell**

Sl. No.	Pressure in kbar	SET I		
		Transition temperatures in °C		
		$S_B - S_C$	$S_C - S_A$	$S_A - N$
1	0.10	51.8	54.0	62.8
2	0.17	52.9	55.0	64.0
3	0.20	53.2	55.5	64.2
4	0.25	54.0	56.3	65.0
5	0.34	55.2	57.8	66.1
6	0.85	62.7	66.4	73.4
7	1.0	64.7	68.8	75.5
8	1.20	67.4	72.1	78.3
9	1.40	70.3	75.8	81.1
10	1.55	72.5	78.2	83.2
11	2.03	79.0	86.3	90.0
12	2.20	81.8	89.0	92.7
13	2.54	86.3	94.8	97.3
14	2.91	91.6	100.8	102.7
15	3.02	93.0	102.2	104.1
16	3.25	96.3	106.1	107.7
17	3.40	98.3	108.5	109.8
18	3.56	99.9	110.4	111.5
19	3.87	105.0	115.7	116.5
20	4.02	107.0	118.0	118.8
21	4.15	109.0	119.9	120.5
22	4.47	113.4	134.5	125.1
23	4.63	115.4	126.7	127.3
24	4.72	117.0	128.0	128.6
25	5.23	123.9	134.8	135.3
26	5.52	127.9	138.7	139.2
27	5.6	129.0	139.8	140.3
28	5.94	133.5	144.0	144.6

Table 5.3

Transition temperatures of 50.6 as a function of pressure
using diamond anvil cell

Set II

Sl. No.	Pressure in kbar	Transition temperatures in °C		
		$S_B - S_0$	$S_0 - S_A$	$S_A - N$
1	2.22	81.8	87.5	93.0
2	2.24	82.1	90.0	93.2
3	2.35	83.6	91.8	94.8
4	2.38	84.1	92.1	95.0
5	2.43	84.7	93.0	96.0
6	2.52	85.9	94.6	97.2
7	2.66	88.1	97.0	99.1
8	3.02	93.0	102.4	104.5
9	3.32	97.2	107.0	108.8
10	4.36	112.1	122.0	122.7
11	4.50	114.1	124.9	125.5
12	5.10	122.3	133.0	133.6
13	5.25	124.3	135.0	135.6
14	5.43	126.8	137.2	137.8
15	5.48	127.5	138.1	138.7
16	5.94	133.5	144.0	144.5
17	6.17	136.4	146.9	147.4
18	6.78	144.6	153.8	154.3
19	7.08	148.4	157.0	157.5
20	7.50	153.70	161.1	161.6
21	7.75	156.0	163.0	163.5

Table 5.3

Transition temperatures of 50.6 as a function of pressure
using Diamond Anvil Cell

Set III

Sl. No.	Pressure in kbar	Transition temperatures in °C		
		$S_B - S_C$	$S_C - S_A$	$S_A - N$
1	0.15	52.7	54.8	63.6
2	1.05	65.2	69.7	76.2
3	1.34	69.4	74.8	80.9
4	1.42	70.5	76.0	81.6
5	1.55	72.3	78.1	83.2
6	1.90	77.2	84.2	88.2
7	2.15	81.0	88.4	92.0
8	2.27	82.5	90.5	93.7
9	2.42	84.5	93.0	95.8
10	2.55	86.5	95.0	97.6
11	2.63	87.4	96.2	98.8
12	2.7	88.7	97.5	99.8
13	2.80	89.9	99.0	101.0
14	2.90	91.2	100.8	102.7
15	3.12	94.3	104.0	105.8
16	3.34	97.6	107.8	109.0
17	3.38	98.1	108.0	109.1
18	3.48	99.6	109.8	110.8
19	3.67	102.2	112.8	113.5
20	3.73	102.8	113.5	114.2
21	3.80	103.9	114.6	115.3
22	4.02	107.09	118.0	118.6
23	4.05	107.31	118.3	119.0
24	4.43	112.65	123.7	124.3
25	5.67	130.0	140.8	141.2
26	5.77	131.3	142.0	142.5
27	6.0	134.45	144.8	145.3
28	6.12	136.01	146.1	146.6

Table 5.3

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Transition temperatures of 50.6 as a function of Pressure
using Diamond Anvil Cell

SET IV

Sl. No.	Pressure in kbar	Transition Temperatures in °C			
		$S_B - S_C$	$S_C - S_A$	$S_A - N$	$N - I$
1	0.20	53.25	55.5	64.2	
2	0.27	54.37	56.4	65.2	
3	0.3	54.81	57.0	65.6	79.2
4	0.35	55.26	58.0	66.2	
5	0.4	56.15	58.7	67.0	
6	0.49	57.48	60.2	68.1	
7	0.62	59.26	62.6	70.0	
8	0.93	63.49	67.5	74.5	
9	1.38	69.94	75.6	80.8	
10	1.56	72.39	78.1	83.3	
11	1.83	76.39	83.0	87.3	
12	2.23	81.95	89.9	93.0	
13	2.67	89.96	96.7	99.0	
14	2.78	89.99	99.0	101.0	
15	3.0	92.7	102.0	104.0	132.2
16	3.48	99.6	109.5	110.6	140.6
17	3.67	102.2	112.8	113.5	
18	3.73	102.86	113.5	114.2	
19	3.80	103.98	114.6	115.3	
20	3.85	104.8	115.2	116.2	147.2
21	4.05	107.31	118.3	119.0	
22	4.1	108.3	119.0	119.8	151.7
23	4.43	112.65	123.7	124.3	
24	4.7	116.80	127.7	128.2	161.2
25	5.07	121.77	132.5	133.0	
26	5.16	123.0	133.7	134.2	168.7
27	5.67	130.0	140.8	141.2	
28	5.77	131.3	142.0	142.5	
29	6.0	134.45	144.8	145.3	
30	6.12	136.01	146.1	146.6	
31	6.13	135.9	146.2	146.7	182.5
32	6.92	146.24	155.7	156.2	
33	7.01	147.58	156.3	156.8	
34	7.54	153.59	161.6	162.0	

Table 5.4

Transition temperatures ($^{\circ}\text{C}$) of nBBCA
(Reference 17)

n	Cr	RN	S _C	S _A	N	I
4	• 137.5	–	–	• (101)	• 299	•
5	• 122.0	–	–	• (102)	• 280	•
6	• 115.0	–	–	• (84)	• 272	•
7	• 115.0	–	–	• (68)	• 265	•
8	• 108	• 152	–	• 198	• 255	•
9	• 97	(• 94)	–	• 224	• 247	•
10	• 100	(• 66	• 79)	• 232	• 242	

Cr : solid crystal

S_A, S_C : smectic A, smectic C

N : nematic

C : isotropic

The numbers are the transition temperatures ($^{\circ}\text{C}$).

Brackets denote monotropic phases.

Table 5.5

Heats of transition of 10 BBCA

Transition	<u>Transition temperatures (°C)</u>		Heats of transi- tion in kJ/mole
	Mettler	DSC	
K - S _A	99.8	98.3	39.92
S _A - N	231.8	231.6	0.72
N - I	242.1	241.9	1.32
S _A - S _C	(76.2)	(76.6)	0.0236*
S _C - RN	(65.1)	(64.7)	0.0485

() indicates monotropic transition

*The transition peak is not sharp and hence the value is not very accurate

Table 5.6

Transitions temperatures of 10 BBQA as a function
of pressure

SET I.

Sl. No.	Pressure in kbar	Transition temperatures in °C				
		heating			cooling	
		$S - S_A$	$S_A - N$	$N - I$	$S_A - S_0$	$S_0 - RN$
1	room pr.	99.8	231.8	242.1	76.2	65.1
2	0.10	108.0			78.17	69.2
3	0.14	109.23			79.33	70.79
4	0.17	109.46			79.83	71.8
5	0.21	109.93			80.34	72.8
6	0.24	110.63			80.84	74.06
7	0.28	112.03			81.34	75.32
8	0.31	113.20			82.34	78.07
9	0.35	114.13			82.85	79.33
10	0.38	114.83			83.35	80.59
11	0.41	115.77			83.60	81.34
12	0.43	116.0			84.10	82.5
13	0.45	116.23			85.38	83.86
14	0.48	117.4			85.86	84.60
					<u>$S_A - RN$</u>	
15	0.55	119.26			87.62	
16	0.62	121.37			89.63	
17	0.69	123.47			92.05	
18	0.83	126.03			95.91	
19	0.97	130.7			102.45	
20	1.10	133.5			108.22	
21	1.24	137.94			112.49	
22	1.38	140.98			116.76	
23	1.52	144.98			120.02	
24	1.66	147.48			123.54	
25	1.8	151.0			128.31	
26	1.93	154.5			132.08	

Table 5.6

Transition temperatures of 10 BBGA as a function of
pressure

Set 11

Sl. No.	Pressure in kbar	Transition temperatures (°C)				
		heating			cooling	
		S - S _A	S _A - N	N - I	S _A - S _C	S _C - R _N
1	room pr.	99.8	231.8	242.1	76.2	65.1
2	0.07	106.63	-	-	77.42	67.78
3	0.10	108.30	235.8	-	78.17	69.53
4	0.14	108.9	-	-	79.33	71.09
5	0.17	109.5			79.58	72.55
6	0.21	110.16	240.0		80.34	73.80
7	0.24	110.87			80.84	74.80
8	0.28	111.56			81.34	75.86
9	0.31	112.97			82.09	77.07
10	0.35	113.9			82.6	78.33
11	0.38	114.37			82.85	79.33
12	0.40	114.6			82.85	81.4
13	0.41	115.77			84.35	82.04
14	0.43	115.83			84.8	83.05
15	0.45	116.93			85.06	83.35
16	0.47				85.2	84.0
17	0.48	117.87			85.86	84.6
18	0.50				85.9	
19	0.52	118.80			86.11	S _A -R _N .
20	0.55	119.97			87.37	
21	0.59				88.37	
22	0.62	121.13			89.63	
23	0.66	122.54			90.63	

continued...

Table 5.6 continued

Sl. No.	Pressure in kbar	Transition temperatures(°C)			
		heating		cooling	
		S - S _A	S _A - N	N - I	S _A - RN
24	0.69	123.24			91.89
25	0.76	125.10			93.6
26	0.90	127.67			97.42
27	1.07	131.17			
28	0.72	124.1			93.01
29	0.79	126.0			95.09
30	0.86	127.5			96.5
31	1.17	136.5			109.6
32	1.31	139.4			112.96
33	1.45	143.1			116.7
34	1.59	147.1			121.6
35	1.72	150.15			126.5
36	1.86	153.5			129.07
37	2.28	160.3			146.4
38	2.48	165.0			151.4
39	2.62	167.0			159.97
40	2.76	169.5			164.48
41	2.90	171.32			169.5
42	3.03	173.18			175.29

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