CHAPTER V

HIGH PRESSURE STUDIES ON SOME SMECTIC LIQUID CRYSTALS

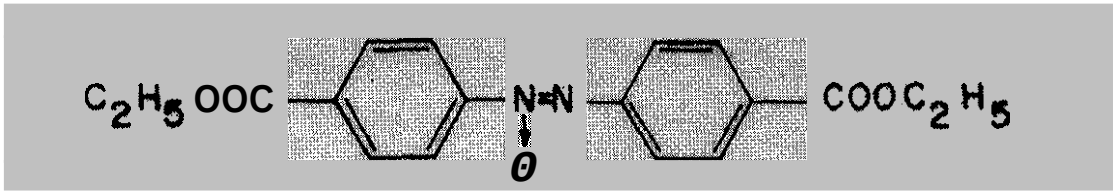
1. Introduction

The majority of high pressure experiments on Liquid crystals have been devoted to the study on nematics, [1] although with the recent discovery of re-entrant hehaviour, [2] there have been some studies on compounds having a smectic A phase. Regarding smectic C phase, there have been two pressure studies, both on 4,4 ' –di-n-heptyloxyazoxybenzene **(HOAB).** [3,4] It was therefore thought worthwile to investigate the behaviour of some smectic liquid crystals under pressure. Experiments were undertaken on a few compounds (whose structural formulae are given in the next section) exhibiting different kinds of smectic mesophases. While these experiments were in progress, Spratte and Schneider [5] reported results on the effect of pressure on smectic polymorphism of some bis-(4'-n-alkoxybenzylidene)- 1, 4-phenylenediamines by DTA technique up to 3kbars. Their results will be referred to briefly later in this chapter.

2. Comaounds studied

a. Di- ethyl-p-azoxybenzoate (EPAB)

This compound is one of the earliest liquid crystalline materials to be synthesized and studied. [6] It exhibits only one mesophase, viz., smectic A and has the structural **Formula** :

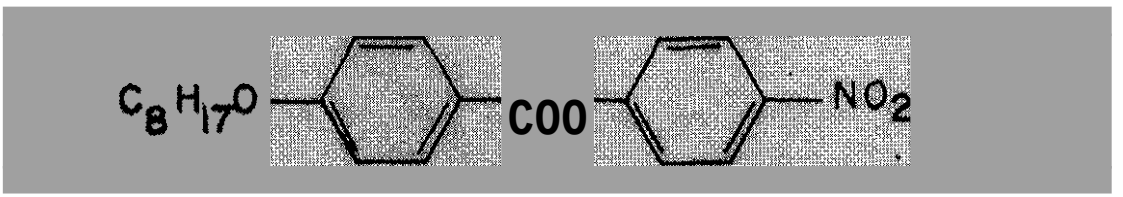


Some pressure studies have also been done on this compound, but only up to a pressure of 100 bars. [7] The compound used in our experiments was obtained from Eastman Kodak, USA, and recrystallised several times in benzene, till the smectic-isotropic transition temperature was constant. The transition temperatures at atmospheric pressure were determined using a polarising microscope with a Mettler FP-52 hot stage and FP-5 temperature control. The heats of transition (H) for the

various transitions were determined by differential scanning calorimetry using Perkin-Elmer DSC-2. The accuracy of H is reckoned to be about + 5 %. The data are given in table I.

b. 4-Nitro~henvl - 4 ' –n-octvloxbenzoate **(NPOOB)**

This compound is the eighth member of the homologous series 4-notrophenyl-4 '-n-alkoxybenzoates synthesized by Griffin et al. [8] and Demus et al. [9] independently. This compound exhibits nematic and smectic **A** phase in addition to two solid phases and has the following molecular structure:

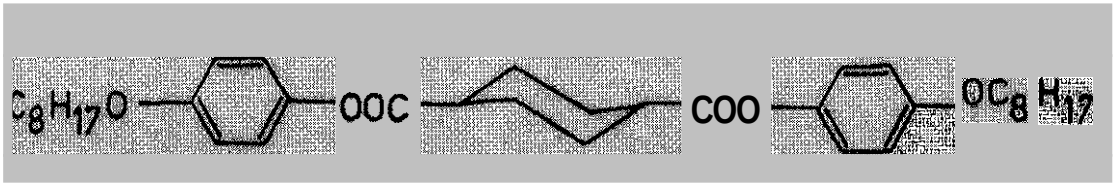


The interest generated in this compound can be gauged by the fact that it has formed the subject matter of an entire monograph edited by Demus, wherein 17 experimental papers have been published. [7]

The transition temperatures and the heats of transition are given in table I . After the completion of our experiments, we learnt that Cladis et al. [11] have also studied this compound as a function of pressure. However, our phase diagram is completely different from that obtained by Cladis et al. We shall make a comparison of the two phase diagrams when we discuss the results. Further, it should be mentioned that there is a significant difference between our value of the heat for the solid-smectic A transition and that of Cladis et al. The combined heat that is given in table I, viz., 32.4 kj/mole, for the solid II ⟶ solid I and solid I ⟶ smectic A transitions agree well with the value of Demus et al [10] (34.56 kj / mole) while it differs very much from the value of Cladis et al. [11] (18.45 kj / mole).

c) trans-1.4-Cvclohexane-di-n-octvloxvbenzoate **(TCOB)**

This compound was synthesized by Neubert et al. [12] with a view to studying the effect of replacing the benzene ring by a cyclohexane ring on the enhancement of smectic properties. This compound having the structural formula



exhibits two solid phases, two smectic B phases, a smectic C phase and a smectic A phase. The temperatures and the heats of H of the various transitions are given in table I. De Vries et al.[13] have conducted a detailed X-ray investigation on this compound to test the long standing belief in the existence of ‘ tilted' smectic A phases A in which 'd' is significantly less than the molecular length. We have carried out high pressure studies on this compound to understand the behaviour of smectic mesophases under pressure.

3. Experimental details

All the transition temperature except that of the C-A transition in TCOB were detected using the DTA cell as described in Chapter II. As regards the second order C-A transition in TCOB, which could not be detected and monitored as a function of pressure by DTA, the transition temperatures were detected by the optical transmission technique using an opposed diamond anvil cell. This is similar to the one used by Shashidhar and Rao (14) for their X-ray studies. The phase transitions were detected by monitoring the intensity of laser light (He-Ne Spectra Physics) transmitted by the sample using a photo transistor (Motorola MRD-300). The intensity was fed to the y-axis and the temperature of the sample (which was varied at a slow rate of about 1C per minute during the experiement) to the x-axis of a Ricken-Denshi X-Y recorder (model F-43). At the phase transmission there was an abrupt change in intensity of the transmitted light.

4. Results and discussion:

(i) EPAB

The data for this compound are given in table II and the phase diagram in figure 1. It is seen from the phase diagram, that the range of the smectic A phase increases with increase of pressure. The dT/dP values evaluated from the phase diagram for the solid-smectic A dn smectic A-isotropic phase boundaries are 25C/kbar and 27C/kbar respectively. It is interesting to note that the dT/dP for the two transitions are about the same, which is in contrast with what is observed in the case of nematogens like PAA or PAP (see chapter III), wherein the dT/dP for the N-I transition is always greater than that of the solid-nematic transition.

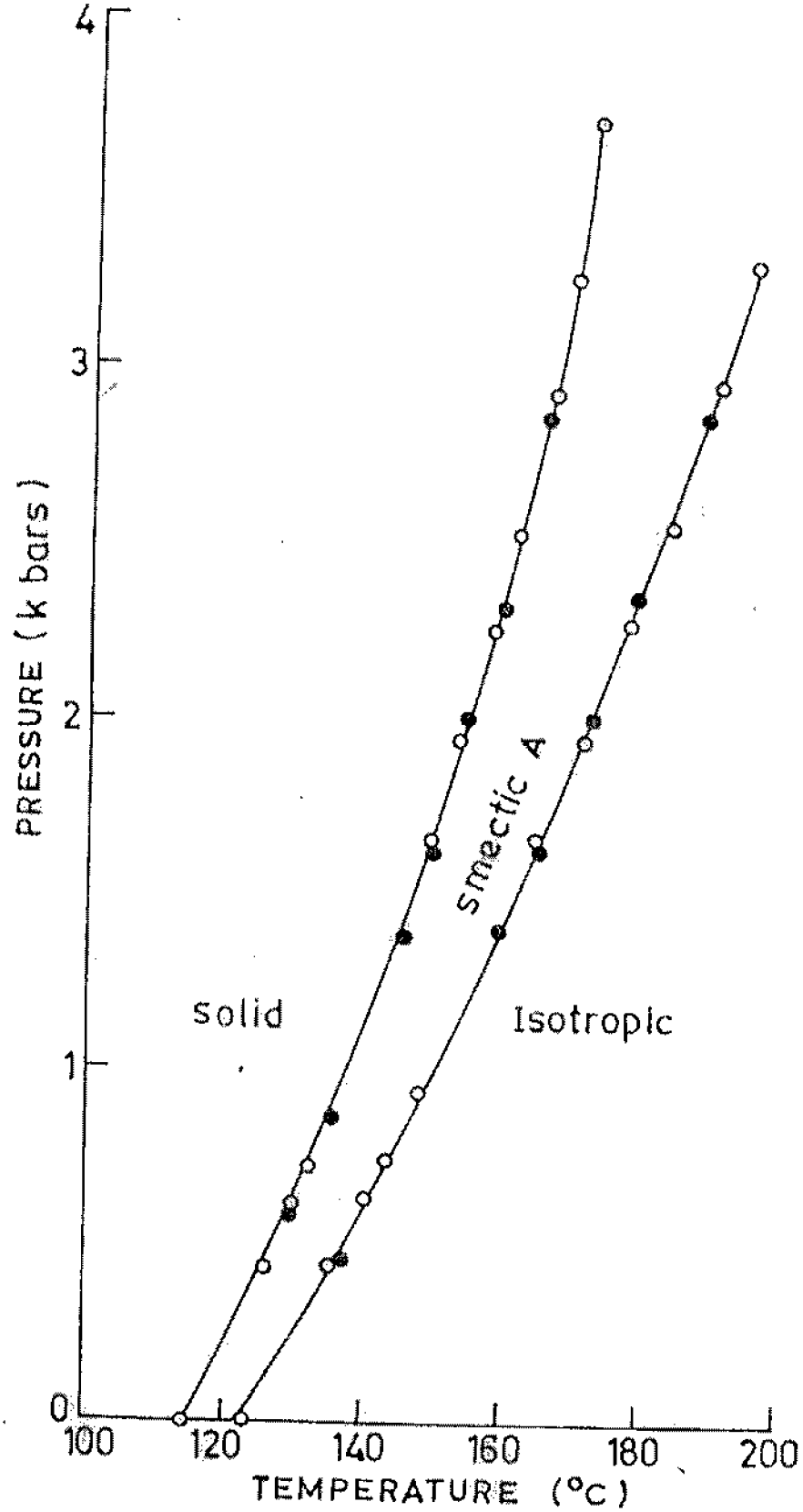


Figure 1: Phase diagram of di-ethyl-p-azoxybenzoate

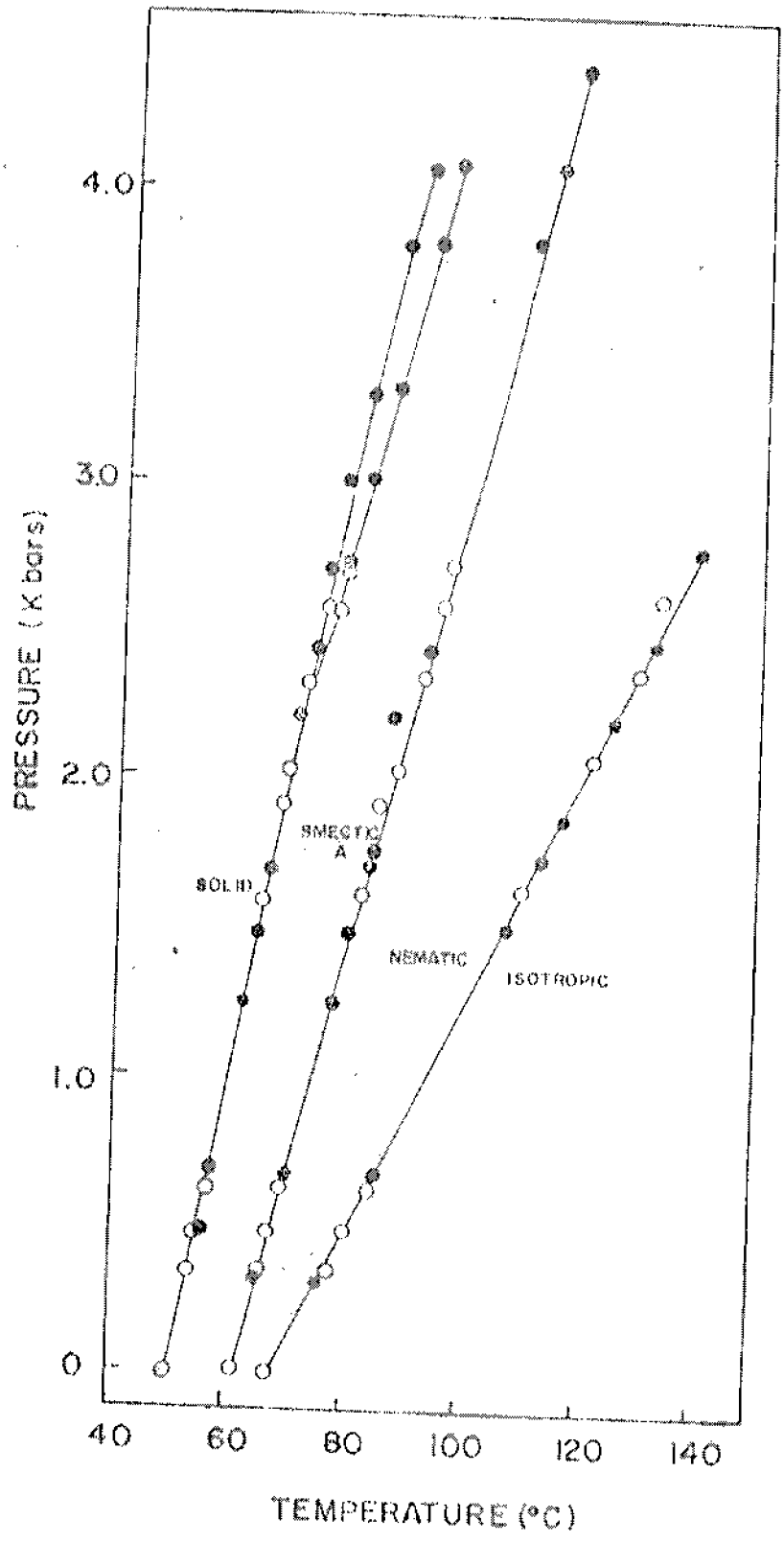


Figure 2: Phase diagram of 4-nitrophenyl-4'-n-octyloxybenzoate

O and ● represent two independent sets of measurements.

(ii) NPOOB

The data for this compound are given in table III and the phase diagram in figure 2. This compound has a nitro end group and therefore has a strong positive dielectric anisotropy. It exhibits a smectic A phase and in addition it has been noted that the measured X-ray layer spacing of the smectic A phase is 31.4 A, whilst the molecular length as obtained from a scaled model is 27.4A (15). This indicates,

Therefore, a bi layer arrangement for the mesophase. Pressure studies were undertaken to see if, like 8 OCB, which is also a strongly polar compound forming a bi layer arrangement, NPOOB exhibits re-entrant behaviour under pressure. (2)

However, as can be seen form the phase diagram (figure 2) there is no indication for re-entrant behaviour under pressure, in spite of the fact that its smectic A layer spacing is 'incommensurate' with the molecular length. There is, nevertheless an interesting feature in the phase diagram in that the solid-smectic A phase boundary, branches beyond a pressure of about 2.3 kbars. The new pressure induced phase could not, however, be identified. It could be an induced higher order smectic phase or it could as well be a new solid phase. The triple point wherein the solid, the new pressure induced phase and the SA phase coexist is at 2.28 + 0.08 kbar, 72 + 1.5 C. The range of the SA phase as well as the nematic phase increase with increasing pressure, the increase in the case of the latter being more pronounced. After the triple point, the range of the SA phase appears to be constant up to the highest pressure studied (4 kbars) indicating a saturation of the stability of the SA phase. The dT/dP for the solid-smectic A, A-N and N-I transitions are 9 .0 Clkbar, 12 .7 C/kbar and 26 Clkbar respectively.

As mentioned earlier, Cladis et al (11) have also studied this compound as a function of pressure. Their phase diagram is reproduced in figure 3. The values of dT/dP obtained by Cladis et al for the A-N and N-I phase boundaries are respectively 12 .2C/kbar and 25 Clkbar which are in good agreement with our values. But there is a marked difference as far as the solid – Sa phase boundary is concerned. Firstly the dT/dP for this transition obtained by Cladis et al is 22 Cikbar while our value is 9.6C/kbar. Secondly the pressure induced phase that we have observed beyond a pressure of 2.3 kbar., has not been observed by them. Thirdly, the solid – SA and the A-N phase boundaries intersect in their case while no such intersection is observed by us.

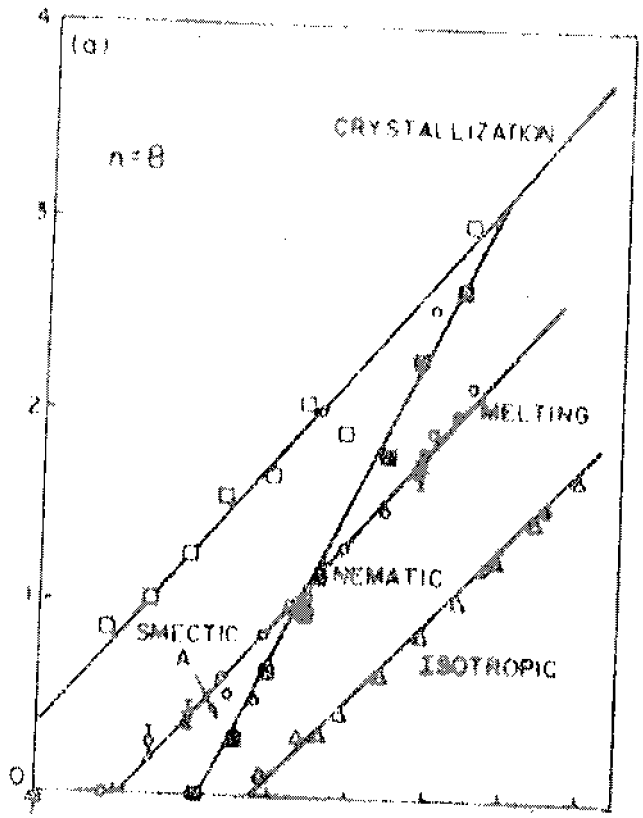


Figure 3: Phase diagram of NPOOB
(After Cladis et al[11])

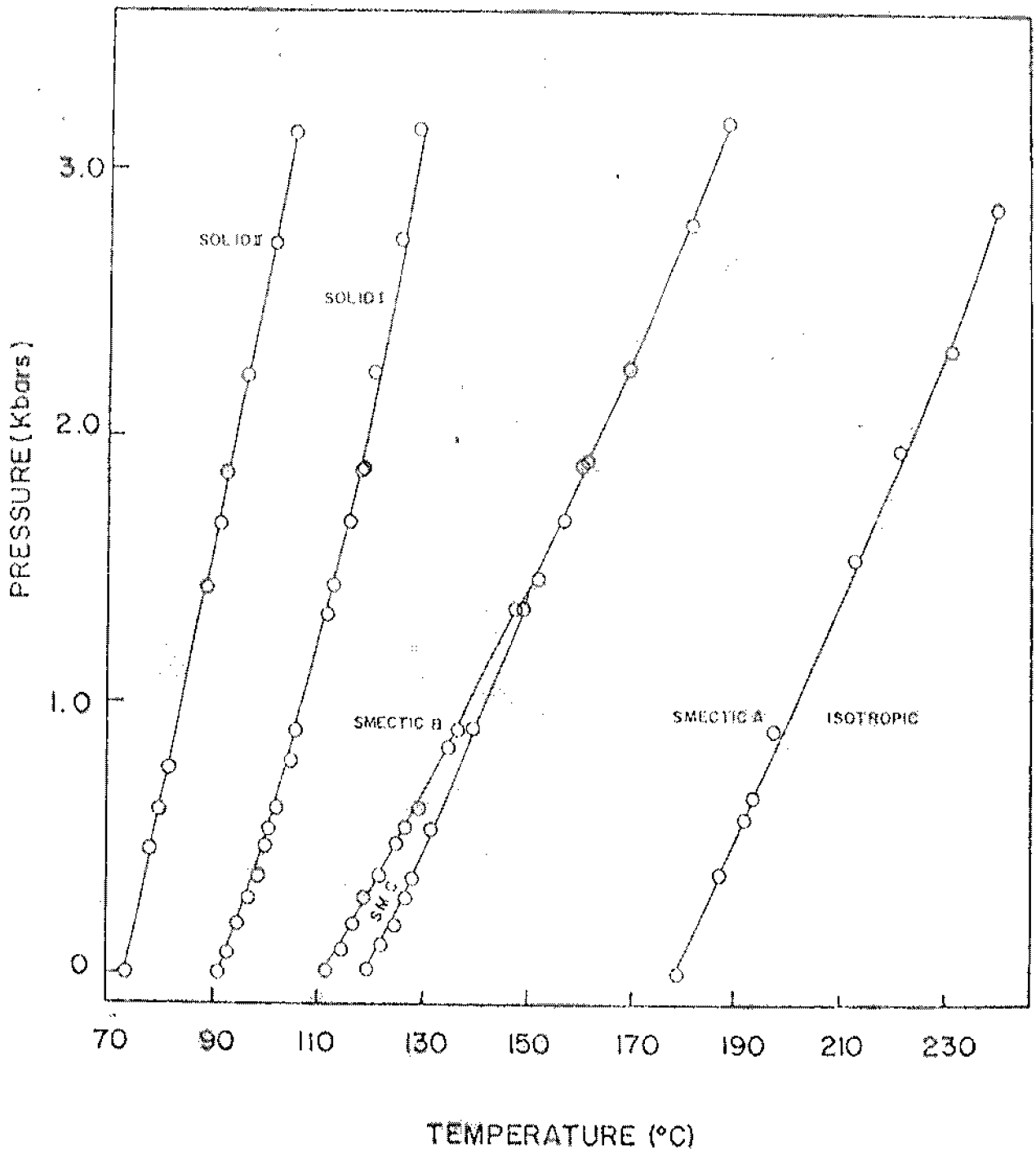


Figure 4: Phase diagram of trans-1,4-cyclohexane-di-n-octyloxybenzoate

The failure of the A-N phase boundary to show any curvature towards the pressure axis even up to 4 k bars, as is observed in 8 OCB (2) or CBOOA, (16) indicates that although all of them have a bi layer arrangement there must he a significant difference in the packing of the molecules between the alkoxy cyano compounds and the nitro compounds.

(iii) TCOB

The data for this compound are given in table IV and the phase diagram in figure 4. Though the two smectic transitions in TCOB, viz., solid I-SB(biaxial) and SB(biaxial) – SB(uniaxial) could be clearly detected in the DSC traces at atmospheric pressure, they could not be resolved in the high pressure DTA experiments. Hence we have marked this as just a single transition in our phase diagram (figure 4)

It is seen from the phase diagram that the range of the smectic B and smectic A phases increase with increase of pressure. The increase in the range of smectic B phase is very much more (from 20 C at atmospheric pressure to about 50 C at a pressure of 3.2 kbar) than that of the smectic A phase. After the suppression of the smectic C phase beyond a pressure of about 1.4 khars, the range of the smectic A phase remains practically a constant in the pressure range of our study. The smectic C phase gets bounded with the resulting triple point at 1.44 + 0.08 kbar, 150 + 1 C. Such a bounded smectic C phase has already been observed by Shashidhar and Chandrasekhar in the case of HOAB. (4)

The dT/dP evaluated from the experimental phase diagram are respectively 11.5 c/kbar, 16.9 Ckbar, 28.4 C/kbar, 27.7 Cikbar and 21.9 C/kbar for the solid II __ solid I, solid I__ SB, SB__ SC, SC__SA and SA__Iphase boundaries.

5. General Remarks

As mentioned earlier, Spratte and Schneider (5) have studied the smectic polymorphism of some Bis-(4, 4'-n-alkoxy-benylidene)1, 4-phenylenediamines as a function of pressure up to **3** kbars. They have concluded, from their experiments, that the range of the smectic phases reduce with increase of pressure and in some cases the highly ordered smectic phases disappear at higher pressures. However, in the case of the compounds studied by us, no such trend is observed, while the smectic C phase disappears at high pressures in the case of TCB, the range of the smectic A phases either increases (as in the case of EPAB) or remains almost constant (as in the case of NPOOB or TCOB) with increase of pressure. It is therefore difficult to draw general conclusions regarding the behaviour of smectic phases under pressure. More experimental results are needed.

6. Evaluation of the volume change (V) at transition using the Clausius-Clapeyron equation

From the experimental dT/dP values and from H values of the DSC measurements, we have evaluated V, the volume change associated with each transition using the Clausius-Clapeyron equation. These data are given in table V along with the dT/dP values.

7. Variation of transition temperatures with pressure and application of the Simon equation

The data of the transition temperatures for each transition obtained as a function of pressure were fitted to a polynomial of the form

$$T = TO + AP = BP2$$

where T is the transition temperature at a pressure P and TO is that at atmospheric pressure. The constants A and B were evaluated using HP9845B programmable calculator with a graphic plotterldisplay facility. The constants thus obtained are given in table IV along with the RMS error. The graphic plots for each compound and for each transition are given separately in figures 5 to 10. The solid lines in these diagrams represent the theoretical curve obtained from the iterated A and B values and the circles are the experimental data points fed to the computer.

Further the constants a and c of the Simon-Glatzel equation (17) as modified by Kraut and Kennedy, (18) viz.,

$$\underline{Pm} = \underline{(Tm)}\, c - 1$$

a To

have also been evaluated for each compound and for each transition. The graphic plots of this equation are given in figures 11 to 16. These constants along with the RMS error are also given in table VI.

The accuracy in the pressure as per the calculated fit from the Simon-Glatzel equation is +20 bars and that of the temperature from the polynomial equation is + 0.20 C. thus the absolute accuracy for each phase transition boundary can be estimated quite reliably.

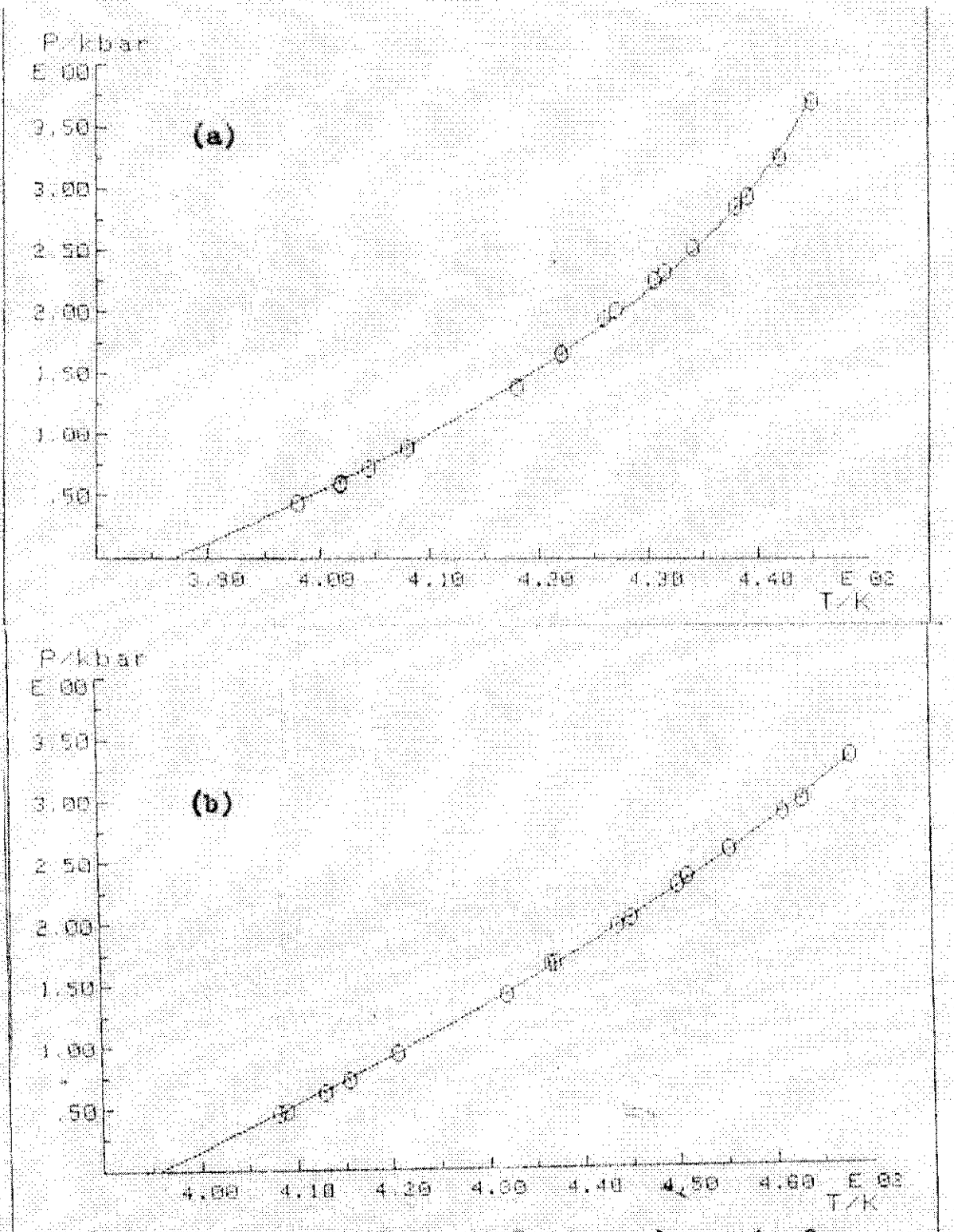


Figure 5: Phase diagram of di-ethyl-p-azoxybenzoate for (a) solid-smectic A, and (b) smectic A-isotropic transitions. The solid lines represent the theoretical curves obtained from the iterated A and B values of the polynomial equation and the circles represent the experimental data points fed to the computer.

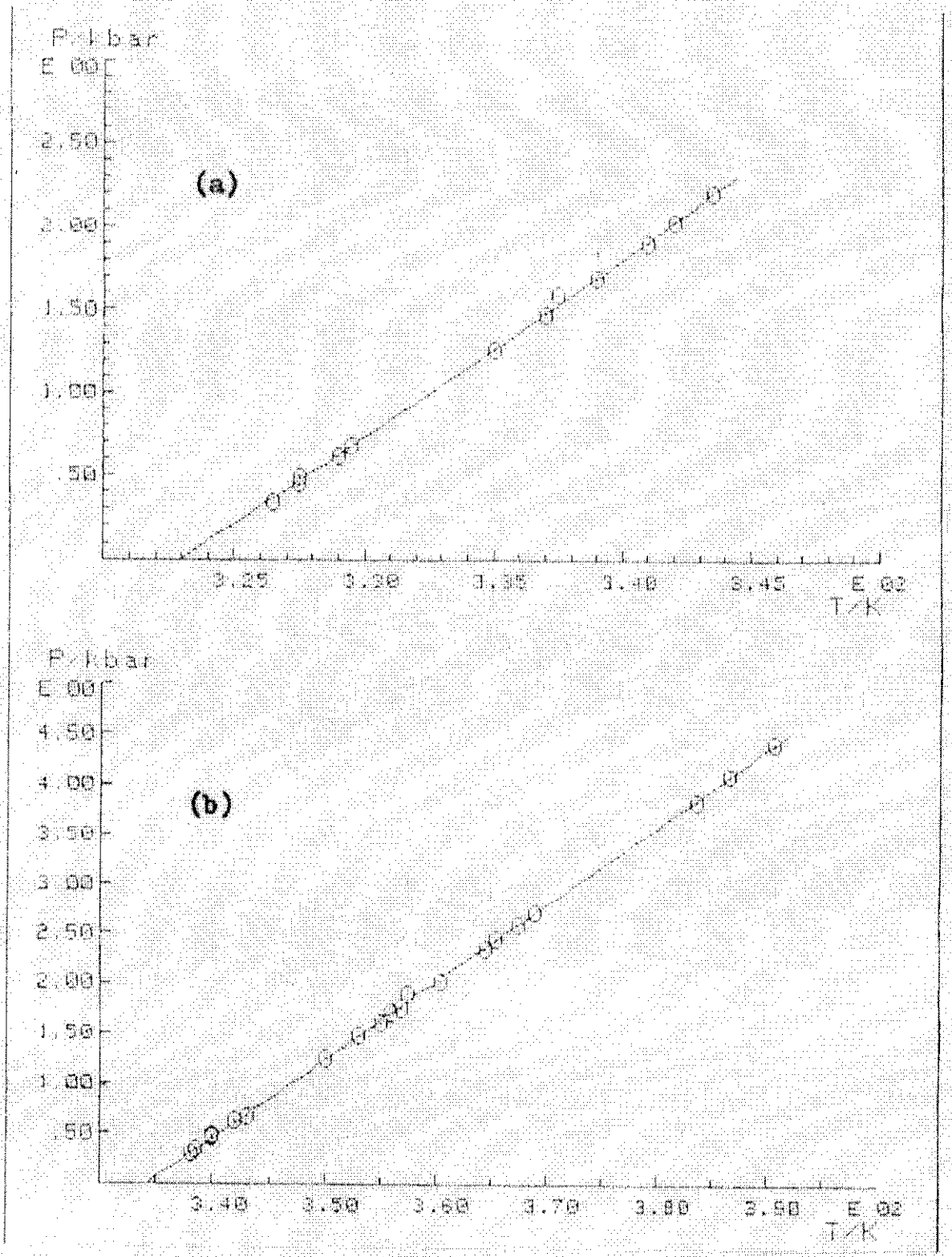


Figure 6: Phase diagram of 4-nitrophenyl-4'-n-octyloxybenzoate for the (a) solid-smectic A, and (b) smectic A-nematic transition The solid lines represent theoretical curves obtained from the iterated A and B values of the polynomial equation and the circles represent the experimental data points fed to the compute

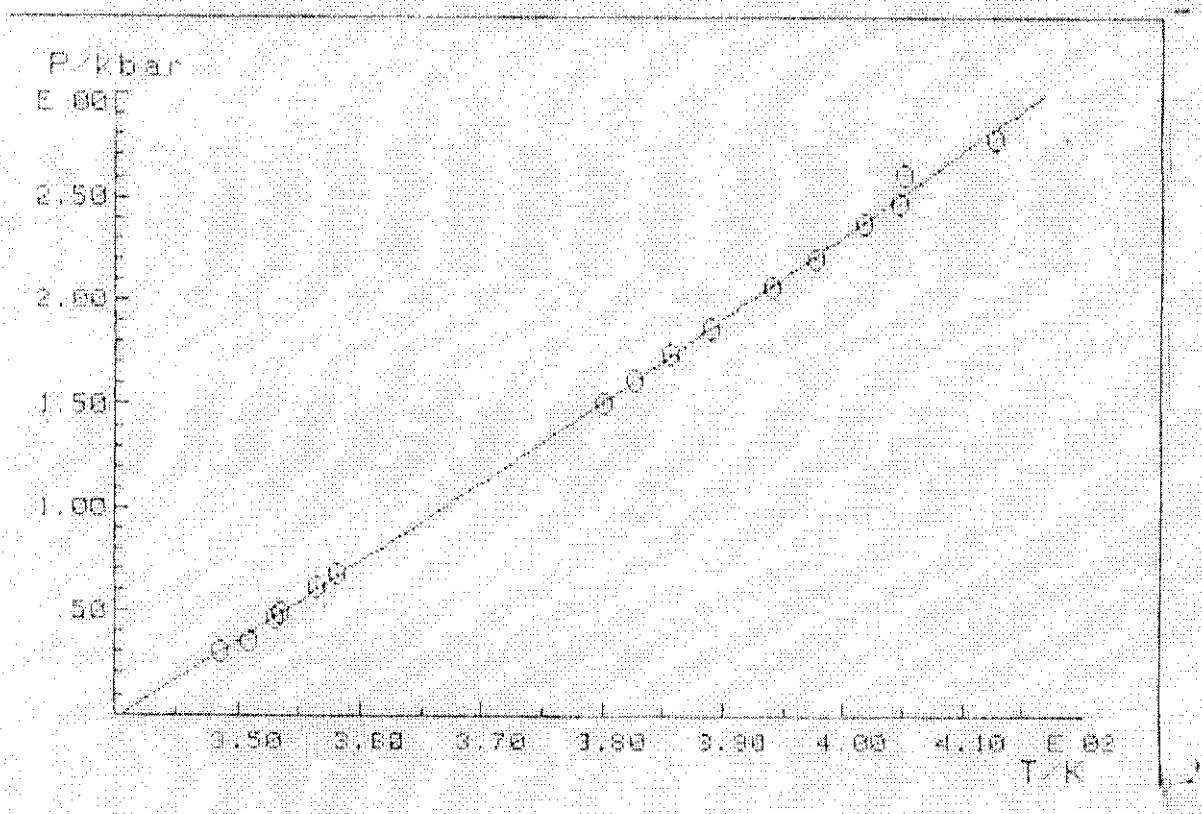


Figure 7: Phase diagram of 4-nitrophenyl-4'-n-octyloxybenzoate for the nematic-isotropic transition. The solid line represent the theoretical curve obtained from the iterated A and B values of the polynomial equation and the circles represent the experimental data points fed to the computer.

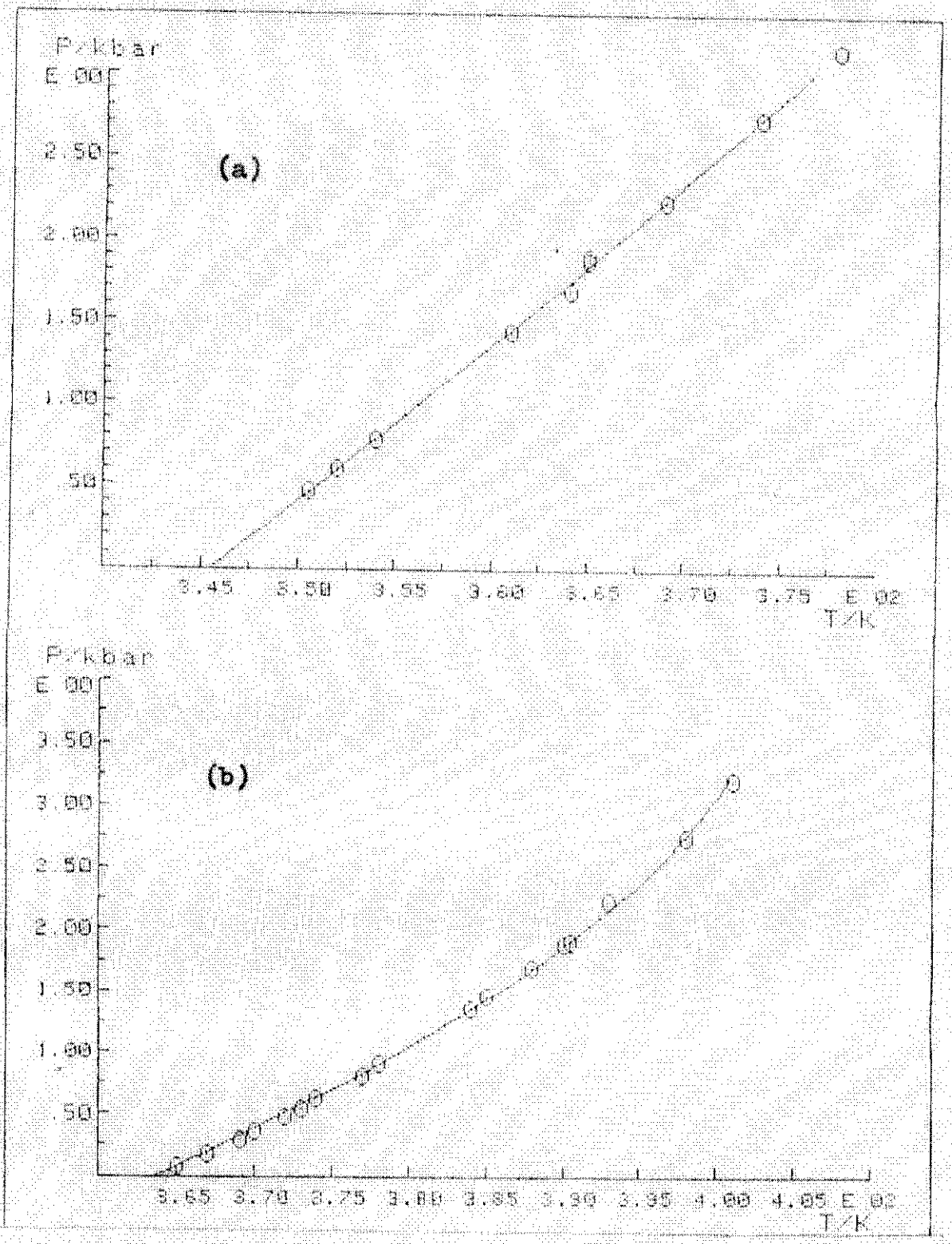


Figure 8: Phase diagram of trans-1,4-cyclohexane-di-n-octyloxybenzoate for (a) solid II-solid I, and (b) solid I-smectic B transitions. The solid lines represent the theoretical curve obtained from the iterated A and B values of the polynomial equation and the circles represent the experimental data points fed to the computer.

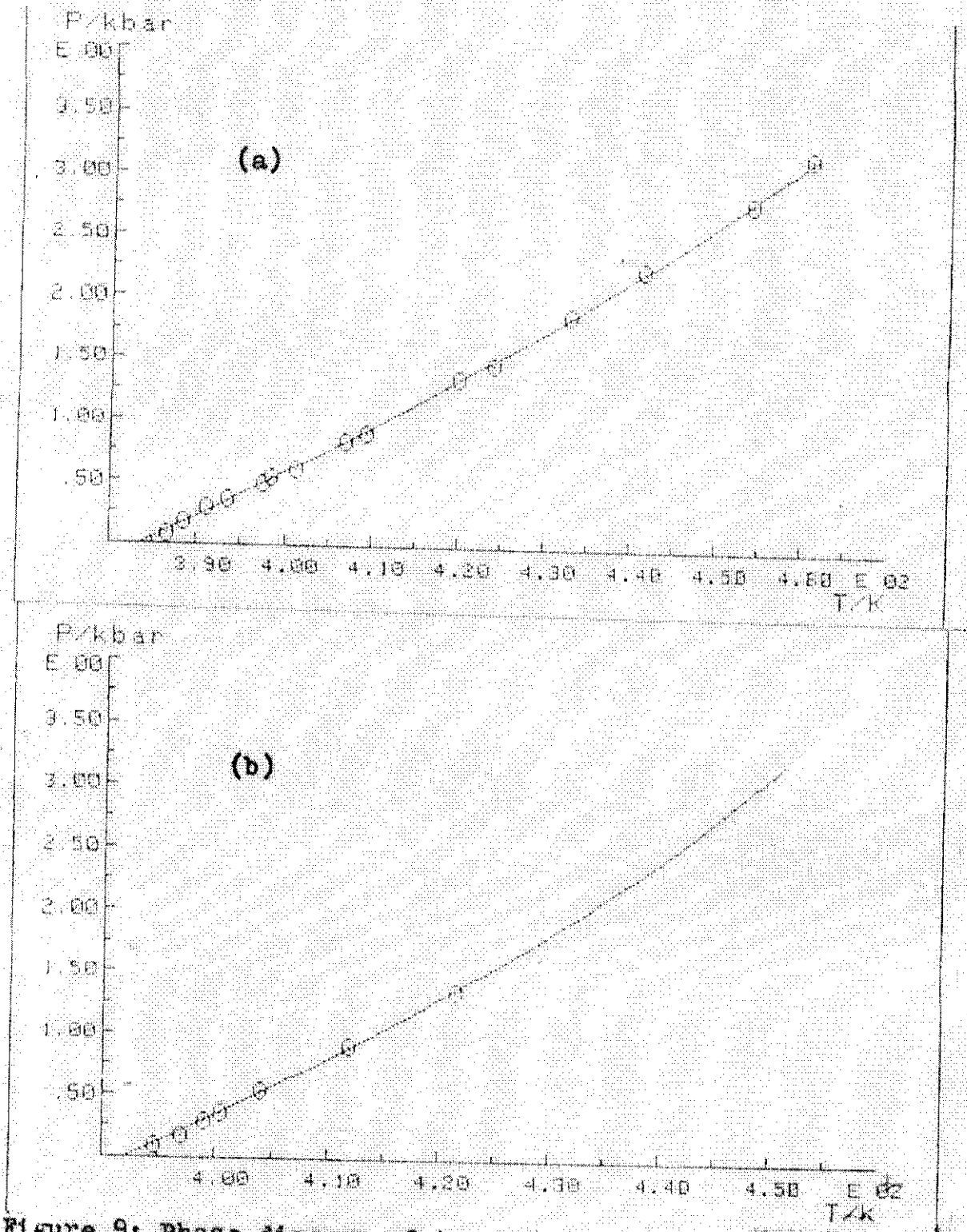


Figure 9: Phase diagram of trans-1,4-cyclohexane-di-n-octyloxy-benzoate for (a) smectic B-smectic C, and (b) smectic C-smectic A transitions. The solid lines represent the theoretical curves obtained from the iterated A and B values of the polynomial equation and the circles represent the experimental data points fed to the computer.

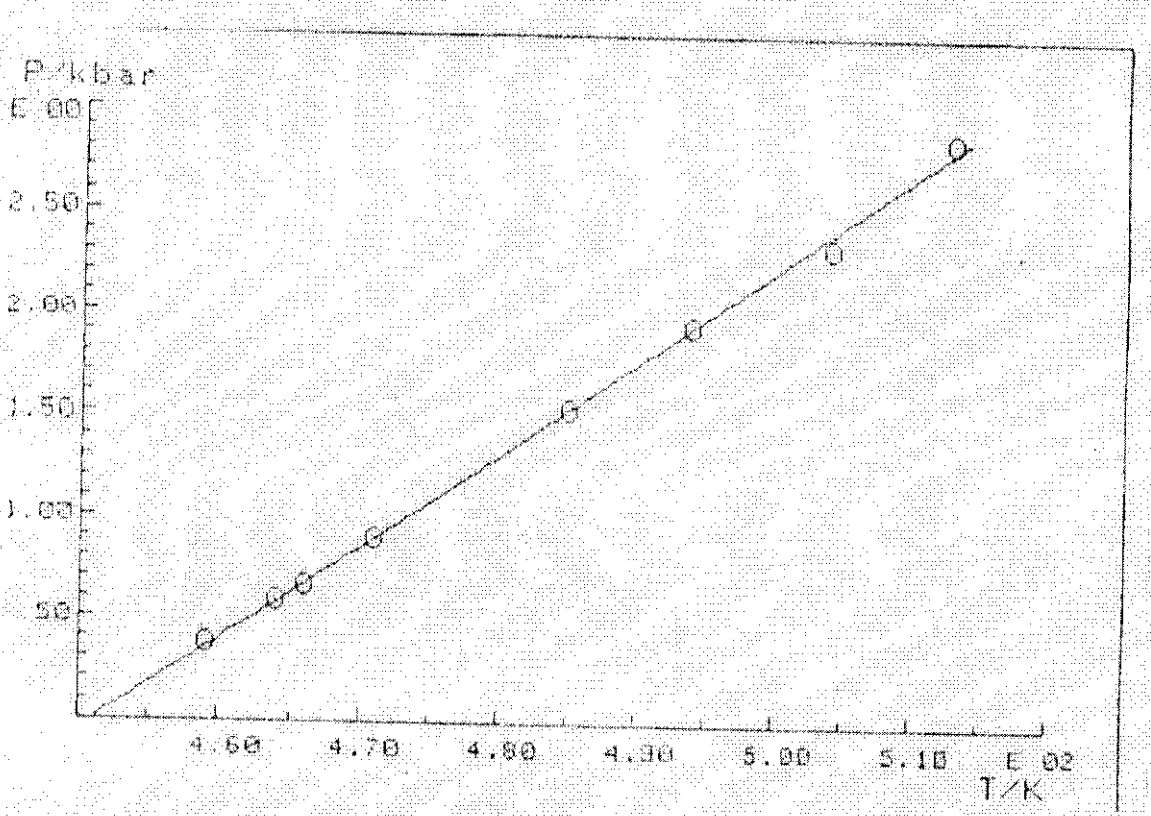


Figure 10: Phase diagram of trans-1,4-cyclohexane-di-n-octyloxybenzoate for the smectic A-isotropic transition. The solid line represents the theoretical curve obtained from the iterated A and B values of the polynomial equation and the circles represent the experimental data points fed to the computer.

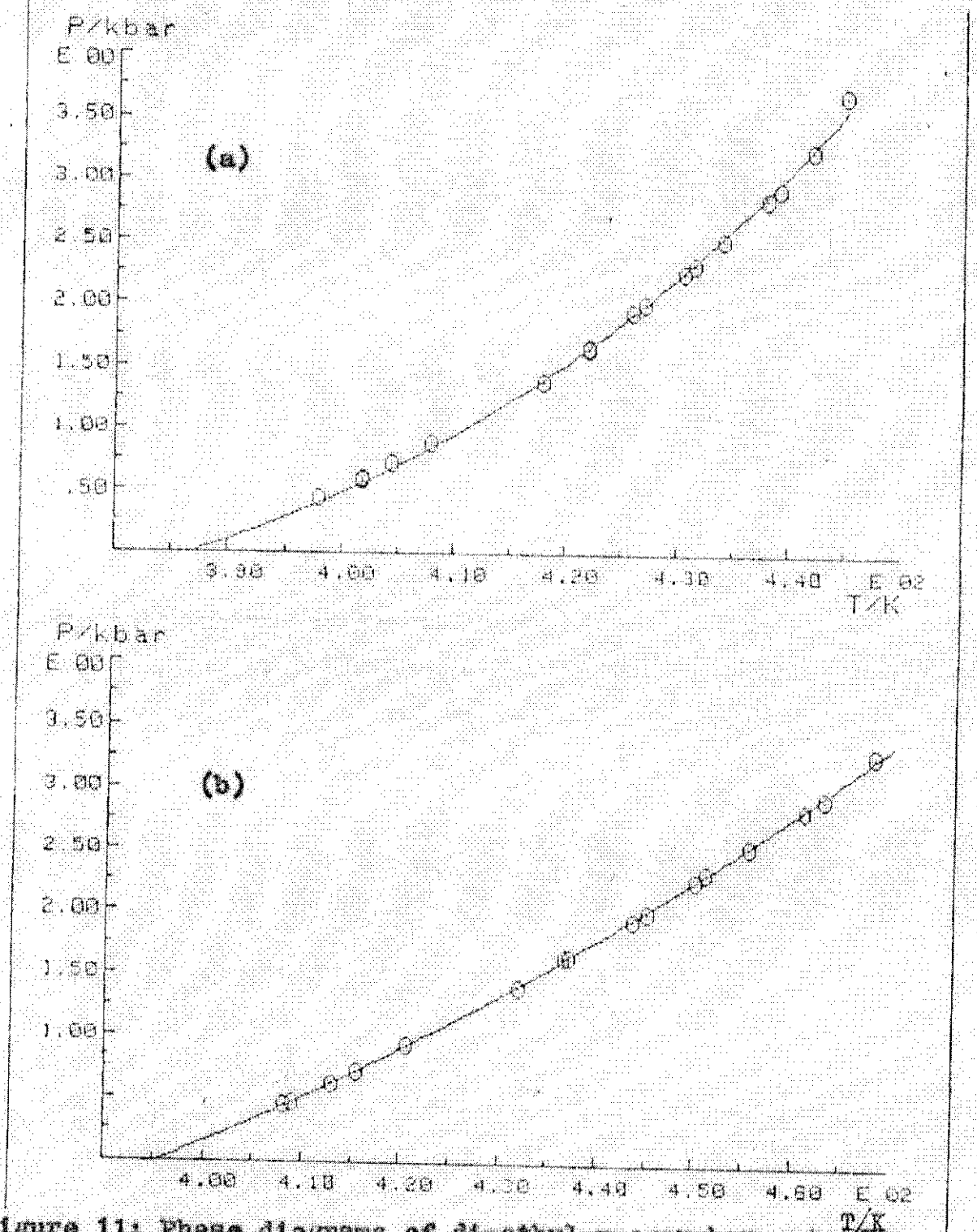


Figure 11: Phase diagrams of di-ethyl-p-azoxybenzoate for (a) solid-smectic A, and (b) smectic A-isotropic transitions. The solid lines represent the theoretical curves obtained from the iterated a and c values of the Simon-Glatzel equation and the circle represents the experimental data points fed to the computer.

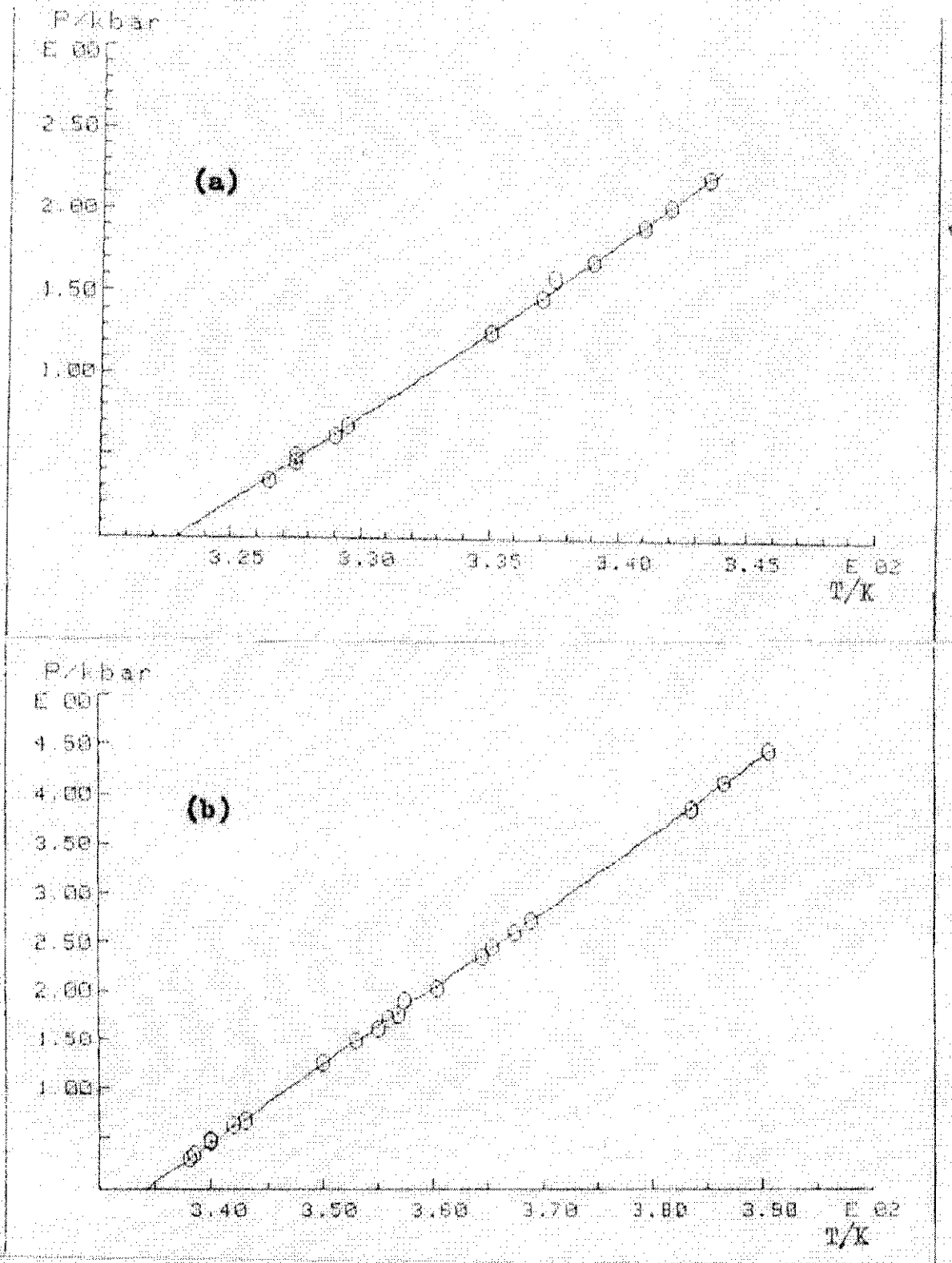


Figure 12: Phase diagram of 4-nitrophenyl-4'-n-octyloxybenzoate for (a) solid-smectic A, and (b) smectic A-nematic transitions. The solid line represents the theoretical curve obtained from the iterated a and c values of the Simon-Glatzel equation and the circles represent the experimental data points fed to the computer.

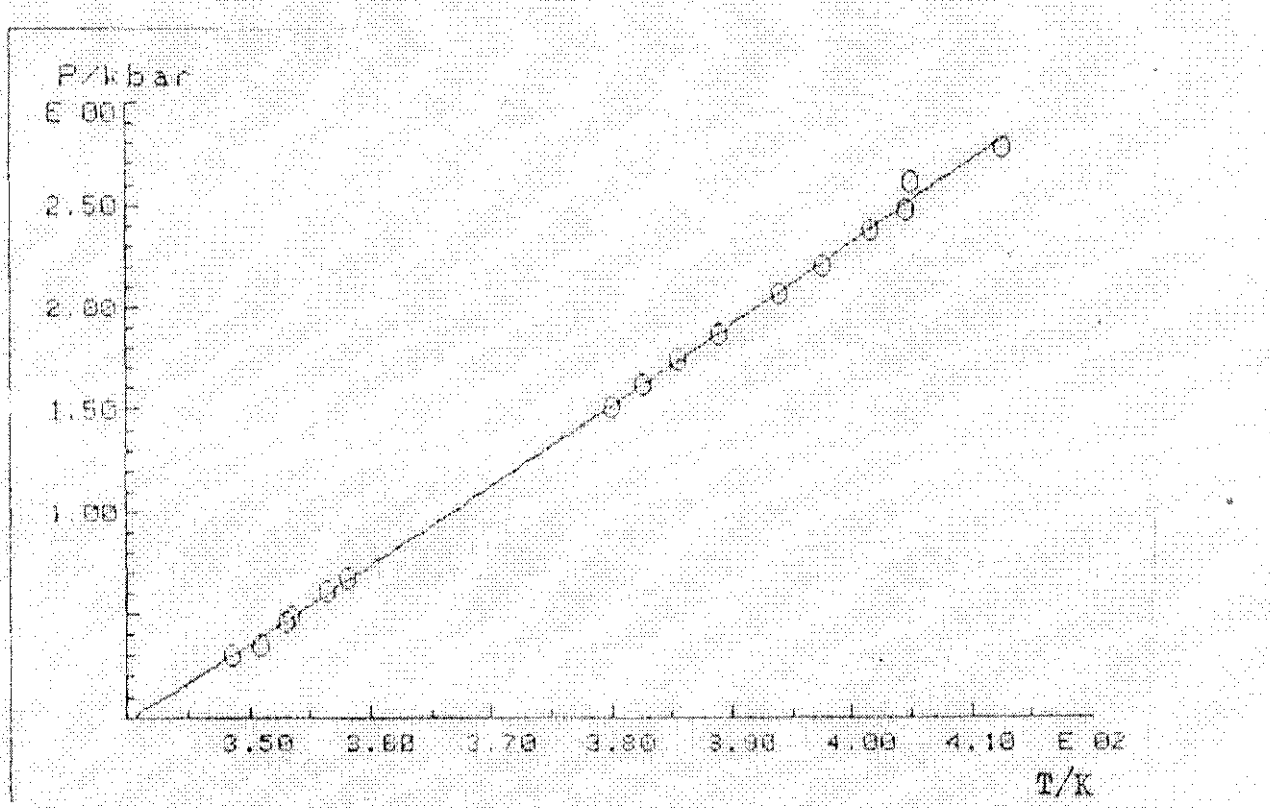


Figure 13: Phase diagram of 4-nitrophenyl-4'-n-octyloxy-benzoate for the nematic-isotropic transition. The solid line represents the theoretical curve obtained from the iterated a and c values of the Simon-Glatzel equation and the circle represents the experimental data points fed to the computer.

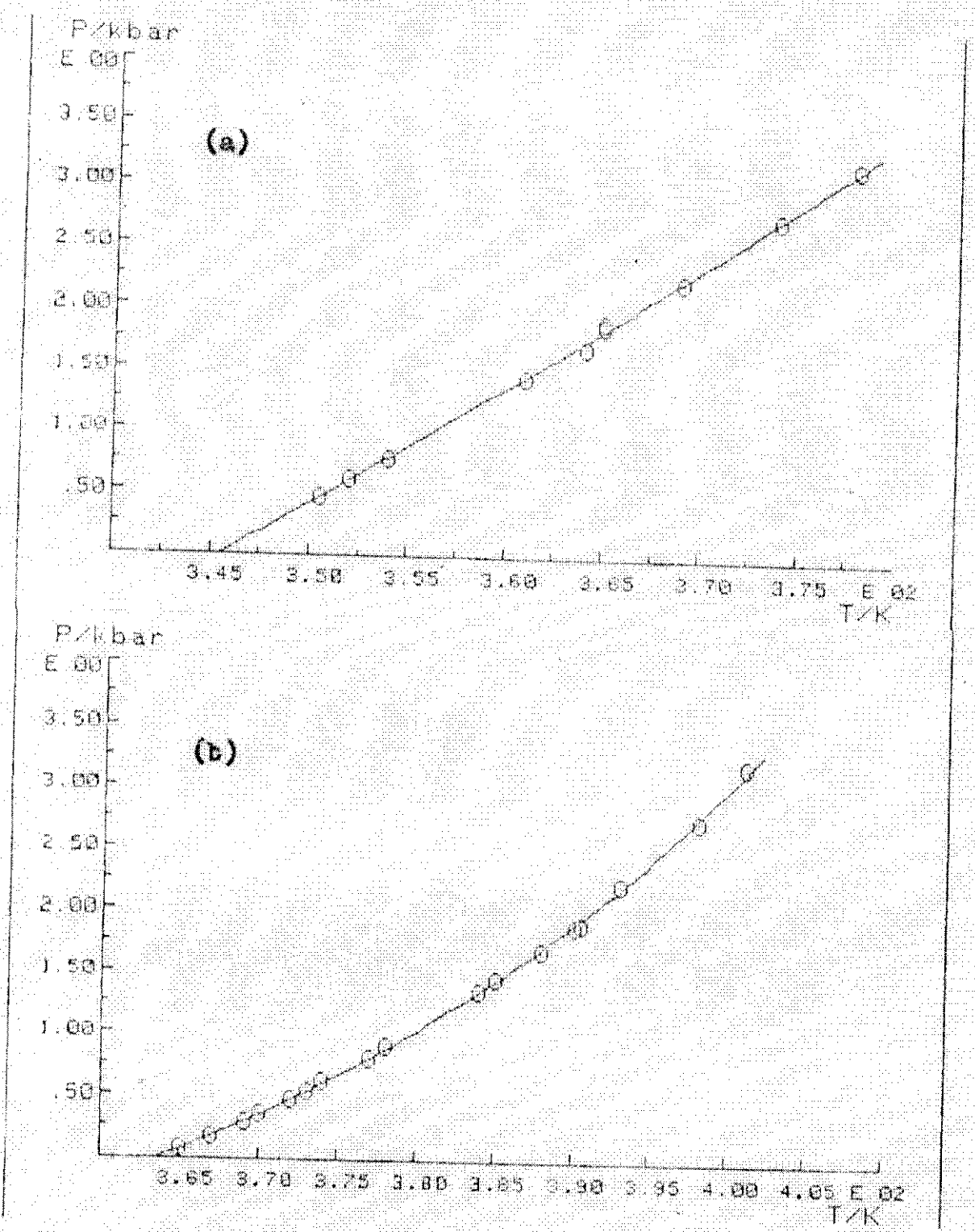


Figure 14: Phase diagrams of trans-1,4-cyclohexane-di-n-octyloxy-benzoate for (a) solid II-solid I, and (b) solid I-smectic B transitions. The solid lines represent the theoretical curve obtained from the iterated a and c values of the Simon-Glatzel equation and the circles represent the experimental data points fed to the computer.

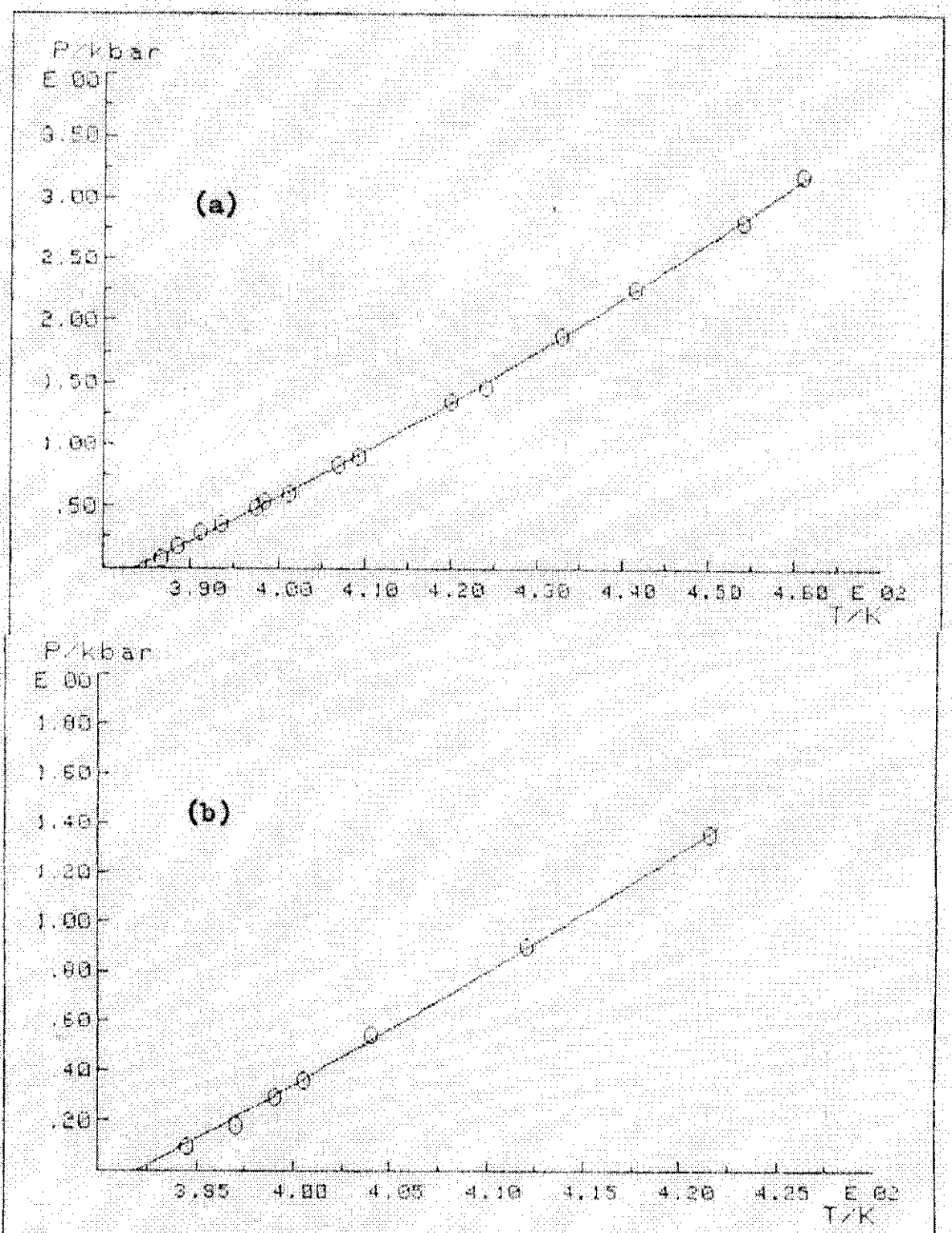


Figure 15: Phase diagrams of trans-1,4-cyclohexane-di-n-octyloxy-benzoate for (a) smectic B-smectic C, and (b) smectic C-smectic A transitions. The solid lines represent the theoretical curves obtained from the iterated a and c values of the Simon-Glatzel equation and the circle represent the experimental data points fed to the computer.

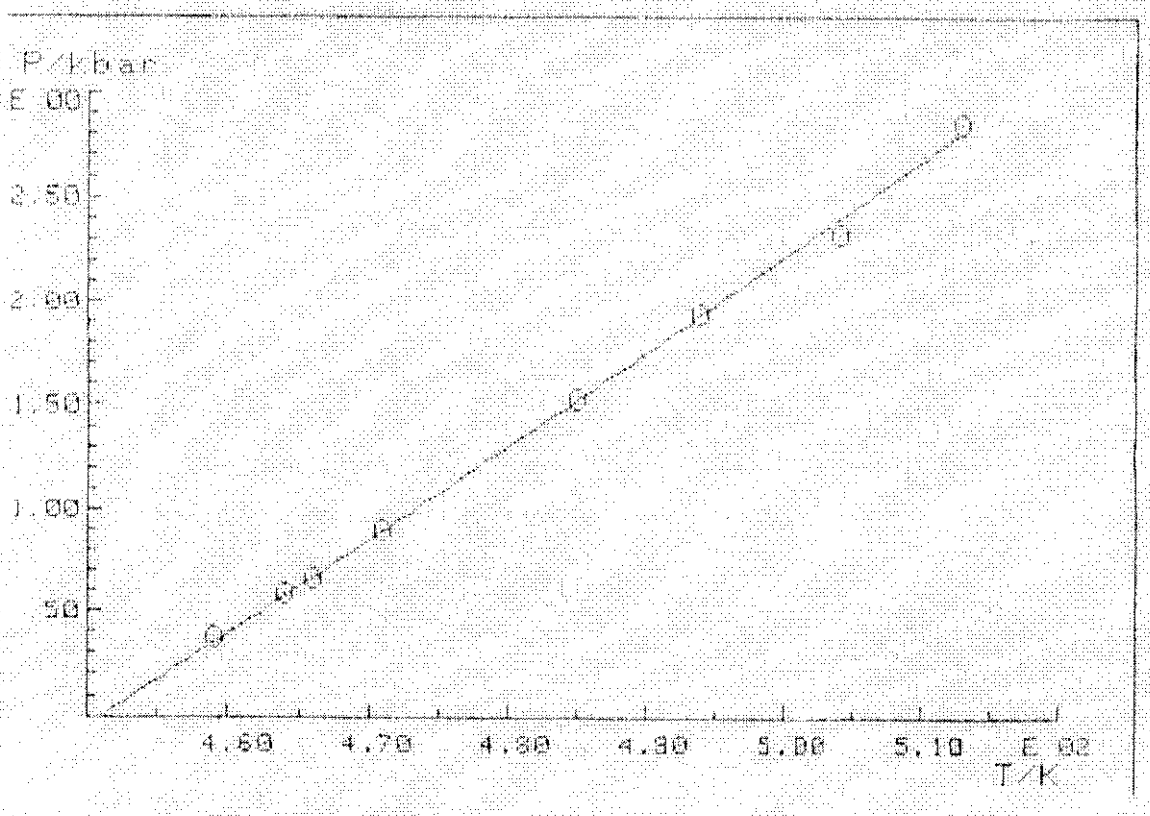


Figure 16: Phase diagram of trans-1,4-cyclohexane-di-n-octyloxybenzoate for the smectic A-isotropic transition. The solid line represents the theoretical curve obtained from the iterated a and c values of the Simon-Glatzel equation and the circles represent the experimental data points fed to the computer.

TABLE I

Transition temperatures and heats of transitions (H) for the compounds studied

Compound	Transition	Temperatures in C	Heat of transition (H) in kJ/mole
a) EPAB	S – SA	114	19.6
	SA – I	122.5	4.8
b) NPOOB	SII – SI	47.6	32.4
	SI – SA	49.8	
	SA – N	61.2	0.2
	N – I	67.5	0.5
c) TCOB	SII – SI	72.5	18.3
	SI – SB (biaxial)	90.5	18.0
	SB (biaxial) – SB (uniaxial)	92.5	0.4
	SB (uniaxial) – SC	110.5	2.2
	SC – SA	119.0	0
	SA – I	178.0	7.8

TABLE – II

Transition temperatures of EPAB as a function of pressure

Solid – Smectic A		Smectic A - Isotropic	
Pressure in kbars	**Temperature in C**	**Pressure in kbars**	**Temperature in C**
0.437	125.0	0.454	135.0
0.446	125.0	0.472	136.0
0.596	129.0	0.622	140.0
0.605	129.0	0.728	142.5
0.719	131.5	0.940	147.5
0.878	135.0	1.400	159.0
1.381	145.0	1.664	163.0
1.638	149.0	1.947	170.5
1.655	149.0	2.008	172.0
1.937	153.0	2.264	177.0
2.000	154.0	2.344	178.0
2.247	157.5	2.547	182.5
2.317	158.5	2.847	188.0
2.520	161.0	2.953	190.0
2.847	165.0	3.297	195.0
2.926	166.0		
3.244	169.0		
3.695	172.0		

TABLE – III

Transition temperatures of NPOOB as a function of pressure

Solid – smectic A		Smectic A – nematic		Nematic – isotropic		Solid-pr. induced		Pr. Induced-smectic A	
Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C
0.344	53.5	0.309	65.0	0.309	75.5	2.46	73.5	2.30	73.0
0.459	54.5	0.344	65.5	0.352	78.0	2.60	74.0	2.60	76.0
0.490	55.0	0.468	67.0	0.468	80.0	2.74	75.0	2.70	78.0
0.615	56.0	0.490	67.0	0.490	80.5	3.02	77.5	3.02	82.0
0.671	56.5	0.622	69.0	0.609	83.5	3.32	81.0	3.34	87.0
1.253	62.0	0.671	70.0	0.671	85.0	3.84	87.0	3.84	94.0
1.474	64.0	1.253	77.0	1.500	107.0	4.10	91.0	4.10	96
1.587	64.5	1.483	80.0	1.615	109.5				
1.686	66.0	1.606	82.0	1.739	112.5				
1.898	68.0	1.695	83.0	1.863	116.0				
2.022	69.0	1.748	84.0	2.065	121.0				
2.200	70.5	1.898	84.5	2.200	124.5				
2.340	72.0	2.022	87.5	2.366	128.05				
		2.340	91.5	2.472	131.5				
		2.445	92.5	2.606	132.0				
		2.587	94.5	2.780	139.5				
		2.711	96.0						
		3.828	110.0						
		4.087	113.0						
		4.414	117.5						

TABLE – IV

Transition temperatures of TCOB as a function of pressure

Solid II – Solid I		Solid I – Smectic B		Smectic B – Smectic C		Smectic C – Smectic A		Smectic A - Isotropic	
Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C	Pressure in kbars	Temp. in C
0.463	77.5	0.080	92.0	0.080	113.5	0.100	121.0	0.384	186.0
0.604	79.0	0.180	94.0	0.180	115.5	0.180	124.0	0.591	191.0
0.722	81.0	0.290	96.0	0.290	118.0	0.290	126.0	0.666	193.0
1.435	88.0	0.360	97.0	0.360	120.5	0.360	127.5	0.896	198.0
1.680	91.0	0.472	99.0	0.490	124.5	0.540	131.0	1.532	212.0
1.862	92.0	0.540	100.0	0.540	125.5	0.900	139.0	1.940	221.0
1.890	92.0	0.614	101.0	0.604	128.5	1.350	148.5	2.317	231.0
2.220	96.0	0.799	104.0	0.834	134.5			2.856	240.0
2.732	101.0	0.900	105.0	0.900	136.0				
3.156	105.0	1.350	111.0	1.350	147.0				
		1.443	112.0	1.461	151.0				
		1.680	115.0	1.680	156.0				
		1.870	117.0	1.876	160.0				
		1.890	117.0	2.247	168.0				
		2.229	120.0	2.794	181.0				
		2.741	125.0	3.171	188.0				
		3.174	128.0						

TABLE – IV

dT/dP and volume change (V) at transition

Compound	Transition	dT/dP C/kbar	V cm3/mole
EPAB	S – SA	25.0	53.4
	SA – I	27.0	13.8
NPOOB	S – SA	9.6	40.5
	SA – N	12.7	0.3
	N – I	26.0	1.6
TCOB	SII – SI	11.5	25.6
	SI – SB	16.9	35.8
	SB – SC	28.4	6.8
	SC – SA	27.7	
	SA – I	21.9	16.2

TABLE VI

Constants of the Polynomial and Simon equations

Compound	Transition	T = TO + AP – BP2			Simon equation P/a = (T/TO)c-1		
		Constants A In kbars	B	RMS error	Constants A In kbars	C	RMS error
EPAB	S – SA	25.7	2.74	+ 0.41	1324.1	9.4	+ 4.3 x 10-2
	SA – I	28.6	2.00	+ 0.35	3054.5	4.3	+ 1.66 x 10-2
NPOOB	S – SA	9.9	- 0.25	+ 0.19	11712.3	2.8	+ 2.05 x 10-2
	SA – N	12.8	- 0.001	+ 0.33	25004.5	1.0	+ 2.55 x 10-2
	N – I	26.9	0.51	+ 0.71	8361.7	1.5	+ 2.86 x 10-2
TCOB	SII – SI	11.1	0.25	+ 0.28	10595.0	2.9	+ 2.74 x 10-2
	SI – SB	17.9	1.97	+ 0.33	1637.2	10.9	+ 2.10 x 10-2
	SB – SC	29.5	1.58	+ 0.49	4328.5	3.0	+ 1.99 x 10-2
	SC - SA	24.2	1.78	+ 0.38	4136.9	3.9	+ 1.62 x 10-2
	SA – I				14809.3	1.3	+ 3.37 x 10-2

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