

APPENDIX

PIEZO THERMAL STUDIES IN THE VICINITY OF SMECTIC A - NEMATIC (AN) TRANSITION IN 4'-n-OCTYLOXY-4- CYANOBIPHENYL (8 OCB)

1. Introduction

Although the first observation of the reentrant nematic behaviour in a pure compound was at high pressure,¹ the subsequent observation of this behaviour at atmospheric pressure^{2,3} led to the fact that most of the experimental studies that are being conducted on the reentrant nematogens are almost exclusively atmospheric pressure experiments. In fact, apart from the P-T diagrams of Gladis et al,^{1,4} there are only a few high pressure experimental studies on reentrant nematics. Chandrasekhar et al⁵ have studied the pressure variation of the layer thickness of smectic A phase of 8 OCB using a high pressure X-ray cell, while Garland et al⁶ and Lushington et al⁷ have carried out high pressure calorimetric studies on the same compound. In chapter IV, we have discussed the method of estimating the ratio of thermodynamic parameters like $\Delta\alpha/\Delta\beta$, $\Delta\beta/\Delta C_p$ by fitting the experimental P-T data of the AN phase boundary to an ellipse, but the calculation

of individual parameter requires the accurate knowledge of any one of the three parameters, viz., thermal expansion (α), isothermal compressibility (β) and specific heat (C_p).

The piezothermal or heat of compression method provides the basis for a precise determination of thermal expansion (α) directly as a function of pressure. It is to be noted that to obtain ' α ' with the same accuracy by conventional method like piezometry, one would have to determine the volume change to an accuracy of one in 10^{-4} which is very difficult to achieve in high pressure experiments. We have carried out piezothermal studies on 8 OCB as a function of pressure along 4 different isotherms.

2. Experimental

A. Principle: The piezothermal or heat of compression method^{8,9} is based on the thermodynamic equation of Maxwell, viz.,

$$(\partial S / \partial P)_T = - \alpha V \quad (1)$$

where S and V are the molar entropy and volume respectively, and α is the thermal expansion. Taking into account the

thermal effects due to the elastic deformation of the container one can write the equation (1) in terms of the quantity of heat **Q liberated** by a volume V_s of the sample under isothermal variation of **pressure ΔP** as^{10,11}

$$Q = - (\alpha - \alpha_r) TV_s \Delta P \quad (2)$$

where α_r is the coefficient of expansion of the **container** material. Hence knowing α_r and V_s by the appropriate **calibration** experiment, ' α ' the thermal **expansion** of the material can be determined with the help of the equation (2).

B. Apparatus and Calibration: **Figure 1 is the schematic** diagram of the conventional Flux calorimeter (**SETRAM**) adopted for high **pressure** experiments. **The sample is taken** in a high pressure (HP) tube of **uniform cross** section. Its length is several **times the height** of the calorimetric **element** in which it is vertically positioned. The lower end of the tube is fitted with a high pressure cone to **cone type** closure which **is push-**fitted into **the** internal cell of the element. This ensures the necessary thermal junction between H.P. tube and the internal cell. Another thermal junction is **made** between H.P. tube **and** the thermostat by **means** of a **copper** cylinder, sliding along the H.P. tube, positioned a **few cm**

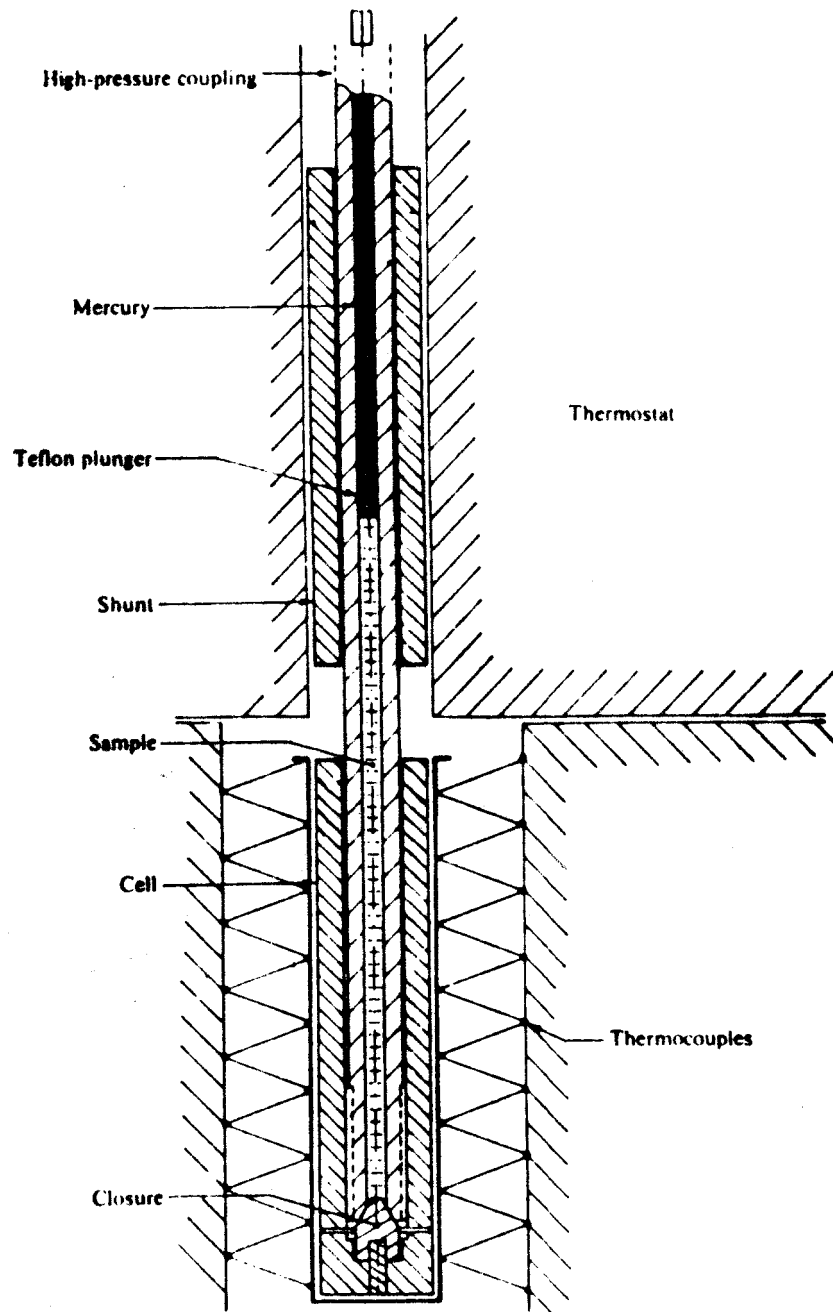


Figure 1: Schematic diagram showing vertical section of a high pressure cell in a calorimetric element.

above the cell. This junction acts as a thermal shunt, thereby keeping the portion of tube which is in contact with it at the temperature of the thermostat. Pressure is generated by a capstan driven high pressure pump (from Nova Swiss) connected to the upper end of the tube, As a result, heat is liberated uniformly in the inner volume of the H.P. tube and propagates towards the thermostat by the two already established thermal junctions. One of the junctions is the calorimetric element itself with its many thermocouples whose overall thermal resistance is 2 KW^{-1} , whereas the other junction namely the thermal shunt is of negligible thermal resistance. The thermal fluxes, one along the tube in the direction of the shunt (J_o) and the other along the thermocouple (J_e), are of the same order of magnitude and practically independent of the contents of the thick high pressure tube. Moreover, due to the large value of the thermal time constant which is usually of the order of a few minutes, the fluxes J_e and J_o vary slowly with time, thereby maintaining the quasi-stationary condition. Moreover, the ratio between two fluxes is constant, and hence it is possible to estimate the overall heat liberated by estimating simply J_o with the help of the thermocouples. Pressure is measured with a strain gauge to

an accuracy of ± 0.5 bar.

Equation (2) also allows the calibration of the containers and of the calorimetric devices by making use of a gas close to the ideal conditions. In this case, we have $\alpha = 1/T$. Since $\alpha_r \ll \alpha$, we have,

$$Q = -V_s \Delta P.$$

Therefore, the piezothermal set up is first calibrated by varying the pressure of helium or nitrogen by a few bar. The resulting heat liberated is measured as an e.m.f. by a set of 500 thermocouples which are electrically in series but thermally in parallel. The combined e.m.f. of the thermocouples is recorded and integrated as a function of time. The area A under the 'thermogram' gives the quantity of heat liberated due to isothermal change in the pressure by ΔP . Hence, we have $\Sigma V_r = A/\Delta P$ where Σ is the sensitivity of the thermocouples for unit thermal flux, which can be determined independently by conventional methods. Therefore, knowing α_r and V_s , the thermal expansion ' α ' of the sample can be obtained by equation (2).

The absolute pressure and temperature were measured to an accuracy of ± 0.5 bar and $\pm 0.01^\circ\text{C}$ respectively.

They were also maintained to the same accuracies.

C. Measurement of a for 8 OCB: The sample used in the present study was purchased from BDH, England and was used without further purification. The transition temperatures at 1 bar were 67.0°C for the smectic A - nematic and 81.0°C for the nematic - isotropic transitions. Figure 2 represents the phase boundary of smectic A - nematic transition obtained using a high pressure optical cell described in chapter II using light transmission technique as the probe. The value of P_m , the maximum pressure up to which smectic A exists is 1.98 kbar which is in good agreement with the earlier data of Gladis¹ and Garland et al⁶. The experiment has been conducted along 4 different isotherms, viz., 68.7, 71.4, 75.1 and 77.6°C . Before commencing the experiment at any temperature, the piezothermal set up was allowed to attain thermal equilibrium for at least 24 hours. Then the pressure was increased very slowly to about 200 bar above the smectic A - nematic transition pressure at that temperature. Pressure was then decreased by small steps (a few bars) and the area of the potential versus time curve was integrated at each step. Initially, at pressures not close to the smectic A - nematic transition,

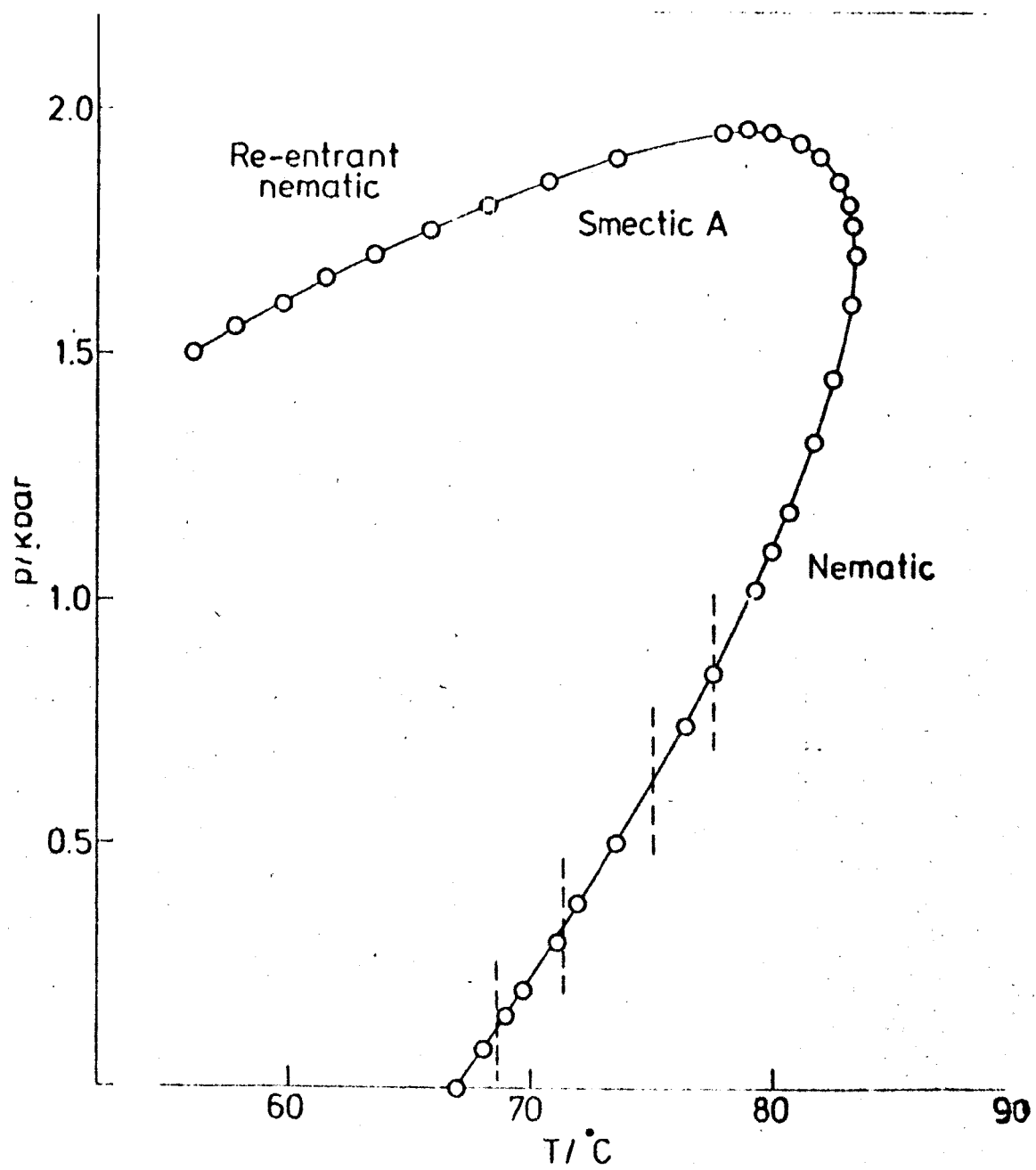


Figure 2: AN phase boundary of 8 OCB

the time necessary for **each** step **was** about 40 minutes. However, in the vicinity of the A-N transition, the **recording** and integration **had** to be carried out for much longer periods of **time**. No experiments could be conducted on the reentrant **nematic** phase **owing** to the rapid **crystallization** of the supercooled **smectic A** phase.

3. Results and Discussion

The data of the thermal **expansion** at **various pressures** measured **along** different isotherms are given in Tables I to IV. Figures 3 to 6 **show** the variation of **thermal expansion** with **pressure** at 4 different temperatures **studied**. From the figure it is found that ' α ' exhibits **an anomaly** at the A-N transition. The height of this **peak decreases** with **increasing** temperature and at the highest **temperature** studied, **viz.**, **77.6°C**, there is hardly any **anomaly** (Fig.6).

Generally, it is far more difficult to achieve a fine variation of pressure than of temperature. To that extent, the **experimental value** of α , particularly **close** to the smectic A - nematic **phase** boundary, do not have the required precision to make a good estimate of the **exponent** (γ) **associated** with the pressure variation of α . **Nevertheless**, an attempt **has** been made to fit **all the data**

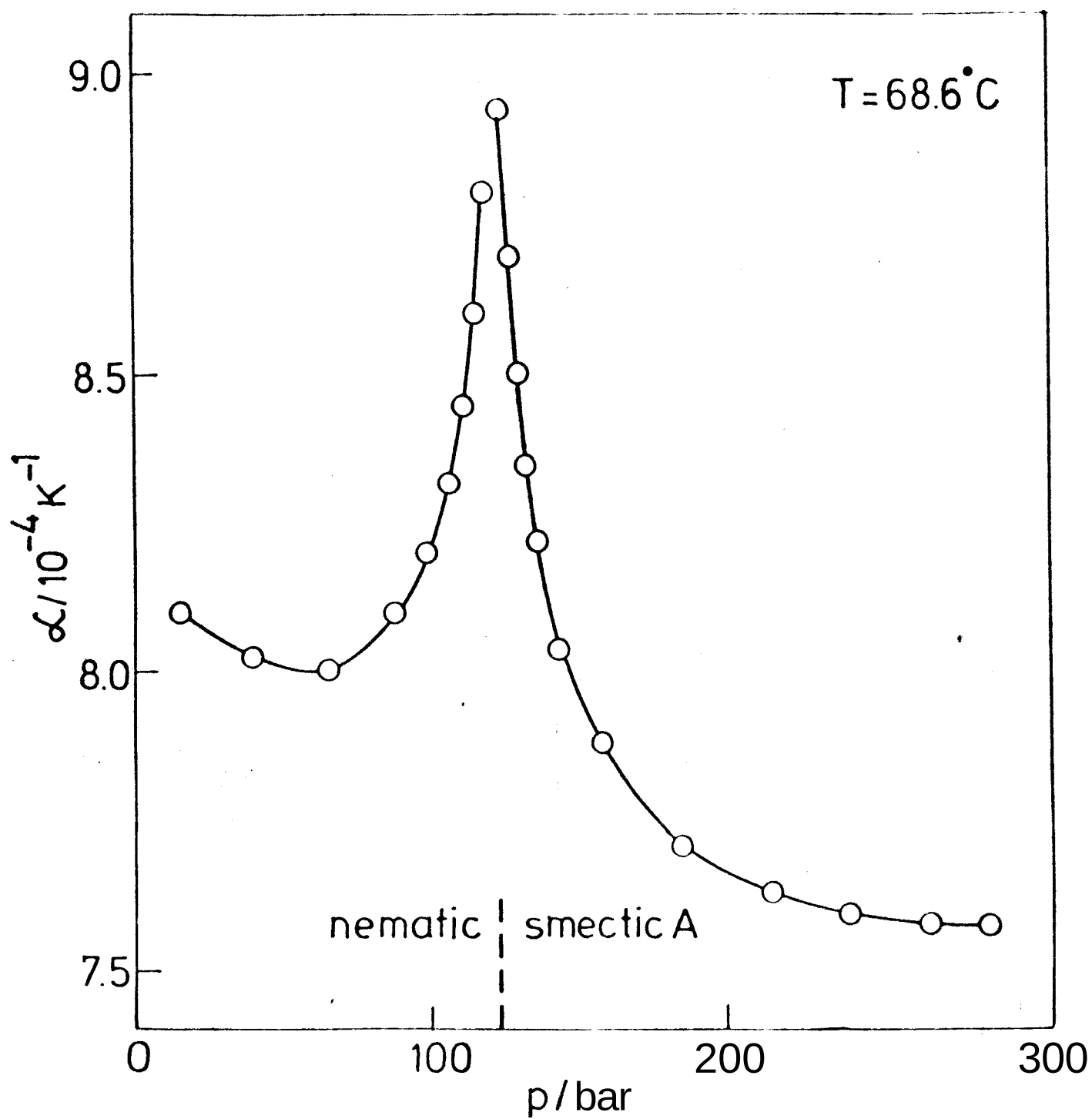


Figure 3: Variation of α with pressure at 68.6°C .

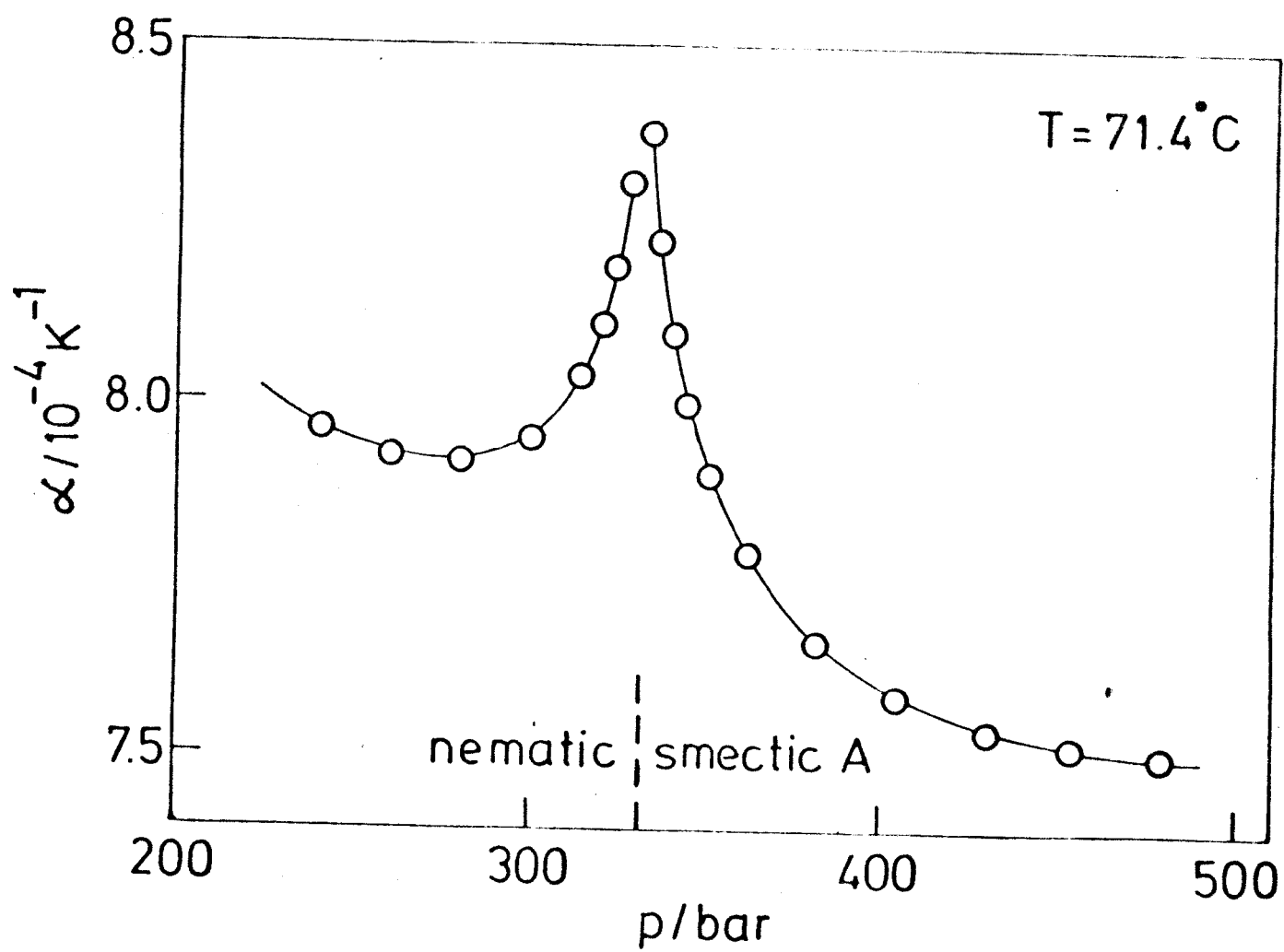


Figure 4: Variation of α with pressure at 71.4°C

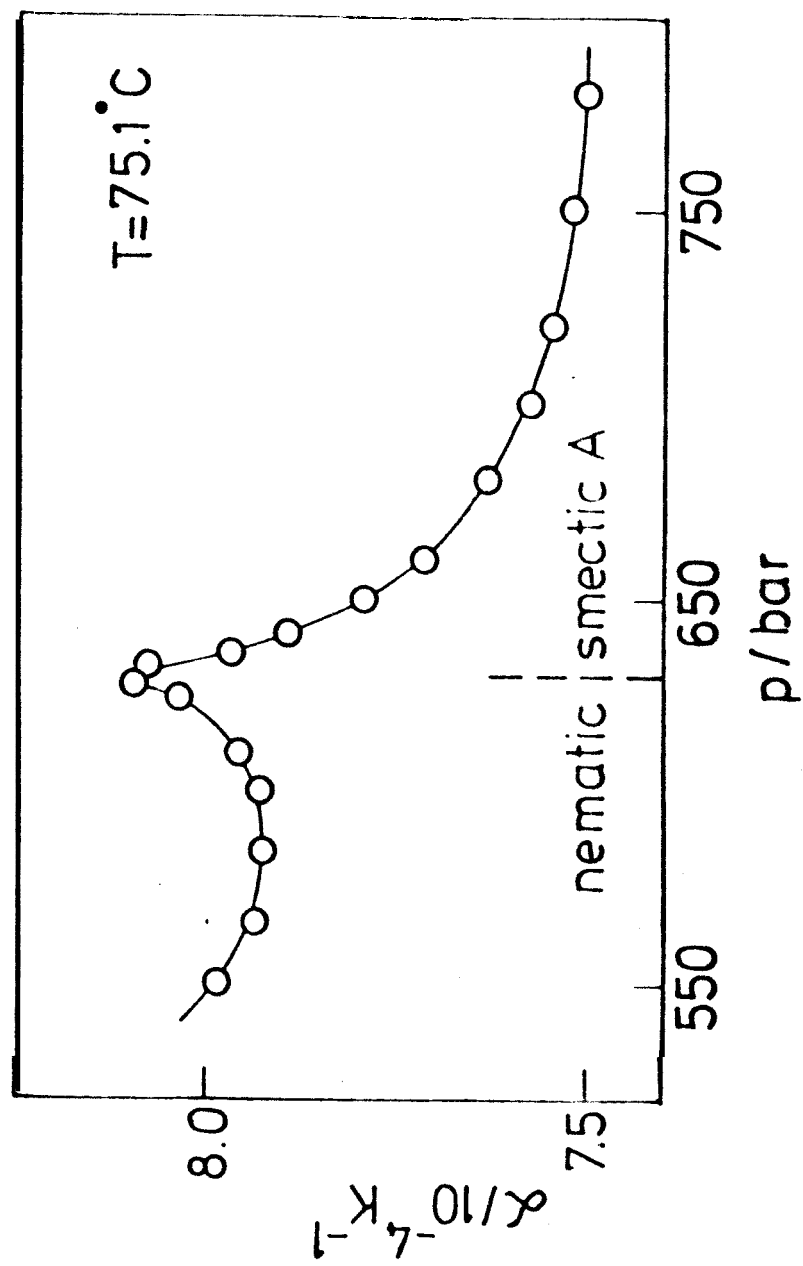


Figure 5: Variation of α with pressure at 75.1°C .

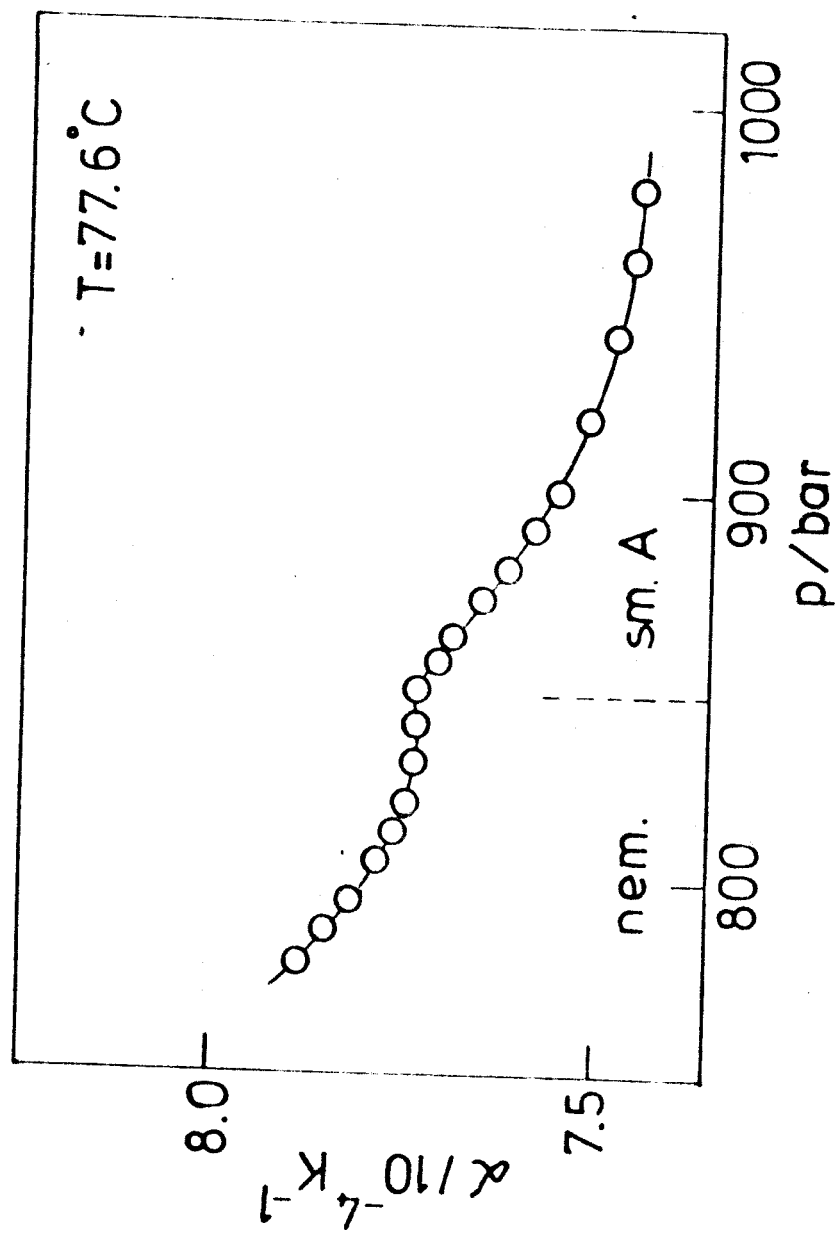


Figure 6: Variation of α with pressure at 77.6°C .

points for $T = 68.6^\circ$ to the equations of the type:

$$\alpha = a_0 + P_r a_1 + A |P_r|^\gamma \quad \text{for } P < P_0$$

and

$$\alpha = a'_0 + P_r a'_1 + A |P_r|^\gamma \quad \text{for } P > P_0$$

where a_0 , a_1 , a'_0 and a'_1 are all adjustable parameters, P_0 is the pressure corresponding to the smectic A - nematic transitions at 68.6° , $P_r = |(P - P_0)/P|$ is the reduced pressure. The base lines with respect to which the expansion coefficients have been evaluated for this fitting consist of two linear parts, one in the nematic and the other in the smectic A phases. The data points at pressures farthest from P_0 have been used to obtain these two linear base line parts which intersect at P_0 , the pressure corresponding to the smectic A - nematic transition. This appears to yield a reasonably good fit over the entire range of pressure investigated and is shown in figure 7. The value of the exponent (γ) for such a fit is 0.22. Attempts were also made to fit the same set of data points in another manner, i.e., by taking the two baseline parts to have a discontinuity (and not intersect) at P_0 . Such a fitting procedure gave a very poor fit which is shown in figure 8, indicating thereby that the smectic A - nematic transition may be

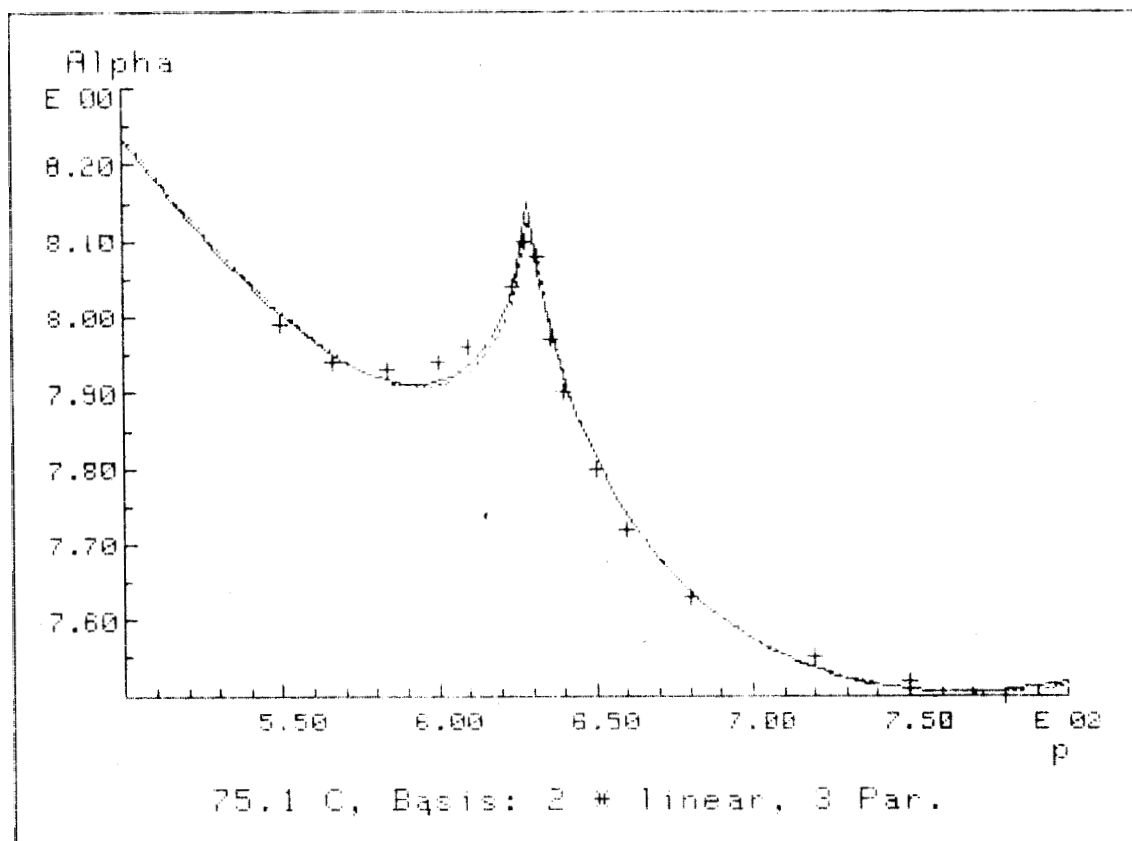


**Figure 7: Computer fit of the experimental data to the equation $\alpha = a_0 + P_x a_1 + A |P_x|^Y$ for $P < P_0$
 $\alpha = a'_0 + P_x a'_1 + A |P_x|^Y$ for $P > P_0$
 taking 2 baselines one in SA and the other in N which intersect at P_0 , the pressure corresponding to AN transition.**

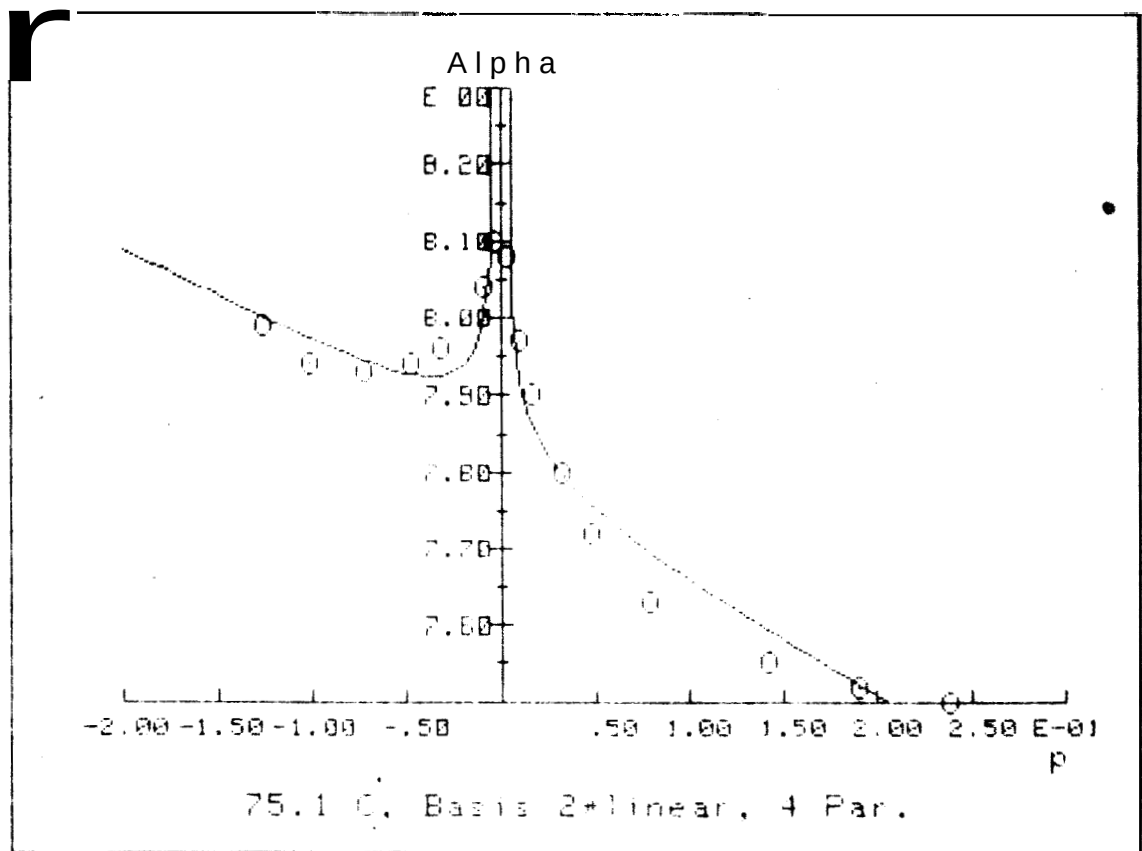


Figure 8f Computer fit of the experimental data with two baselines having a discontinuity at P_0 .

more **aptly** described as a **higher** order transition than a first order one,

Figure 9 **represents** the **variation** of C_p with temperature **along** an **isobar** corresponding to $P = 1$ bar, 500 bar, 1 kbar, 1.5 kbar and 2 kbar respectively obtained for the same compound by Garland et al.^{5,6} It may be mentioned that an integration of the a versus **pressure curve** essentially leads to a term which should be a function of entropy. Thus it is not surprising that the trends of a versus pressure curves with **increasing** temperature resemble generally the ΔC_p versus **temperature curves** with increasing pressure.

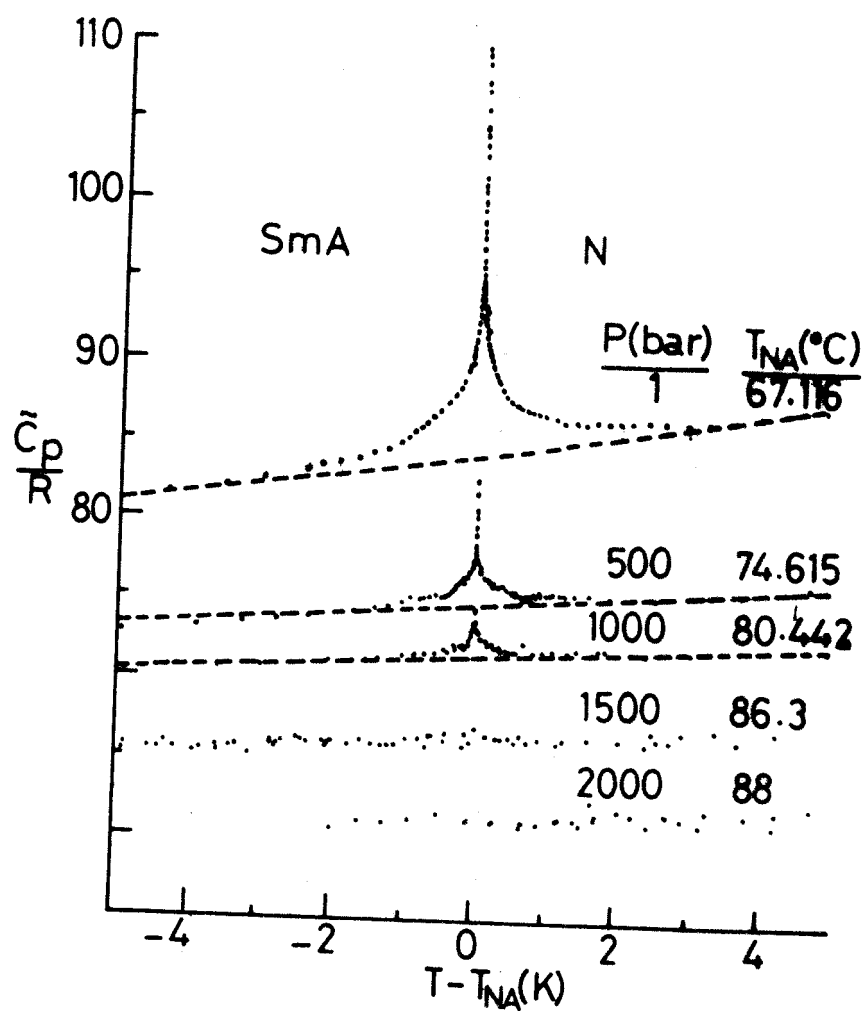


Figure 9: Variation of C_p with temperature (after Garland et al⁶).

Table I

Piezothermal coefficient of 8 OCB as a
function of pressure. Temperature 68.6°C

$P_0 = 122$ bars

Pressure in bars	Piezothermal coeff. $\alpha \times 10^{-4}/K$
290	7.57
270	7.57
242	7.63
186	7.71
158	7.88
144	8.04
136	8.22
133	8.35
130	8.50
127	8.70
124	8.94
117	8.80
116	8.60
112	8.45
106	8.32
100	8.20
88	8.40
66	8.00
40	8.03

Table II

Coefficient of thermal expansion of 8 OCB as
a function of pressure. Temp. = 75.1°C

$P_0 = 630$ bars

P in bars	Coefficient of thermal expansion $\alpha \times 10^{-4}/^{\circ}\text{K}$
780	7.50
750	7.52
720	7.55
680	7.63
660	7.72
650	7.80
640	7.90
636	7.97
632	8.08
628	8.10
624	8.04
610	7.96
600	7.94
584	7.93
566	7.94
550	7.99

Table III

Coefficient of thermal expansion of 8 OCB as a function of pressure. .Temperature = 71.4°C

$$P_0 = 322 \text{ bars}$$

Pressure in bars	Coefficient of thermal expansion $\alpha \times 10^{-4}/K$
480	7.51
454	7.52
430	7.54
405	7.57
382	7.67
362	7.79
351	7.90
344	8.00
340	8.10
336	8.23
333	8.38
328	8.31
324	8.19
320	8.11
314	8.04
300	7.95
280	7.92
260	7.93
240	7.96

Table IV

Coefficient of thermal expansion of 8 OCB as a
function of pressure. Temperature 77.6°C

$$P_0 = 848 \text{ bars}$$

Pressure in bars	Coefficient of thermal expansion $\alpha \times 10^{-4}/K$
980	7.45
960	7.46
940	7.48
920	7.53
900	7.55
890	7.58
880	7.62
872	7.65
863	7.69
856	7.71
849	7.74
840	7.73
830	7.74
820	7.77
810	7.82
800	7.87
790	7.97
780	8.04
770	8.13

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