

CHAPTER III

PRESSURE STUDIES ON REENTRANT NEMATOGENS

3.1 Introduction.

As was pointed out in chapter I, the general sequence of phase transitions on heating a polymeric compound would be solid $\rightarrow$ amectic $\rightarrow$ nematic $\rightarrow$ isotropic. However, a remarkable exception to this sequence was found by Gladis.¹ She found that in the mixtures of N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA) and p-[(p-hexyloxybenzylidene)-amino]benzonitrile (HBAB), the nematic - smectic A transition temperature becomes the multivalued, nematic phase occurring at higher as well as lower temperatures relative to the smectic A phase. The phase diagram of these mixtures is given in figure 3.1. It is seen that for a concentration range of about 5 to 15% of HBAB, the sequence of phase transitions on cooling is

isotropic $\rightarrow$ nematic $\rightarrow$ smectic A $\rightarrow$ nematic $\rightarrow$ solid.

This lower temperature nematic phase was later designated as reentrant nematic phase. The reentrance of a higher symmetry phase at a temperature below the less symmetric

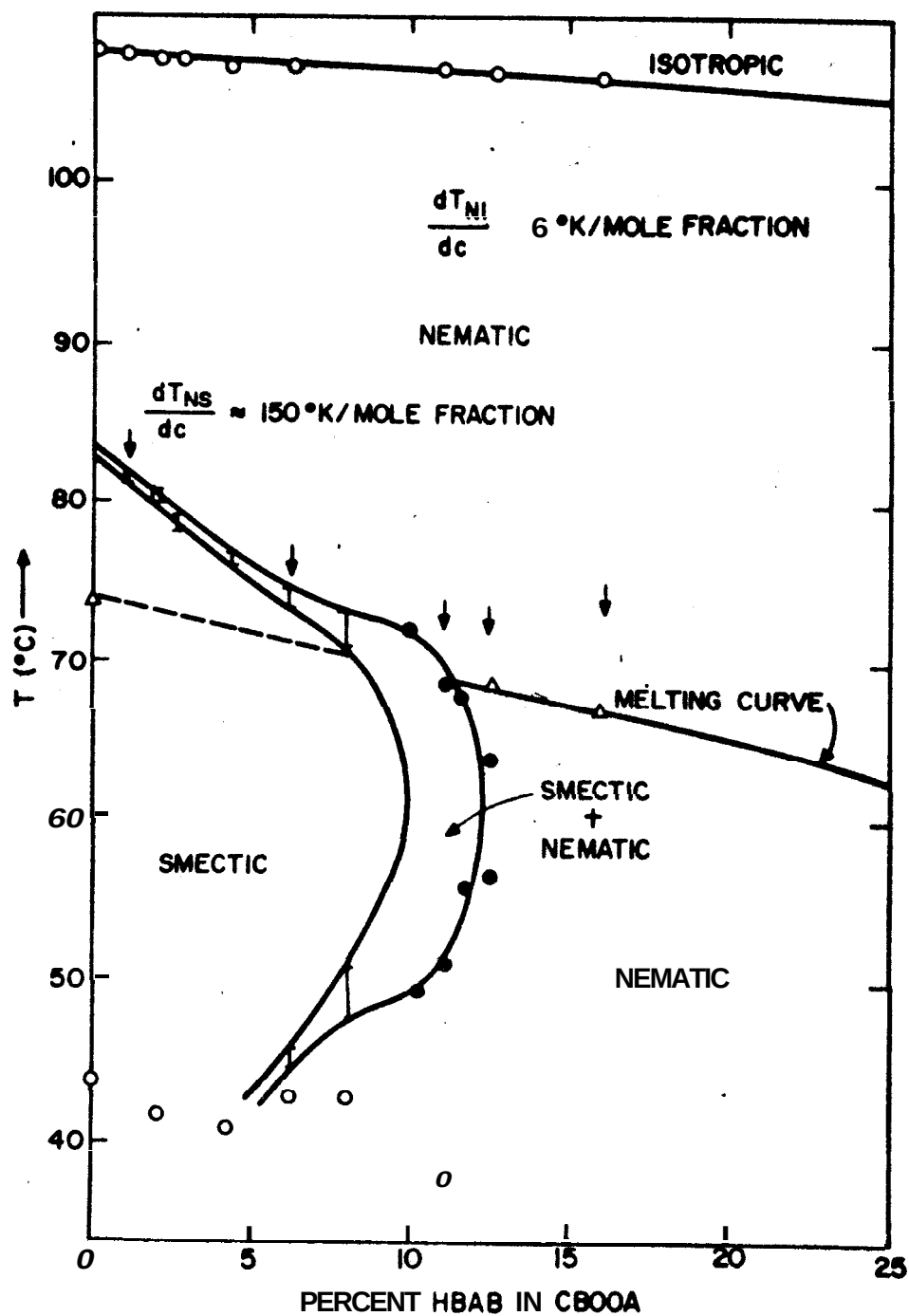


Figure 3.1: Isobaric phase diagram of the binary mixtures of CBOOA and HBAB (after Uladis¹).

one is encountered in several other systems. The pressure dependence of He^3 melting temperature³ was perhaps the earliest example of reentrant behaviour. The reentrance of the normal phase in superconductors doped with Kondo impurities was predicted theoretically⁴ and was immediately established experimentally.⁵ Other systems such as the naturally occurring proteins like metmyoglobin and chymotrypsinogen water systems^{6,7} exhibit similar P-T diagrams (at constant pH). More recently, a reentrant nematic-isotropic phase boundary has been predicted in poly- γ -benzyl-L-glutamate dissolved in denatured solvents.⁸

Thus, although the phenomenon of reentrance was known for quite some time, it came as a surprise in the field of liquid crystals. Cladis¹ found that the bend elastic constant K_{33} of OBOOA and HBAB mixtures exhibited a similar behaviour on both sides of the smectic A phase, namely, it showed a sharp pretransitional increase on approaching the smectic A phase either from the high or from the low temperature side. It was concluded, therefore, that there is no macroscopic difference between a high temperature (normal) nematic and the reentrant nematic phases.

Subsequently, Gladis et al.² found for the first time reentrant behaviour in a single component system (pure compound) at elevated pressures. They found that the compound 4'-n-octyloxy-4-cyanobiphenyl (8 OCB) exhibits reentrant nematic phase in the pressure range of about 1.6 to 1.8 kbar, in the cooling mode. They also observed reentrant nematic phase in CBOOA, mixtures of 8 OCB and 6 OCB, and also mixtures of n-p-cyanobenzylidene-p-nonylaniline (CBNA) with n-p-cyanobenzylidene-p-heptyl aniline (CBHA)⁹ under high pressure.

In all these high pressure investigations wherein reentrant nematic phase has been observed, there is an unusual behaviour of nematic-smectic A phase boundary. Figure 3.2 shows the P-T diagram of 8 OCB obtained by Gladis et al.² It is seen that the nematic-smectic A phase boundary curves towards the pressure axis resembling the arc of an ellipse. The reentrant nematic phase exists, over a pressure range of 1.6 to 1.8 kbar. Beyond this pressure smectic A ceases to exist and there is only a nematic phase.

Very recently, reentrant nematic phase has been observed in pure compounds at atmospheric pressure by Madhusudana et al.¹⁰ in our laboratory and at about the

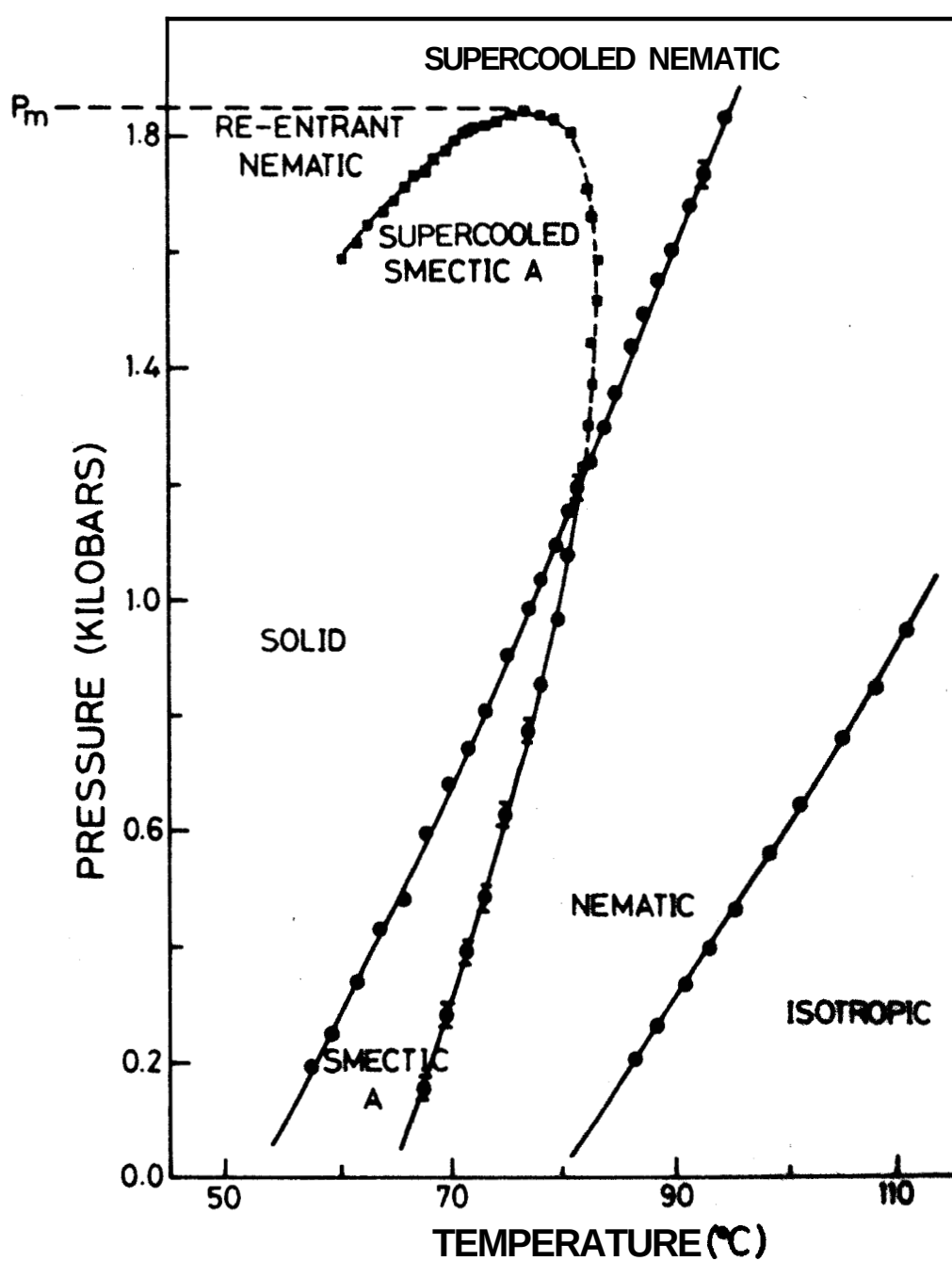


Figure 3.2: P-T diagram of 8 OOB (after Gladis et al²).

same time by Hardouin et al¹¹ at Bordeaux. The discovery of compounds which show reentrant behaviour at atmospheric pressure has led to the tremendous surge of activity in the synthesis of such materials and a number of substances, pure compounds as well as the binary mixtures, are now known which exhibit the reentrant nematic behaviour at atmospheric pressure.¹²⁻²⁸ The synthesis of these compounds have also led to a variety of experimental studies on this phenomenon.²⁹⁻³³

In spite of the fact that a number of pure compounds are now known which exhibit the reentrant nematic phase at atmospheric pressure, so far there has been only a single pressure study on such a compound, this being, due to Gladis³⁴ who studied the P-T diagram of 4-n-octyloxybenzoyloxy-4'-cyanostilbene (T8), the compound synthesised by Bordeaux group. We have studied the 11th and 12th members of four different homologous series. Six of the compounds studied, exhibit monotropic reentrant nematic phase, whereas in the other two compounds, the reentrant nematic phase is enantiotropic. All the compounds studied have been synthesised in our laboratory.^{25,26}

3.2 Compounds

The compounds studied are listed in Table 3.1 along with their structural formula.

All the compounds have three phenyl rings with a lateral methyl or methoxy substituent attached to the middle phenyl ring and a cyano end group. The purity of the compound was checked by elemental analysis and thin layer chromatography. The phases were identified by observing the textures using a polarising microscope fitted with a heating stage (FP5 Mettler). The transition temperatures were determined both optically and by differential scanning calorimetry and the heats of transition were determined using a differential scanning calorimeter (Perkin-Elmer DSC-II). These data are given in Table 3.2. The heat associated with smectic A - reentrant nematic transition is given only for four compounds since in the case of the other substances, the heats are too small to be determined with sufficient accuracy. The reentrant nematic phase is enantiotropic in two compounds, viz., the 11th homologue of series II and III. The other six compounds studied exhibit only a monotropic reentrant nematic phase.

3.3 Experimental

The phase transitions were detected by the optical transmission technique. The sapphire cell described already in chapter II was used for the experiments. The liquid crystalline sample was sandwiched between two optically polished sapphire cylinders which fit snugly inside the fluran tube, Fluran being an elastomer material, transmits pressure very well, but does not permit oil to seep through it. Further, it prevents the sample from coming into direct contact with the pressure transmitting medium. The line pressures measured therefore also correspond to the pressure experienced by the sample,

The transmitted light intensity was monitored by a photocell. Experiments were always conducted along isobars, i.e., to determine the transition temperatures at any pressure, the pressure was kept constant and the temperature was varied at a constant rate of 1 to 2°C per minute. The temperature at which there was an abrupt change in the intensity of transmitted light was taken as the transition temperature. There was however a difficulty in that all the compounds studied have a natural tendency for a homeotropic

alignment which **makes** the detection of **the** transition by this technique rather difficult. **To** avoid such an **alignment**, silicon monoxide was deposited at an oblique **angle** on the surface of the sapphire cylinders **sand-**wiching the sample. **This** resulted in **large intensity jumps** at the **transition**. Even the **smectic A - reentrant** nematic **transitions** which were rather difficult to detect by DSC were easily **detected** by this technique. **Pressures** were maintained **and** measured to an **accuracy** of ± 10 bars while the **transition** temperature would be read correct to $\pm 0.025^\circ\text{C}$.

The self consistency of **the** results **is** proved by the fact that the data points obtained by 2 independent measurements on fresh **samples** of different **thickness** fall on the **same** curve. The transition **temperatures** at room pressure **measured** before and after the **experiment** were identical showing **that** there **was** no contamination or deterioration of the sample.

3.4 Results and Discussion

From the **P-T** diagrams of the compounds **studied**, it **is** found that the melting **as** well **as** the nematic - isotropic (**N - I**) **phase** boundaries are **straight** lines

while the smectic A - nematic (A - N) phase boundary is elliptic in shape in all the cases. ' P_m ' the maximum pressure and T_m the maximum temperature up to which smectic A exists are listed in Table 3.12.

3.4.1 8 OCB

In order to estimate the possible pressure hysteresis in the determination of smectic A - nematic phase boundary particularly where the curving is rapid i.e., where the A-N transition temperature is more sensitive to pressure changes, it was thought worthwhile to do experiments first on 8 OCB. The compound used in our experiment was obtained by BDH Chemicals, England and was used without further purification. The transition temperatures of our sample at 1 bar are 67.0°C and 81.0°C for smectic A - nematic and nematic isotropic transitions respectively. The P-T diagram of our 8 OCB sample is shown in figure 3.3 while the P-T data is given in Table 3.3. It was found that when the experiment was performed along an isobar, there was no observable hysteresis in the experimental value. The value of P_m , the maximum pressure for smectic stability, i.e., the maximum pressure up to which the smectic A exists for our sample is 1.98 kbar which is slightly higher than

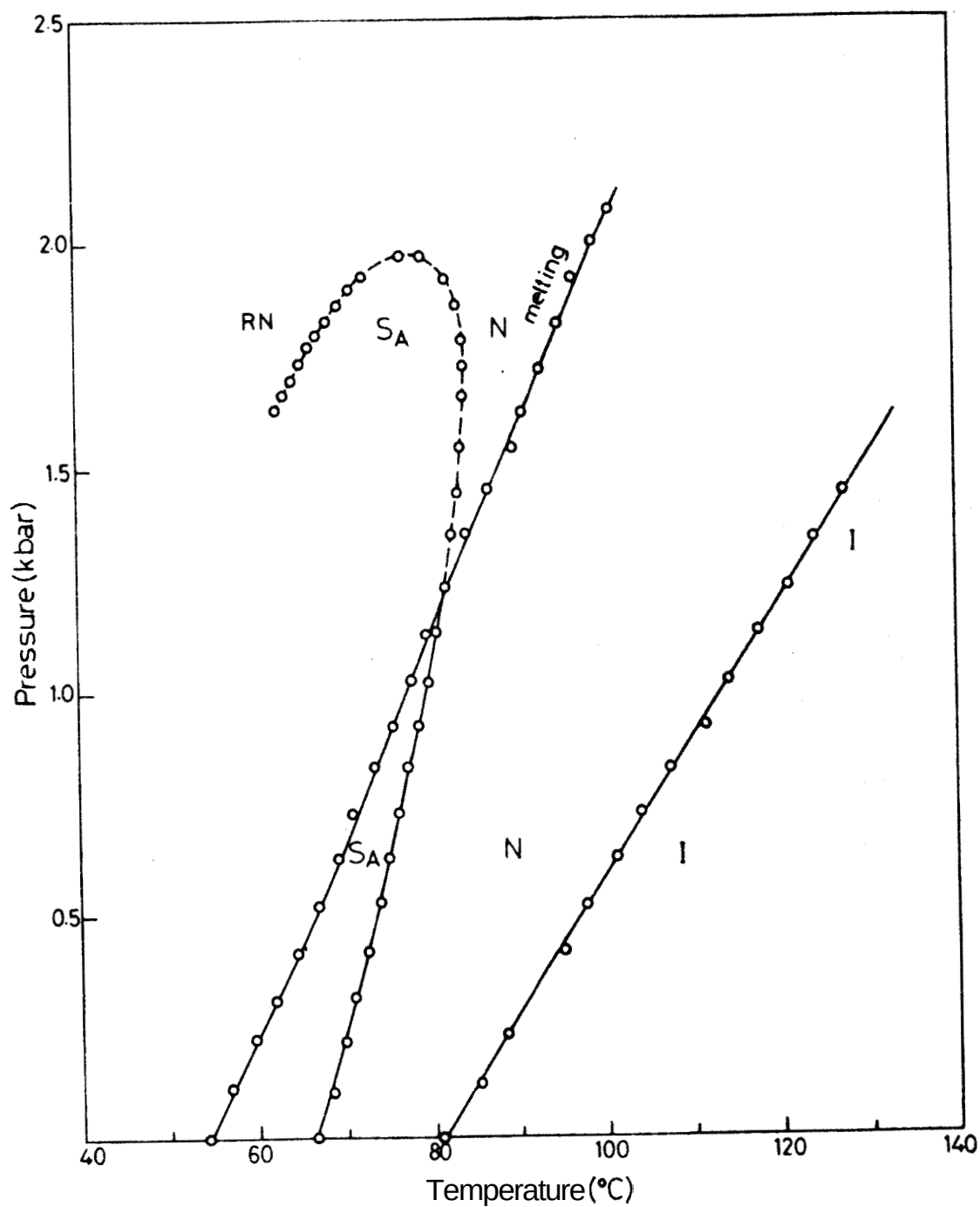


Figure 3.3: P-T diagram of 8 OCB. In this *W* well as in all the following diagrams, the solid curve is a guide to the eye.

the earlier data of **Cladis** et al probably because of a slight difference in the purity of *the* sample. In fact it has been shown that P_m for 8 OCB is extremely sensitive to impurities.⁹

3.4.2 Series I - 11 CPMBB and 12 CPMBB

As said earlier, **Madhusudana** et al¹⁰ observed the reentrant nematic phase in pure compounds at atmospheric pressure, two of these compounds being 11 CPMBB and 12 CPMBB. The synthesis of these compounds has been carried out by **Sadashiva**.²⁵ For these compounds both the bridging groups are carboxyloxy moieties and there is a lateral CH_3 group attached to the middle phenyl ring. Both compounds exhibit monotropic reentrant nematic phases,

The transition temperatures at different pressures for these two compounds are given in Table 3.4 and Table 3.5 respectively, The complete P-T phase diagrams are given in figures 3.4 and 3.5. It is seen that in 11 CPMBB, P_m , the maximum pressure at which the smectic A gets suppressed is quite low, i.e., 0.55 kbar. The melting line intersects smectic A - nematic (A-N) phase boundary at a pressure of 0.50 kbar, thereby resulting in a solid - smectic A - nematic triple point (on heating)

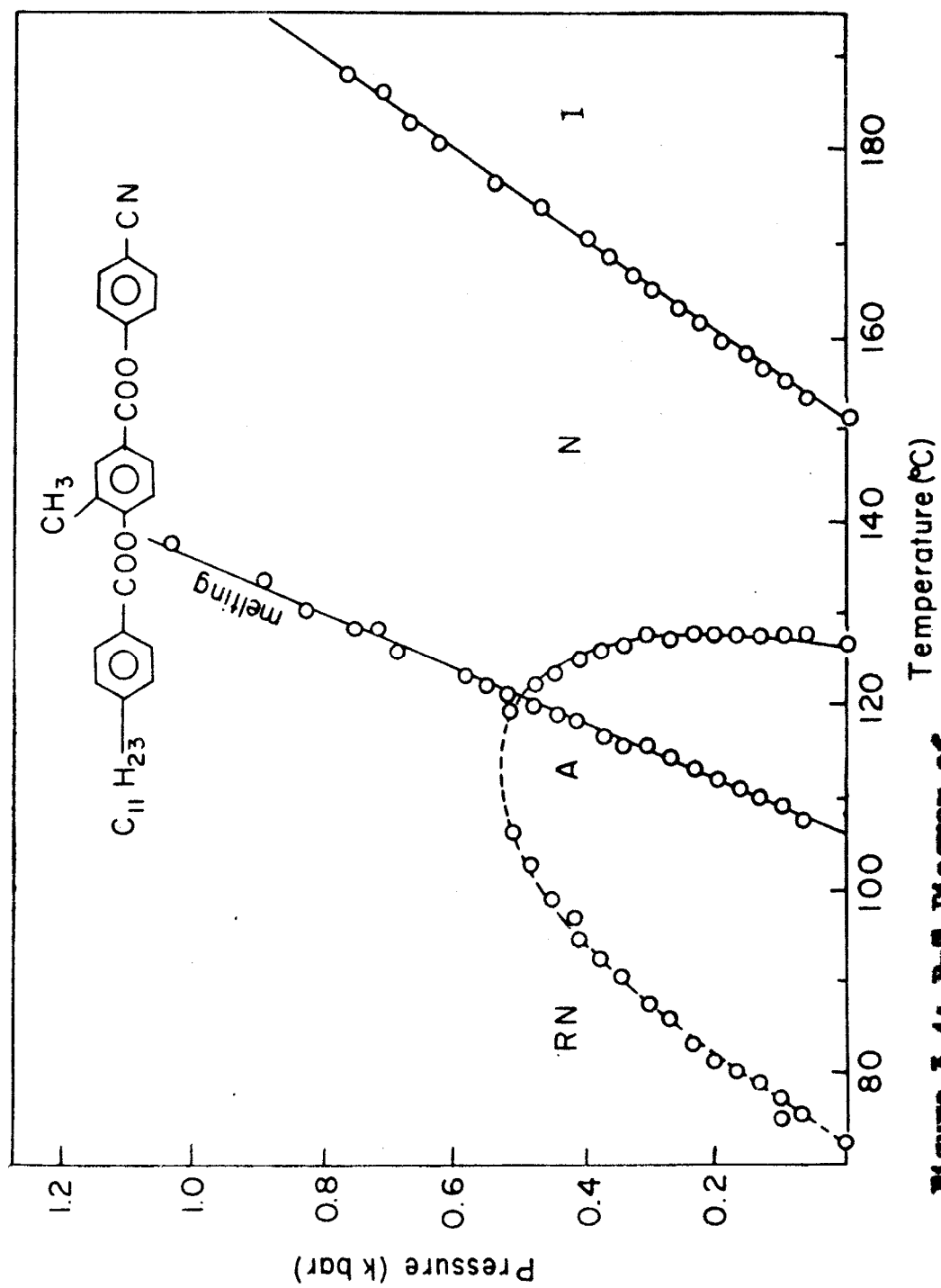


Figure 3.4: P-T Diagram of 11 OPNDB

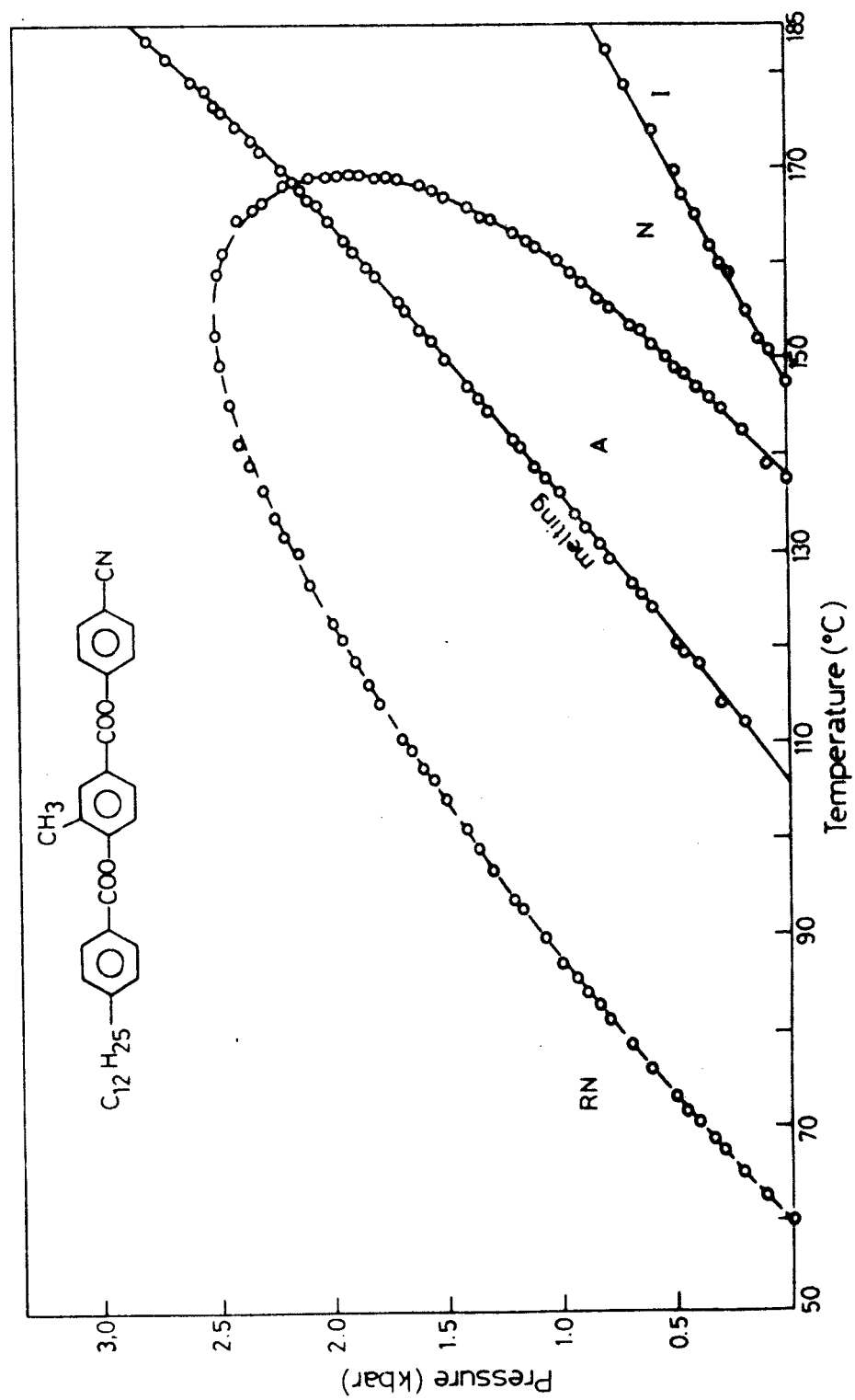


Figure 3.5: P-T diagram of 12 OPMBB

at 0.50 kbar, 120.75°C respectively. This temperature being lower than the temperature corresponding to P_m in the P-T plane, the reentrant nematic phase is monotropic in character at all pressures.

The addition of an alkyl end group enhances the P_m value which is 2.5 kbar for 12 CPMBB (Figure 3.5). It appears, therefore that P_m is very sensitive to changes in molecular length. We shall see that the same is true for all the series studied. The reentrant nematic phase of 12 CPMBB also remains monotropic at all pressures. We have shown in this P-T diagram, data points obtained from two different sets of experiments. They fall on the same ellipse showing thereby the self-consistency of the experimental set up. The emectia A phase is enantiotropic up to 2.16 kbar. The melting line intersects the smectic A - nematic phase boundary at 2.16 kbar and 168.0°C, resulting again in a solid - smectic A - nematic triple point on heating.

3.4.3 Series II - 11 CPMBB and 12 CPMBB

The data for these compounds are given in Tables 3.6 and 3.7 and the complete P-T diagrams in figures 3.6 and 3.7 respectively.

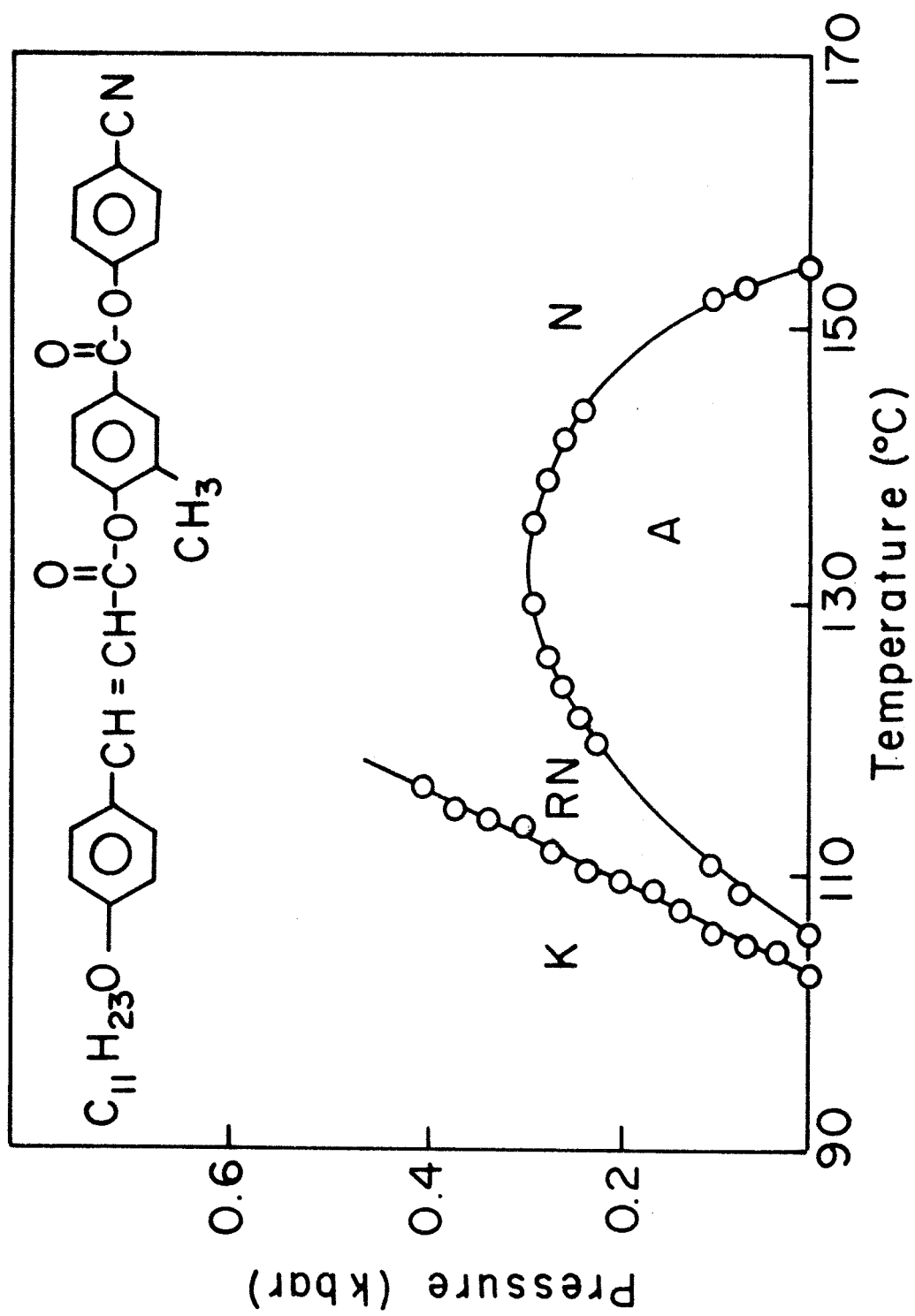
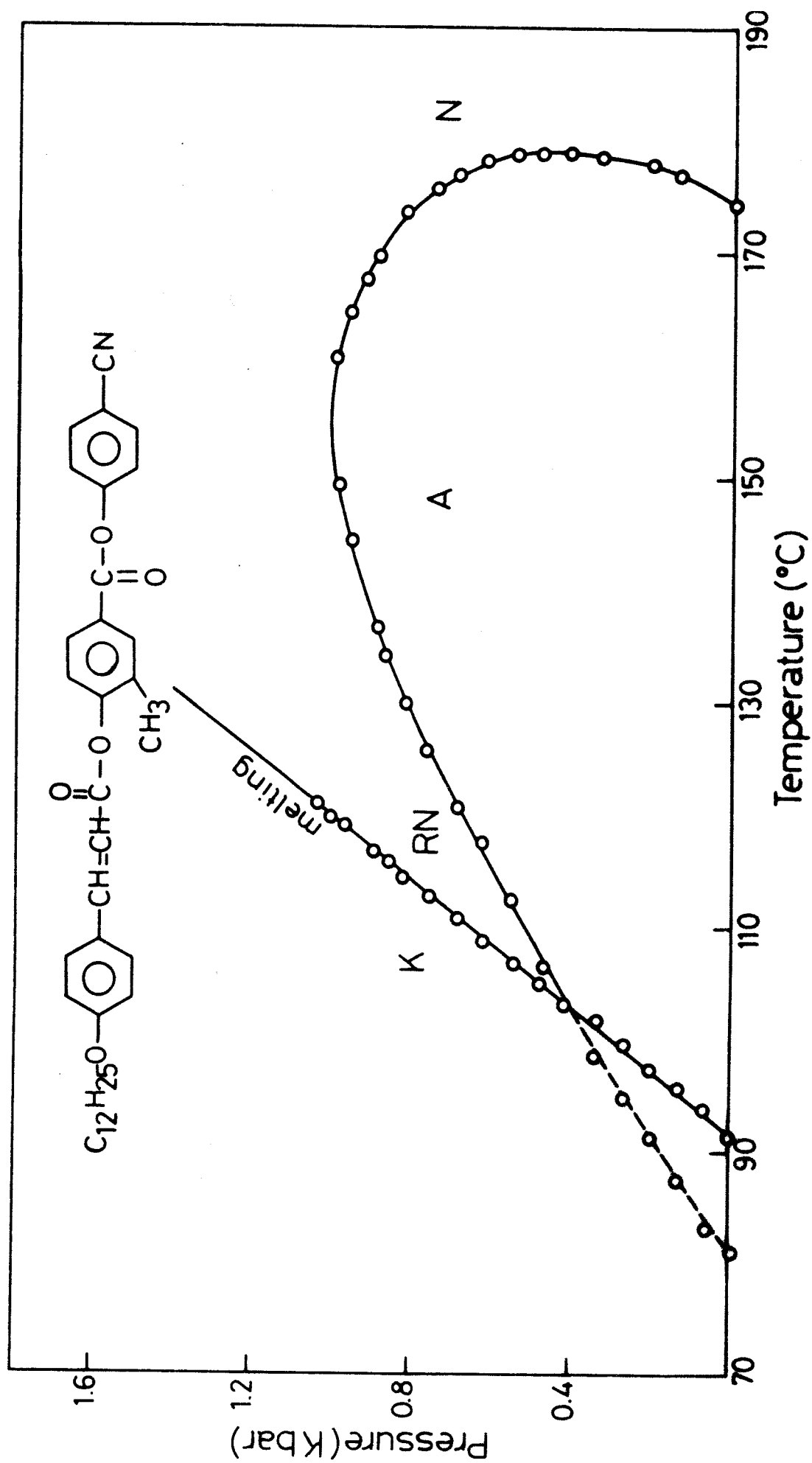


Figure 3.6: P-T diagram of 11 OPNMB

Figure 3.7: P-T diagram of 12 OPNMB



These compounds synthesised by Urs and Sadashiva²⁶ are different from the compounds of Series I in that (1) they have an additional ethylene ($\text{CH} = \text{CH}$) linkage in one of the bridging groups, and (ii) the alkyl end chain is replaced by an alkoxy. This seems to decrease P_m to a large extent. The value of P_m for 11 CPMCB is 0.29 kbar while for the next homologue, viz., 12 CPMCB it is 1.05 kbar. It must also be mentioned that 11 CPMCB has an enantiotropic reentrant nematic phase at 1 bar which remains so at all pressures. On the other hand, in 12 CPMCB the reentrant nematic phase is monotropic at one bar, but with increasing pressure, it becomes enantiotropic. The melting line intersects smectic A - reentrant nematic phase boundary at 0.44 kbar resulting thereby a triple point at 0.44 kbar and 104.5°C . Beyond this pressure, reentrant nematic phase becomes enantiotropic. This case is the first instance 'of' such a change in the character of the transition involving reentrant nematic phase, though a similar change has been observed before for nematic and cholesteric phases.^{35,36} Here again, as in nCPMBB series, increasing the length of the molecule has stabilized the smectic A phase to a large extent as seen by the higher P_m value of 12 CPMCB compared to that of 11 CPMCB.

3.4.4. Series III - 11 CPMA α MCB and 12 CPM α MCB

The P-T diagram for these compounds are given in figure 3.8 and 3.9 and the data in Tables 3.8 and 3.9 respectively.

In these compounds, there is, compared to CPMCB series an additional a methyl group attached to one of the middle groups instead of a hydrogen, This does not affect P_m value very much. The value of P_m for 11 CPMA α MCB is 0.19 kbar and that for 12 CPM α MCB is 1.35 kbar. Hence, here again the maximum pressure of smectic stability is greater for the higher homologue. As in the case of nCPMCB series, the 11th member of this series has an enantiotropic reentrant nematic phase and the next homologue has monotropic reentrant nematic phase which beyond a pressure of 0.57 kbar becomes enantiotropic in character. The solid-reentrant nematic-smectic A triple point is at 0.57 kbar and 96.5°C.

3.4.5. Series IV - 11 CPMeO α MCB and 12 CPM α MeO α MCB

The P-T data for these compounds are given in Tables 3.10 and 3.11 respectively and the corresponding P-T diagram in figures 3.10 and 3.11. These substances have a lateral methoxy group attached to the middle phenyl

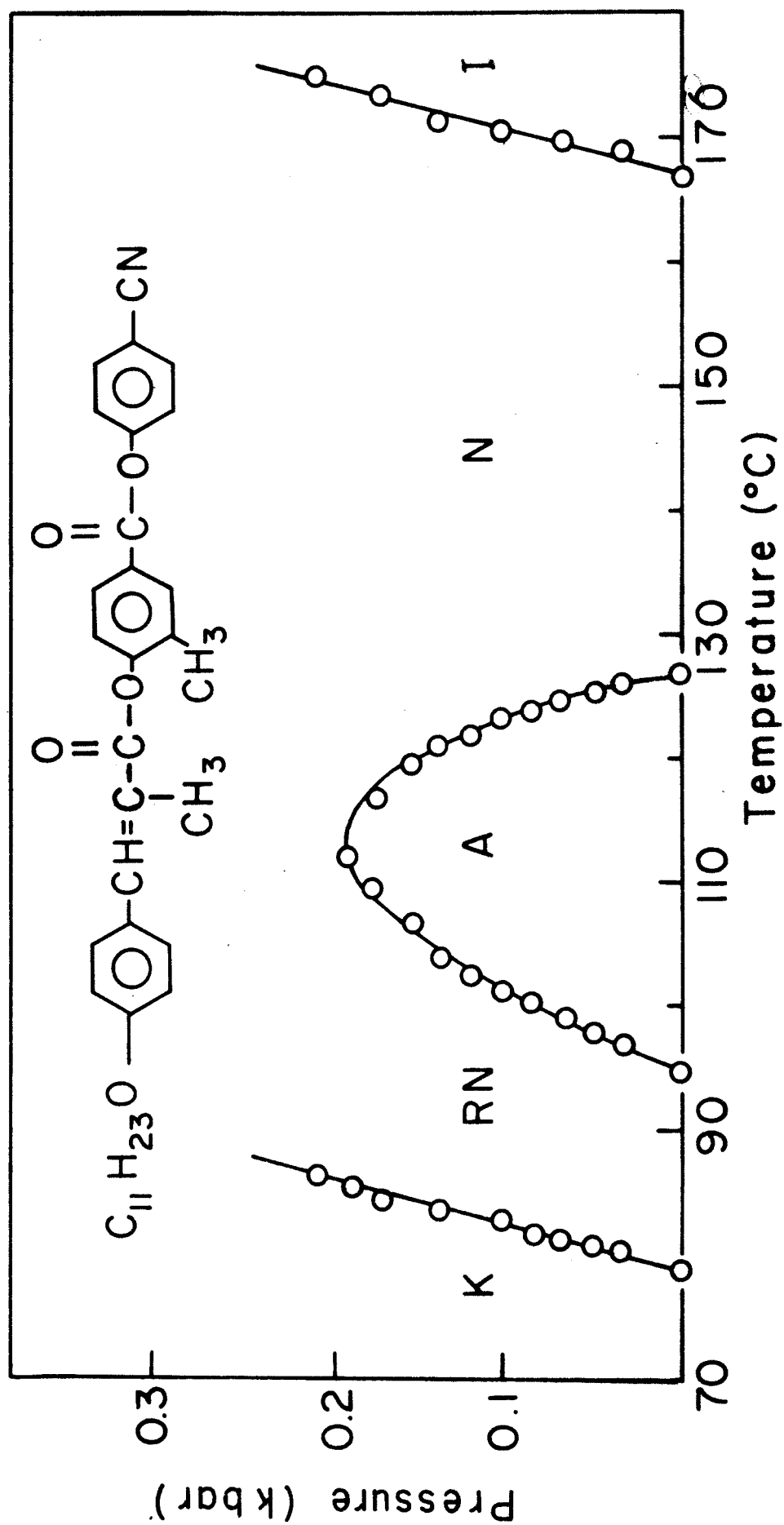
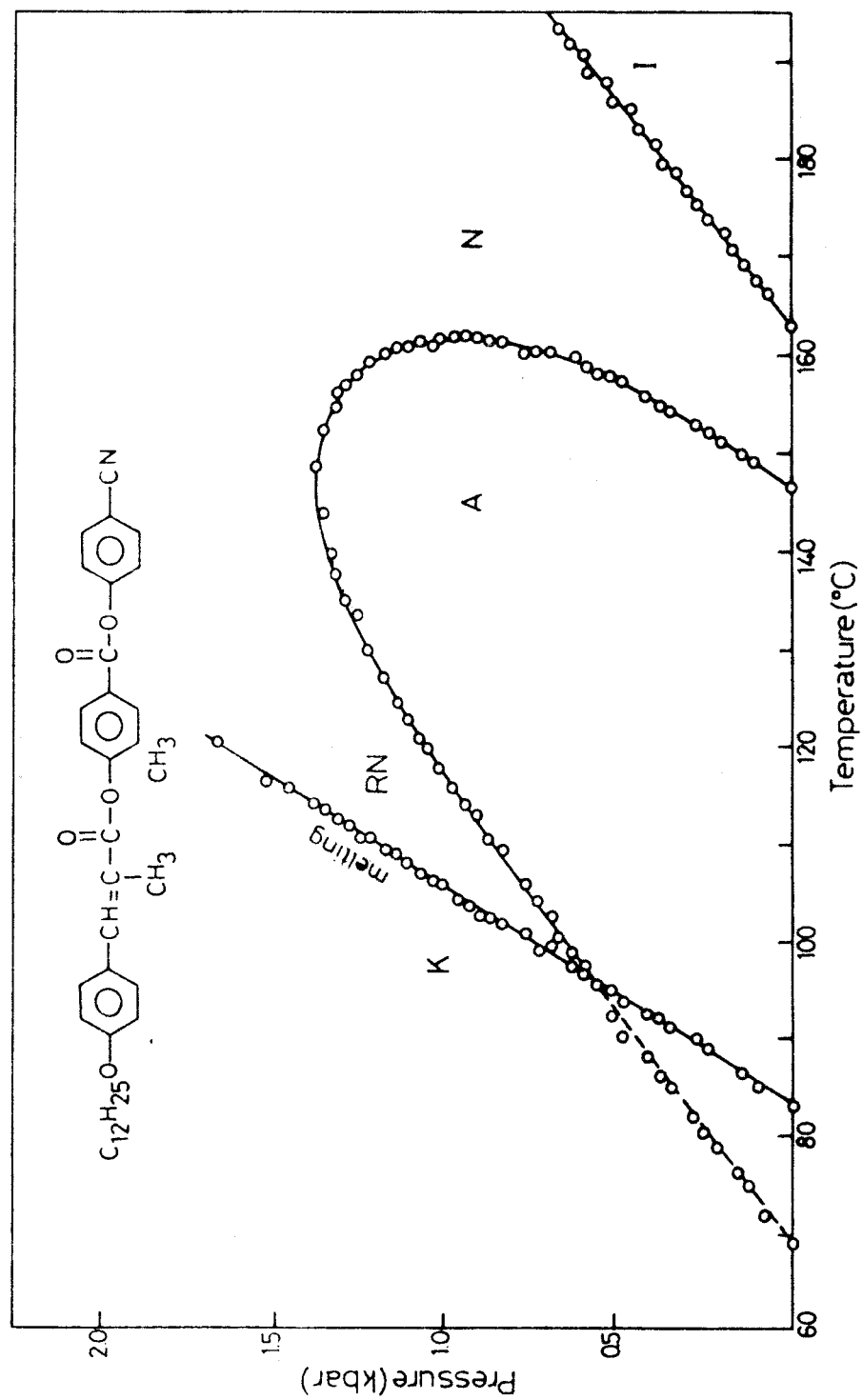


Figure 3.8: P-T diagram of 11 OPNMOB

FIGURE 3.9: P-T diagram of 12 OPNMOB



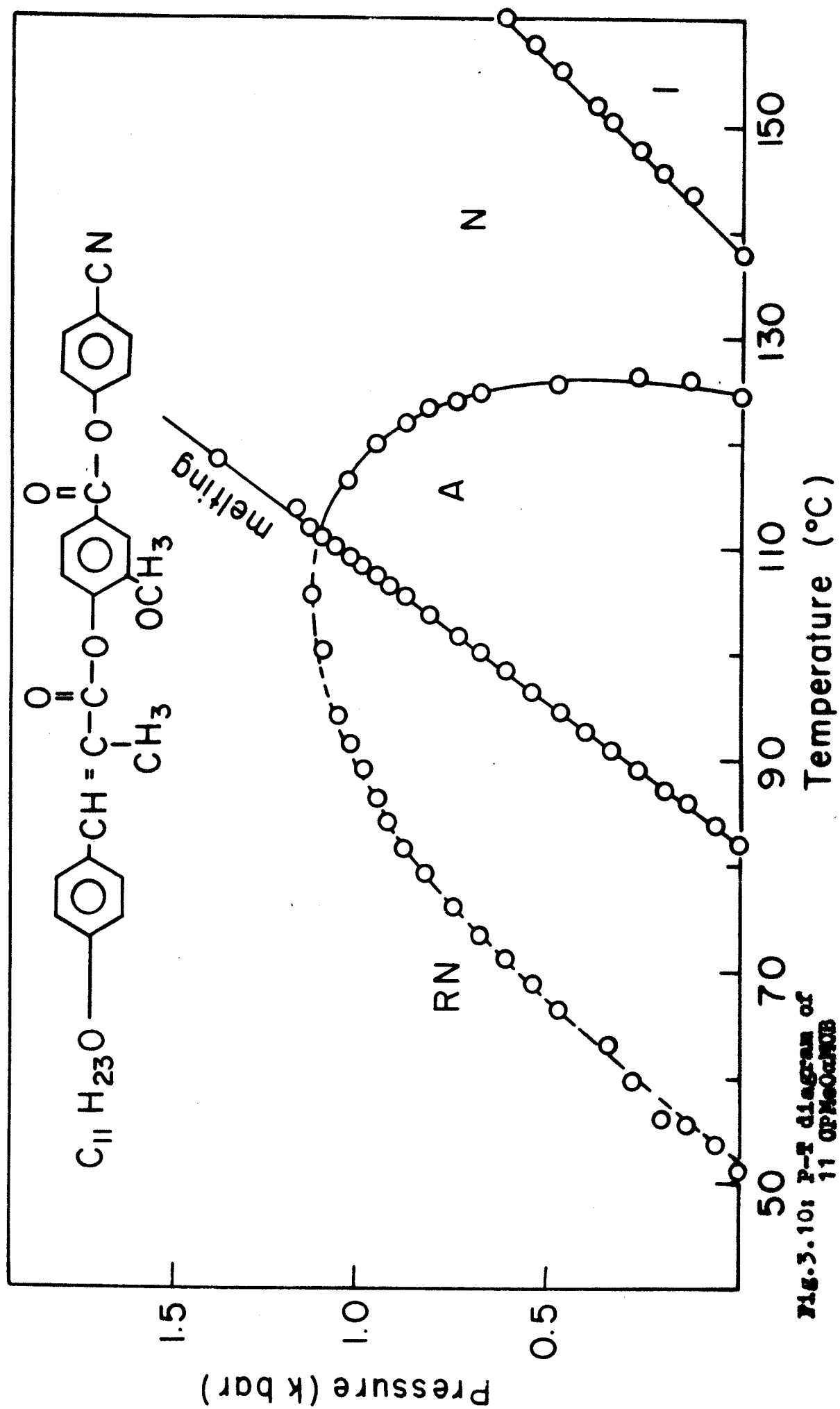


Fig. 3.10: P-T diagram of 11 OPMeOCHNB

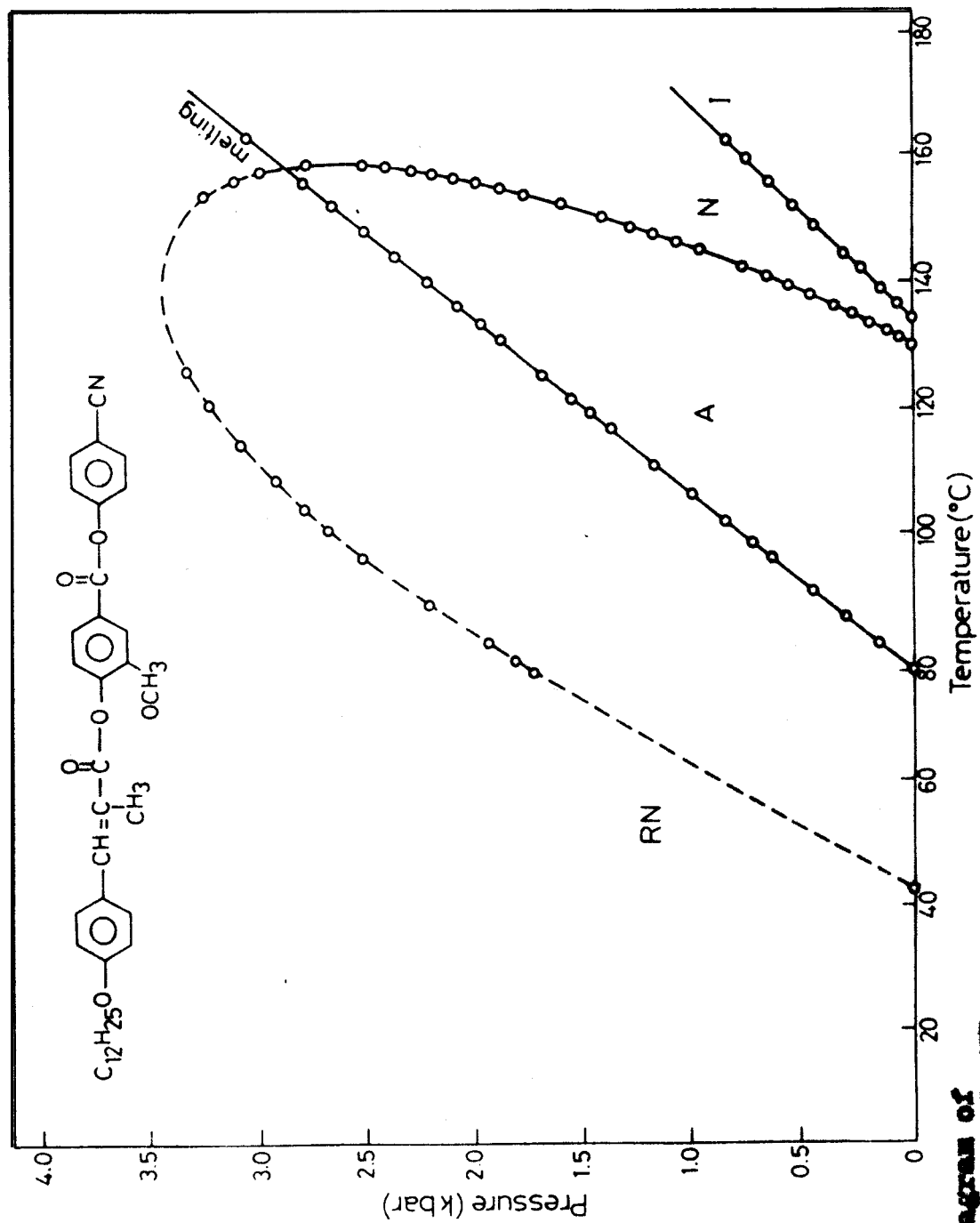


FIG. 3.11: P-T diagram of 12 OPMeOeNCN

ring as compared to the methyl group of nCPMeO α MCB series of compounds. This seems to increase the stability of smectic A phase as seen by a rather high P_m value, namely, 1.14 kbar for the 11th member and 3.45 kbar for the next higher homologue. In both these compounds the reentrant nematic phase at 1 bar is monotropic at all pressures. In the case of 12 CPMeO α MCB, it was just possible to observe the reentrant nematic phase at one bar using a polarising microscope equipped with hot stage Mettler FP5 with great difficulty. However, it was not possible to follow this transition till a pressure of 1.66 kbar in the high pressure optical cell presumably because a rather thick sample (100 μ m to 400 μ m) was used in the pressure experiments which hastens the crystallization before the formation of the reentrant nematic phase. Beyond this pressure, however, reentrant nematic - smectic A transition could easily be observed. In both these cases, the melting line intersects the smectic A - nematic phase boundary and the resulting solid - smectic A - nematic triple points (on heating) being at 1.13 kbar, and 111.50°C for 11 CPMeO α MCB and 2.84 kbar, 158.0°C for 12 CPMeO α MCB. The nematic - smectic A transitions are of course observable during cooling at all pressures.

3.4.6. Relation between P_m and the nematic range 'R'

It has been pointed out by Gladis et al^{9,37} that for the substances studied by them, P_m exhibits a monotonic dependence on the ratio of the nematic - smectic transition temperature to that of nematic - isotropic transition (T_{AN}/T_{NI}), known as the McMillan number.³⁸ For the compounds studied by us, we have attempted to relate P_m with the range of the nematic phase $R = T_{NI} - T_{AN}$ at one bar. Figure 3.12 shows a plot of $\log P_m$ versus R for all the eight compounds. The data points fall on a straight line (Line A) so that they can be represented by the expression $P_m = P_0 \exp(-mR)$. The constant P_0 and m evaluated from a least square fit of the data to a straight line, are 3769 bars and 0.071/°C. This result implies that with increasing nematic range, i.e., with decreasing smectic stability, P_m should decrease.

Since P-T data are known for several other reentrant nematogens, viz., two pure compounds (CBOOA and 8 OCB)⁹ and many binary mixtures - 8 OCB/6 OCB,^{34,39} CBOOA/HBAB,⁹ CBNA/CBHA⁹ and 8 OCB/40.8,⁴⁰ it is worthwhile to see if such a relation between P_m and R is valid in these cases also. Table 3.13 gives the P_m values for these materials. The plot of P_m versus R the nematic range at 1 bar for these

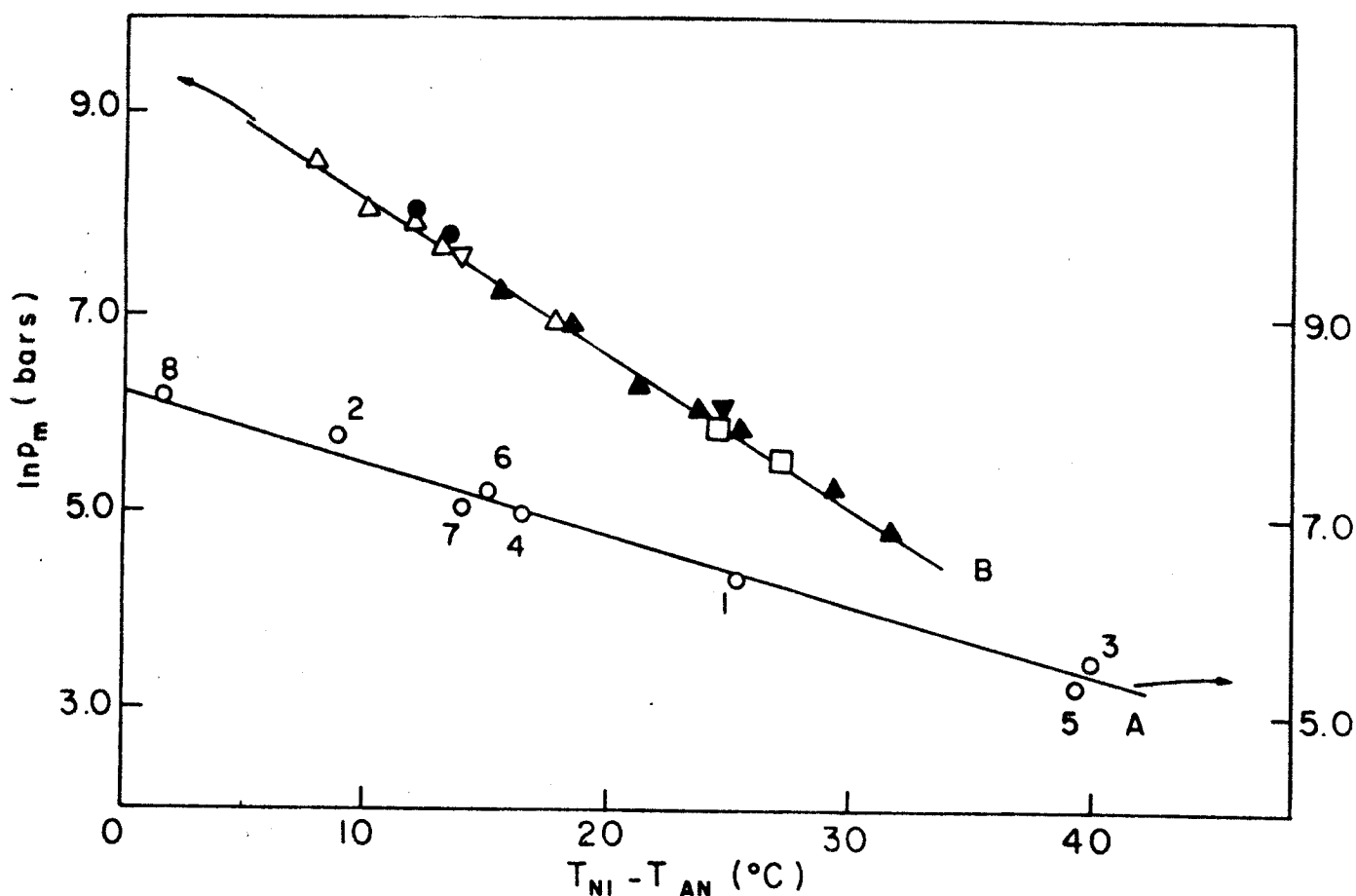


Figure 3.12

Plot of P_m , the maximum pressure of smectic stability versus $(T_{NI} - T_{AN})$, the range of nematic phase at 1 bar. The data points 1,2,3...etc. on line A are for three phenyl ring compounds listed in Table III. The data points on line B are for 2 phenyl ring compounds, viz., ∇ - 8 OCB, ∇ - OBOCA,⁹ Δ 8OCB/6 OCB,^{34,39} $\square$ OBHA/OBNA,⁹ $\triangle$ OBOCA/HBAB,⁹ $\bullet$ 8 OCB/40.8⁴⁰ mixtures.

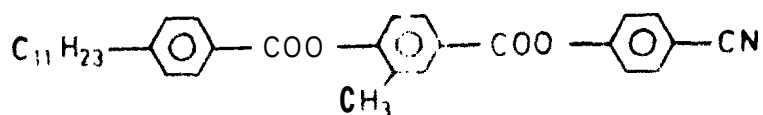
substances is **also** shown in figure 3.12. **These** data **again** fall on a straight **line** (line B) but with a different elope. **The** constants for this line obtained from the least square fit of the data to a straight line are $P_0 = 14050 \text{ bar}$ and $m = 0.140/^{\circ}\text{C}$. It is **interesting** to note **that** **all** the **substances** **whose** data fall on **line B** have two phenyl rings while **all** the **compounds** whose data fall on line A will have three **benzene** rings. We therefore tentatively **conclude** that for a reentrant **nematogen**, P_m is uniquely related to the nematic range **and** hence to the stability of the **nematic** ordering, the **constants** of **proportionality** being dependent on the molecular structure. Also, the higher **value** of the constant P_0 for line B (compared to that for line A) **indicates** that the stability of the **smectic** A phase is **more** in **compounds** with two phenyl rings than the **smectic** **stability** of the **three** phenyl ring compounds. In other words, the reentrant **nematic** phase **is** **more** favoured to **occur** in the three **benzene** ring compounds, a fact which is well supported by experimental **observations**.

TABLE 3.1

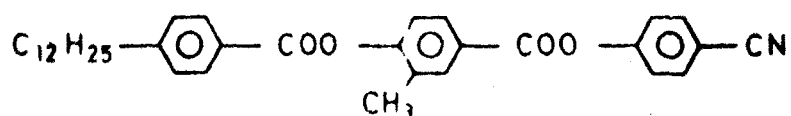
List of reentrant compounds studied with their structural formulae

Series I

4 cyanophenyl - 3'methyl - 4' (4"-n undecyl Benzoyloxy) Benzoate
(11 CPMBB)

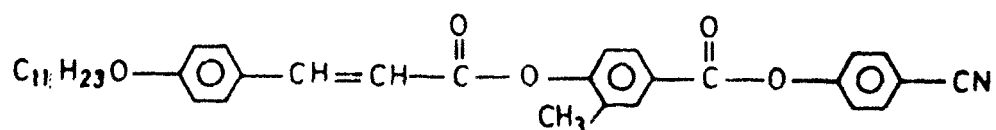


4 cyanophenyl - 3'methyl - 4' (4"-dodecyl Benzoyloxy) Benzoate (12 CPMBB)



Series II

4 cyanophenyl - 3'methyl - 4' (4"-undecyloxy cinnamoyloxy) Benzoate
(11 CPMCB)



4 cyanophenyl - 3'methyl - 4' (4"-dodecyloxy cinnamoyloxy) Benzoate
(12 CPMCB)

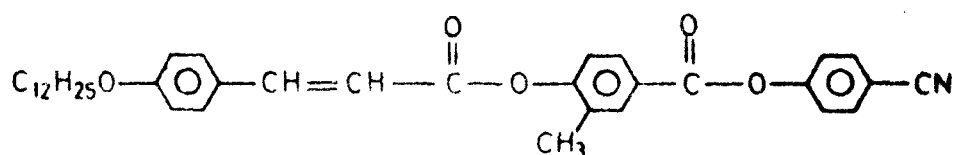
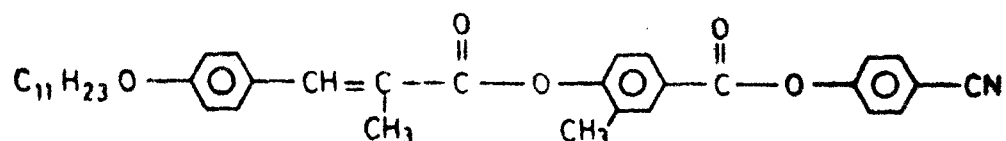


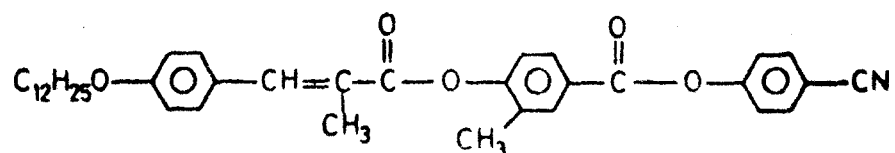
Table 3.1 continued

Series III

4 cyanophenyl - 3'methyl - 4'(4"undecyloxy - α methylcinnamoyloxy)
Benzoate (11CPM α MCB)

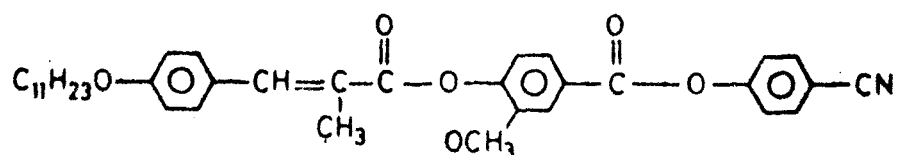


4 cyanophenyl - 3'methyl - 4'-f 4"dedocyloxy - α methyl cinnamoyloxy)
Benzoate (12CPM α MCB)



Series IV

4 cyanophenyl - 3'methoxy - 4'-(4"undecyloxy - α methyl cinnamoyloxy)
Benzoate (11CPMeo α MCB)



4 cyanophenyl-3'methoxy - 4'(4"dodecyloxy - α methyl cinnamoyloxy)
Benzoate (12CPMeo α MCB)

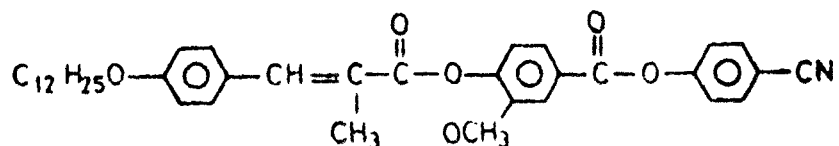


Table 3.2

Transition temperatures and heats of transition of the compounds

Series number	Compound	Transition	Transition temperatures (°C)	ΔH (kJ/mole)
I	11 CPMBB	K - A	103.0	32.49
		A - N	127.0	0.02
		N - I	152.5	1.12
		A - RN	(78.5)	0.02
	12 CPMBB	K - A	102.0	35.55
		A - N	138.5	0.25
		N - I	148.0	1.26
		A - RN	(59.8)	0.05
II	11 CPMCB	K - RN	101.9	56.24
		RN - A	105.1	~0*
		a - N	153.8	0.02
		N - I	193.7	0.92
	12 CPMCB	K - A	89.5	65.45
		A - N	175.6	0.05
		N - I	191.7	1.45
		A - RN	(82.1)	~0*
III	11 CPM α MCB	K - RN	78.2	37.13
		RN - A	101.1	~0*
		A - N	128.4	0.04
		N - I	168.0	1.03
	12 CPM α MCB	K - A	77.5	40.65
		A - N	147.3	0.03
		N - I	162.2	0.94
		A - RN	(69.2)	0.02
IV	11 CPMeO α MCB	K - A	82.9	38.8
		A - N	125.2	0.02
		N - I	138.2	1.16
		A - RN	(53.7)	0.01
	12 CPMeO α MCB	K - A	77.2	59.98
		A - N	134.6	0.13
		N - I	136.4	1.43
		A - RN	(42.8)	~0*

() denotes monotropic transition

*The transition is very weak, no accurate estimation of ΔH can be made.

K - crystal, A - smectic A, N - nematic, RN - reentrant nematic.

Table 3.3

Transition temperatures of 8 OCB as a function of pressure

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Heating			Cooling
		K - A	A - N	N - I	A - RM
1	room pr.	54.5	67.0	81.0	
2	0.10	56.56	67.89	85.0	
3	0.21	59.65	69.87	88.04	
4	0.31	62.21	70.85	91.78	
5	0.42	64.34	72.21	95.12	
6	0.52	67.09	73.84	97.50	
7	0.63	69.08	75.12	101.20	
8	0.73	70.83	76.14	104.25	
9	0.83	73.32	77.12	107.51	
10	0.93	75.31	78.56	111.23	
11	1.03	77.51	80.08	114.22	
12	1.14	79.61	80.89	117.72	
13	1.24	81.80	81.72	121.21	
		<u>K - N</u>			
14	1.35	84.04	83.1	124.45	
15	1.45	86.54	83.43	127.69	
16	1.55	87.53	83.60		
17	1.63	90.53	83.98		62.8
18	1.66	-	84.10		63.56
19	1.69	-	-		64.72
20	1.73	92.77	84.60		65.55
21	1.76				66.5
22	1.79	-	83.98		67.52
23	1.83	95.02	-		68.30
24	1.86	-	83.35		70.02
25	1.90				71.40
26	1.93	96.76	82.34		73.01
27	1.97	-	80.85		77.02
28	2.00	99.26			
29	2.07	101.25			

Table 3.4

Transition temperatures of 11 CPMBB as a function of pressure
SET I

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Heating			Cooling
		K - A	A - N	N - I	A - RN
1	room pr.	103.0	126.30	150.30	76.5
2	0.07	107.24	127.04	154.0	76.84
3	0.10	108.73	127.84		77.35
4	0.14	109.74	128.09	156.85	80.11
5	0.17	110.98	128.30		81.37
6	0.21	111.3	127.34	160.09	81.87
7	0.28	114.22	127.09	163.59	86.65
8	0.31	115.47	126.84		87.15
9	0.35	116.17	126.34	167.08	91.18
10	0.41	118.96	124.82	170.82	94.94
11	0.45	119.61	123.32		99.21
12	0.48	120.25	121.86		102.98
		<u>K - N</u>			
13	0.52	121.35	119.05		106.49
14	0.55	122.70		176.06	
15	0.59	123.45			
16	0.69	125.94		183.23	
17	0.76	127.69			
18	0.83	129.69			

Table 3.4

Transition temperatures of 11 CPMBB as a function of Pressure

SET II

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Heating			Cooling
		K - A	A - N	N - I	A - RN
1	room pr.	103.0	126.30	150.30	76.5
2	0.10		127.04	155.83	77.49
3	0.14	109.74	128.35		79.11
4	0.17		127.59	158.85	80.37
5	0.21	111.23	127.59		81.37
6	0.24	112.98	127.34	162.85	83.63
7	0.31		127.04	166.1	87.40
8	0.35	115.47	126.59		90.66
9	0.38	116.47	126.08	167.33	92.68
10	0.41	118.47	125.08		96.95
11	0.45	118.96	123.32		99.20
12	0.48	115.71	122.32		103.23
		<u>K - N</u>			
13	0.52	120.71	119.81		105.99
14	0.55	122.20			

Table 35

Transition temperatures of 12 CPMBB as a function of pressure
Set I

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Heating			Cooling
		K - A	A - N	N - I	A - RN
1	room pr.	100.8	137.4	147.4	59.8
2	0.10		138.19	149.63	62.78
3	0.21	112.2	143.42	155.0	65.04
4	0.31	113.98	146.68	160.10	66.3
5	0.41	118.21	147.94	165.10	70.57
6	0.52	119.96	149.20	170.10	73.30
7	0.62	123.45	151.45	173.82	75.85
8	0.72	126.44	153.46	178.81	78.86
9	0.83	129.2	155.21	182.55	81.87
10	0.93	132.43	157.98		83.88
11	1.03	136.17	160.50		87.15
12	1.14	138.41	161.25		90.66
13	1.24	141.40	162.75		93.42
14	1.34	144.65	163.25		96.4
15	1.45	147.64	165.80		100.71
16	1.55	149.89	167.28		106.0
17	1.65	153.13	168.28		107.75
18	1.76	156.12	169.54		110.0
19	1.86	158.62	169.00		114.0
20	1.96	161.36	168.28		118.55
21	2.07	164.6	167.78		122.32
	<u>K - N</u>				
22	2.17	166.35	167.13		126.6
23	2.27	169.5	167.0		131.61
24	2.38	171.59	166.53		136.6
25	2.48	174.08	164.3		146.2
26	2.58	176.58	158.94		152.67
27	2.69	158.57			

Table 3.5

Transition temperatures of,12 CPMBB as a function of pressure

SET II

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Heating			Cooling
		K - A	A - N	N - I	A - RN
1	room pr.	100.8	137.4	147.4	59.8
2	0.14	110.53	141.5	152.87	63.5
3	0.28	113.58	144.67	156.85	
4	0.35	115.73	146.78	161.85	69.31
5	0.48	119.21	148.25	168.37	71.57
6	0.69	125.95	152.96	178.8	78.11
7	0.86	130.94	156.23	186.03	83.38
8	0.97	133.68	158.24		85.39
9	1.10	137.17	161.0		89.91
10	1.21	140.66	162.25		92.6
11	1.38	145.89	164.01		99.60
12	1.59	151.85	167.53		106.25
13	1.72	155.1 6	169.29		108.50
14	1.90	159.41	168.78		116.28
15	2.00	162.1	168.28		121.06
16	2.14	166.1	168.28		126.33
		<u>K - N</u>			
17	2.21	167.34	166.78		135.38
18	2.41	172.68	165.32		139.74
19	2.55	175.09	160.24		149.69
20	2.62	178.07			

Table 3.6

Transition temperature of 11 CPMCB as a **function of**
pressure

Sl. No *	Pressures in kbar	Transition temperatures in °C		
		K - RN	RN - A	A - N
1	roompr.	103.2	105.8	155.2
2	0.069	105.5	108.76	153.1 1
3	0.10	106.5	110.63	152.77
4	0.12		112.0	151.77
5	0.16		114.36	150.08
6	0.17	109.0	115.53	149.38
7	0.19		116.93	147.98
8	0.21	110.0	118.57	147.51
9	0.22		119.50	146.34
10	0.24	111.0	121.37	144.24
11	0.26		123.7	142.37
12	0.28	112.0	126.03	139.10
13	0.29		130.0	136.54
14	0.31	113.50		
15	0.41	117.0		

Table 3.7

Transition temperatures of 12 CPMCB as a function of
pressure

Sl. No.	Pressure in kbar	Transition temperatures in °C		
		Heating		Cooling
		K - A	A - N	A - RN
1	room pr.	89.5	175.6	82.1
2	0.07	93.84	177.32	83.1
3	0.14	95.93	178.08	87.62
4	0.21	97.56	178.52	91.64
5	0.28	99.90	178.45	95.16
6	0.34	101.99	178.61	98.68
7	0.41	103.40	179.0	101.69
8		<u>K - RN</u>		<u>RN - A</u>
8	0.48	105.26	179.12	105.96
9	0.55	106.9	179.25	112.73
10	0.62	109.23	178.32	117.87
11	0.69	111.10	176.69	120.90
12	0.76	112.73	175.52	125.30
13	0.83	114.37	174.22	130.00
14	0.86	115.77	171.80	133.97
15	0.90	116.80	169.28	138.64
16	0.93	117.17	167.5	142.7
17	0.97	119.0	164.78	145.18
18	0.98	119.60	160.58	150.31
19	1.00	120.0		
20	1.05	121.0		

Table 3.8

Transition temperatures of 11 CPMαMCB as a function of pressure

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		K - RN	RN - A	A - N	N - I
1	room pr.	78.9	96	126.8	167.9
2	0.04	80.05	97.09	126.03	168.51
3	0.05	80.75	98.02	125.57	
4	0.07	81.46	98.96	124.87	169.36
5	0.09	82.16	100.53	124.0	
6	0.10	82.5	101.3	123.47	170.38
7	0.12	83.09	102.50	122.06	
8	0.14	83.79	103.86	121.13	171.54
9	0.16		107.13	119.50	
10	0.17	84.72	110.13	117.63	172.95
11	0.19	85.43	113.43	114.60	
12	0.21	86.32			174.58
13	0.34	90.32			178.0

Table 3.9

Transition temperatures of 12 CPMαMCB as a function of pressure

Sl. No.	Pressure in kbar	Transition temperatures in °C				
		Heating			Cooling	
		K - A	A - N	N - I	A - RN	
1	room pr.	82.0	147.0	162.0	69.0	
2	0.07		148.05	166.96	72.08	
3	0.14	86.47	149.95	168.94	76.60	
4	0.21		150.90	172.92	79.11	
5	0.28	90.21	152.71	175.91	82.13	
6	0.35	91.20	154.47	178.66	85.14	
7	0.41	92.20	155.73	181.89	88.66	
8	0.48	93.95	156.73	185.39	90.42	
9	0.55	95.94	158.49	188.38	95.94	
		<u>K - RN</u>			<u>RN - A</u>	
10	0.62	97.44	159.75	191.12	99.20	
11	0.69	99.93	160.00	193.86	102.98	
12	0.76	100.91	160.50		105.74	
13	0.83	101.67	161.25		109.76	
14	0.90	102.67	162.0		113.64	
15	0.97	104.67	162.0		114.88	
16	1.03	106.66	161.0		119.11	
17	1.10	107.90	161.0		122.61	
18	1.17	109.65	160.25		126.84	
19	1.24	110.64	158.24		133.08	
20	1.31	112.39	154.72		137.39	
21	1.34	113.39	150.70		146.03	
22	1.52	116.63				

Table 3.9

Transition temperatures of 12 CPMA₂MCB as a function of pressure

SET II

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Heating			Cooling
		K - A	A - N	N - I	A - RN
1	room pr.	82.0	147.0	162.0	69.0
2	0.10	85.05	149.45	167.74	74.84
3	0.17		150.8	170.68	77.5
4	0.24	89.29	151.70	172.68	80.37
5	0.31			176.66	
6	0.38	92.28	154.47	179.90	85.89
7	0.45			183.64	
8	0.52	95.02	157.98	186.13	92.68
		<u>K - RN</u>			<u>RN - A</u>
9	0.59	96.52	158.49	189.37	97.45
10	0.72	98.76	160.24		103.98
11	0.86	102.50	161.25		110.52
12	0.93	104.00	161.76		114.22
13	1.00	105.75	161.25		117.79
14	1.07	106.74	161.50		120.71
15	1.14	109.49	160.75		125.69
16	1.21	110.48	159.24		131.68
17	1.28	117.73	157.23		135.92
18	1.31	112.73	156.73		139.16
19	1.34	113.73	152.46		144.65
20	1.38	114.47			149.64
21	1.45	115.72			
22	1.66	120.71			

Table 3.10

Transition temperatures of 11 CPMeO α MCB as a function
of pressure

Sl. No.	Pressure in kbars	Transition temperatures in °C				
		Heating			Cooling	
		K - A	A - N	N - I	A - RN	
1	roompr.	82.0	124.0	138.1	51.0	
2	0.07	84.26			53.47	
3	0.14	86.12	125.8	148.3	55.27	
4	0.21	87.06		145.41	55.97	
5	0.28	89.16	125.80	147.74	59.74	
6	0.35	91.26		150.54	63.25	
7	0.41		126.04		74.3	
8	0.48	94.53	125.63	155.21	66.02	
9	0.55	96.63	125.50	157.78	68.53	
10	0.62	98.26	125.20	160.11	71.04	
11	0.69	100.13	124.64	162.67	73.05	
12	0.76	101.76	124.16		75.31	
13	0.83	103.63	123.0		78.83	
14	0.93	105.73	121.6		81.34	
15	0.97	106.67	120.85		83.85	
16	1.00	108.30	118.50		89.38	
17	1.04	109.23	116.0		91.39	
18	1.07	110.16	114.50		93.65	
19	1.10	110.87	112.40		100.18	
20	1.14	112.03	109.50		105.4	
21	1.17	113.67				
22	1.38.	118.33				

Table 3.1 1

Transition temperatures of 12 CPMeO α MCB as a function of pressure

Sl. No.	Pressure in kbar	Transition temperatures in °C			
		Heating			Cooling
		K - A	A - N	N - I	A - RN
1	room pr.	77.5	131.8	135.9	43
2	0.10	81.64	132.57	138.99	
3	0.21	83.82	134.51	142.14	
4	0.31	86.12	136.12	145.41	
5	0.41	90.10	138.17	149.84	
6	0.52		139.92	153.34	
7	0.62	95.71	141.56	156.96	
8	0.72	98.12	143.54	161.16	
9	0.83	101.56	144.5	164.08	
10	0.93		146.34		
11	1.03	107.5	147.28		
12	1.14	111.32	148.51		
13	1.24	113.61	149.32		
14	1.35	116.61	150.54		
15	1*45	119.56	151.5		
16	1.55	122.51	152.56		
17	1.66	124.94	153.86		
18	1.76	128.54	155.14		78.31
19	1.86	131.28	156.0		80.21
20	1.97	134.52	157.0		83.2
21	2.07	136.25	158.13		84.85
22	2.17	140.18	158.82		87.50
23	2.28	143.10	159.30		90.05
24	2.34	144.7	159.50		91.11
25	2.48	149.37	160.00		95.51
26	2.62	153.34	159.5		100.90
27	2.76	157.08	159.15		104.2
28	2.90	160.92	159.12		108.57
29	3.03	164.54	157.5		113.50
30	3.17	168.50	155.5		119.70
31	3.31	172.12	152.10		126.55

Table 3.12

Values of maximum pressure (P_m) and temperature (T_m) of smectic A stability for the compounds^{*} studied

Sl. No.	Compound	P_m (bars)	T_m (°C)
1	11 CPMBB	550	127.5
2	12 CPMBB	2510	170.0
3	11 CPMCB	290	155.0
4	12 CPMCB	1050	179.0
5	11 CPM α MCB	190	127.6
6	12 CPM α MCB	1350	162.0
7	11 CPMeO α MCB	1140	126.5
8	12 CPMeO α MCB	3610	160.5

^{*}**All the compounds have 3 phenyl rings (see text)**

Table 3.13

Values of P_m , the maximum pressure of smectic stability for pure compounds and the mixtures having 2 phenyl rings

Sl. No.	Mixture	Molar concentration	P_m in bars	Ref.
1	Pure 8 OCB	—	1960	present work
2	8 OCB + 6 OCB	5% of 8 OCB	1480	34, 39
3	+"	10% of 8 OCB	980	"
4	"	15% of 8 OCB	560	"
5	"	17.5% of 8 OCB	500	"
6	"	20% of 8 OCB	370	"
7	"	23.7% of 8 OCB	210	"
8	CBOOA (pure)	—	600	9
9	CBOOA + HBAB	0.10	490	"
10	"	0.95	520	"
11	CBHA + CBNA	34	4850	"
12	"	46	2950	"
13	"	53	2210	"
14	"	64	1170	"
15	"	83	910	"
16	8 OCB + 40.8	4.5	3190	40
		2.0	2620	

References

- 1 P.E.Cladis, Phys. Rev. Lett. 35, 48 (1975).
- 2 P.E.Cladis, R.K.Bogardus, W.B.Daniels and G.N.Taylor, Phys. Rev. Lett. 39, 720 (1977).
- 3 A.C.Anderson, W.Reese, J.C.Wheatley, Phys. Rev. 130, 1644 (1963) and references therein.
- 4 E.Muller-Hartmann, J. Zittartz, Phys. Rev. Lett. 26, 428 (1971).
- 5 G.Riblet, K.Winzer, Solid State Comm. 9, 1663 (1971).
- 6 A.Zipp and W.Kauzmann, Biochem. 12, 4217 (1973).
- 7 S.A.Hawley, Biochem. 10, 2436 (1971).
- 8 V.T.Rajan and C.W.Woo, Phys. Lett. 73A, 224 (1979).
- 9 P.E.Cladis, R.K.Bogardus and D.Aadsen, Phys.Rev. A18, 2292 (1978).
- 10 N.V.Madhusudana, B.K. Sadashiva and K.P.L.Moodithaya, Curr. Science 53, 613 (1979).
- 11 F.Hardouin, G. Sigaud, M.F.Achard and H.Gasparoux, Phys. Lett. 71A, 347 (1979).
- 12 B.Engelen, G.Heppke, R.Hopf and F.Schneider, Mol.Cryst. Liq. Cryst. Lett. 49, 193 (1979).
- 13 N.H.Tinh, M.J.Dubien, G.Destrade, Mol. Cryst. Liq. Cryst. Lett. 56, 257 (1980).

- 14 D. Demus, G.Pelzl, W.Weigeleben and W Weissflog,
Mol.Cryst.Liq.Cryst. Lett. 56, 289 (1980).
- 15 W.Weissflog, G.Pelzl, A.Weigeleben and D.Demus,
Mol.Cryst.Liq.Cryst.Lett. 56, 295 (1980).
- 16 G.Pelzl and D.Demus, Z.Chem. (to be published).
- 17 G.Pelzl, U.Bottger and D.Demus, Krist und Techn.
(to be published).
- 18 W.Weissflog, N.K.Sharma, G.Pelzl and D.Demus,
Krist. Und Technik 15, 5 (1980).
- 19 G.Pelzl, S.Diele, A.Weigeleben and D.Demus,
Mol.Cryst.Liq.Cryst.Lett. 64, 163 (1981).
- 20 W. Weissflog, G.Pelzl and D. Demus, Cryst.Res. and
Techn. 16(5), K79 (1981).
- 21 G.Pelzl, U.Bottger, K.Kallweit, D.Demus and H.Sackmann,
Cryst. Res. and Techn. 16(9), K119 (1981).
- 22 G.Heppke, R.Hopf, B.Kohne and K.Praefcke,
'Advances in Liquid Crystal Research and Applications',
Ed. L. Bata, Pergamon Press (1980) p.141.
- 23 G. Heppke, R.Hopf, B.Kohne and K.Praefcke,
Z. Naturforsch. 35b, 1384 (1980).
- 24 A. Gobl Wunsch, G.Heppke and R.Hopf, Z.Naturforsch.
36A, 213 (1981).
- 25 B.K.Sadashiva, Mol.Cryst.Liq.Cryst. 53, 253 (1979).
- 26 M.S.Urs and B.K.Sadashiva, Mol. Cryst.Liq.Cryst.Lett.
72, 227 (1982).

- 27 G.Pelzl and D.Demus, *Z.Chem.* 21(4), 151 (1981).
- 28 G.Pelzl, U.Bottger and D.Demus, *Mol. Cryst. Liq. Cryst. Lett.* (in press)
- 29 S.Chandrasekhar, K.A Suresh and K.V.Rao, Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S.Chandrasekhar, Heyden, London (1980) p.131.
- 30 R.Shashidhar and K.V.Rao, Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S.Chandrasekhar, Heyden, London (1980) p.115.
- 31 B. R.Ratna, R.Shashidhar and K.V.Rao, Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S.Chandrasekhar, Heyden, London (1980) p.135.
- 32 K.P.L.Moodithaya and N. V.Madhusudana, Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S.Chandrasekhar, Heyden, London (1980) p. 121.
- 33 B.R.Ratna, R. Shashidhar and K. V. Rao, *Mol.Cryst. Liquid Cryst.* 74, 1743 (1981).
- 34 P.E.Cladis, Proceedings of the International Liquid Crystals Conference, Bangalore (1979), Ed.S.Chandrasekhar, Heyden, London (1980) p.105.
- 35 R.Shashidhar, *Mol.Cryst.Liq .Cryst.* 43, 71 (1977).
- 36 J.Robberecht, *Bull. Soc. Chim. Belg.* 47, 597 (1938).

- 37 P.E.Cladis, D.Guillon, F.R.Bouchet and P.L.Finn,
Phys. Rev. A, 23, 2594 (1981).
- 38 W.L.McMillan, Phys. Rev. A4, 1238 (1971).
- 39 R.Shashidhar, H.D.Kleinhans and G.M.Schneider,
Mol.Cryst.Liq.Cryst. Lett. 72, 119 (1981).
- 40 P.E.Cladis, Mol.Cryst.Liq.Cryst. 67, 177 (1981).