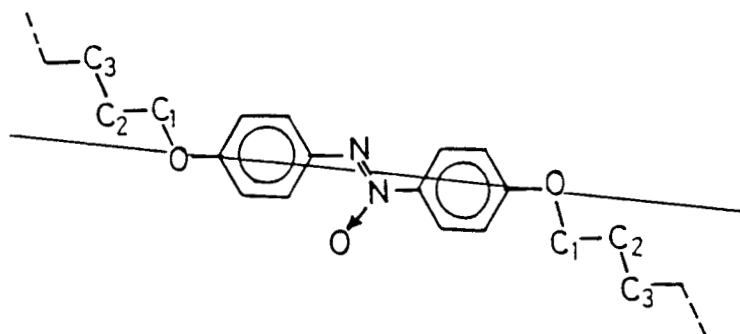


## CHAPTER VII

### PRESSURE STUDIES ON THE NEMATIC-ISOTROPIC TRANSITION IN CYANO CYCLOHEXYL CYCLOHEXANE MATERIALS

#### 7.1 INTRODUCTION

It is well known that the end chains of a molecule play a significant part in the stability of the mesophases exhibited by the compounds. The N-I transition temperature<sup>1</sup> and a number of other properties like order parameter,<sup>2,3</sup> the excess specific heat,<sup>4</sup> transition entropy,<sup>5</sup> splay elastic constant<sup>5</sup> and  $dT/dP$ <sup>6,7</sup> (the rate of variation of transition temperature with pressure at room pressure), etc., show a pronounced alternation as the homologous series is ascended, i.e., as the number of carbon atoms is increased in the end-chain. This is often referred to as the 'odd-even' effect.<sup>8</sup> Qualitatively, the origin of the effect can be understood from a consideration of the molecular structure (Fig.7.1). In the even members of this series the disposition of the end-groups is such as to enhance the molecular anisotropy and hence the molecular order, whereas in the odd-members it has the opposite effect. As the chains get longer their flexibility increases and the odd-even effect becomes less pronounced. A quantitative calculation of the contribution of the end-chains to the order parameter has been made by Marcelja.<sup>9</sup>



**Figure 7.1.** Structure of p,p'-di-n-alkoxyazoxybenzenes. The addition of an even-numbered atom in the preferred trans conformation is along the major molecular axis. This is not the case for an odd-numbered carbon atom (Ref. 9).

The first observation of alternation in  $dT/dP$  for N-I transitions was by Feyz and Kuss,<sup>6</sup> who reported such alternation in five homologous series, all of them being biaromatic thermotropic compounds. Such an alternation was subsequently seen in strongly polar mesogens<sup>7</sup> and thermotropic main-chain polyesters.<sup>10</sup>

Eidenschink et al.<sup>11,12</sup> synthesized a new series of thermotropic liquid crystals called pentyl cyclohexanes wherein the phenyl ring is replaced by cyclohexane ring. Subsequently they synthesized<sup>13</sup> another group of cyclohexanes, viz., alicyclic cyclohexyl cyclohexanes, by replacing both the phenyl rings with the cyclohexane rings. These materials were found to have a negative diamagnetic anisotropy and represent the first thermotropic class of nematic substances with negative diamagnetic anisotropy with the exception of nematic systems of compensated cholesteric liquid crystals.<sup>14</sup> They possess several unique properties such as high photostability, small anisotropy of polarizability (when compared with the aromatic ring systems and conjugated functions groups). The phase behaviour of these compounds is unusual in that the compound with the shortest tail exhibits the greatest smectic stability while the seventh member onwards show only nematic phase. This class of substances also possesses enantiotropic nematic properties and wide nematic phases with relatively high clearing points, in contrast to previous concepts of propor-

tionality between anisotropy and polarizability and clearing point of the liquid crystals. As far as we are aware no systematic pressure study has been carried out on alicyclic cyclohexyl cyclohexane materials although there have been reports on P-V-T<sup>15</sup> and pressure studies<sup>16</sup> on a few phenyl cyclohexanes for which one phenyl ring is replaced by a cyclohexane ring. We shall describe in this chapter our pressure studies on four successive homologous members of the alicyclic cyclohexyl cyclohexane series. Our studies are restricted only to the behaviour of N-I transitions of the four compounds up to a pressure of about 600 bars.

## 7.2 MATERIALS

The materials chosen for our pressure study are n=2,3,4 and 5 members of the homologous series - the trans, the trans-4-alkyl-4'-cyanocyclohexyl cyclohexane (CCH<sub>n</sub>).<sup>13</sup>

The chemical structure of these compounds is shown in the Fig. 7.2 and the transition temperatures are listed in Table 7.1. These compounds were purchased from Merck and used without further purification. The transition temperatures determined by optical microscopy (Table 7.1) are in good agreement with the transition temperatures reported earlier and hence indicates the purity of the materials. All the four homologues exhibit nematic phases. CCH<sub>2</sub> and CCH<sub>4</sub>

Chemical structure of the cyclohexane materials used

the trans , trans - 4-alkyl-4'-cyanocyclohexylcyclohexane (CCH<sub>n</sub>)

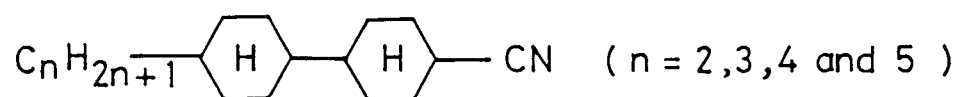


Figure 7.2

TABLE 7.1

Transition temperatures (in °C) of cyclohexane materials

Compound	K	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	N	I
CCH <sub>2</sub>	23			46	47.5	
CCH <sub>3</sub>	58		(42.6)	(55.4)	80.5	
CCH <sub>4</sub>	28			54	79	
CCH <sub>5</sub>	62		(39.8)	(52)	86.4	

( ) denotes that the transitions are monotropic.

S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> are smectic phases. S<sub>3</sub> has been classified as smectic B<sup>17</sup> while S<sub>1</sub> and S<sub>2</sub> are yet to be classified.

exhibit one smectic phase whereas  $CCH_3$  and  $CCH_5$  exhibit three and 2 smectic phases respectively. Of the various smectic phases exhibited by these compounds, only  $S_3$  (high temperature smectic phase) phase of  $CCH_3$  and  $CCH_5$  has been characterised by Brownsey and Leadbetter<sup>17</sup> by the Xray diffraction studies. They identified the  $S_3$  phase of  $CCH_3$  and  $CCH_5$  as bilayer smectic B phase.

### 7.3 PRESSURE STUDIES

An optical high pressure cell was used for the experiments. A brief description of the cell as well as the technique used to determine the transition temperatures have already been given in chapter II and will not be repeated here. Pressure was measured using a Heise gauge to an accuracy of  $\pm 1.5$  bar while the temperature was measured with a precision of  $\pm 100$  mK. About 6 mg of the sample was mounted in the pressure cell. Applying a known pressure, the sample was heated and cooled at a very slow rate of  $0.2^\circ\text{C}/\text{min}$  and the transitions were recorded. The transition temperatures were determined as explained in Chapter II. The pressure was varied in steps of  $-60$  bars and at each pressure the N-I transition temperature was determined. Data were collected in this manner up to a pressure of  $-600$  bars. A least square fit of the data (for the N-I transition) was carried out using a computer (HP 86B). Such a fit yielded  $(dT/dP)$  and N-I transition temperature ( $T_{N-I}$ ) extrapolated to room pressure. The

precision in the determination of  $(dT/dP)$  in our pressure set up is found to be  $\pm 0.2^\circ\text{C/kbar}$ .

The values of  $dT/dP$  obtained for the four compounds are shown in Table 7.2. The P-T diagrams of these materials are shown in Figures 7.3-7.6. The open circles represent the data points and the solid lines represent the computer fit of the data drawn using the constants from the table 7.2. The goodness of the fit is evident from the P-T diagrams. Figure 7.7(a) shows the plot of  $(dT/dP)$  vs.  $n$  (the number of carbon atoms in the end chain) and Fig.7.7(b) shows the plot of (N-I) transition temperature versus 'n'. It is clearly seen from these figures that  $(dT/dP)_{N-I}$  shows an odd-even alternation with  $n$  similar to that exhibited by  $T_{N-I}$ . The alternation is more pronounced for small  $n$  and then decreases with increasing  $n$  as expected. Similar instances of odd-even alternation of  $(dT/dP)_{N-I}$  have been observed earlier for several homologous series<sup>6</sup> of thermotropic liquid crystals, strongly polar mesogens<sup>7</sup> and main-chain polyesters.<sup>10</sup>

Thus, our studies establish the occurrence of odd-even effect for  $(dT/dP)_{N-I}$  in cyclohexane materials. In the absence of data on volume changes associated with N-I transition for these members of the homologous series (CCH $n$ ) we are unable to compare the  $(dT/dP)_{N-I}$  obtained experimentally with the one calculated from the Clausius-Clapeyron equation. More experiments in this direction should throw light on the thermodynamic behaviour of this new class of thermotropic liquid crystals.



TABLE 72

$(T_{N-I})$  at 1 bar and  $(dT/dP)_{N-I}$  values obtained from the least-square-fit of  $(P, T_{N-I})$  data to the equation of a straight line

Compound	$(dT/dP)_{N-I}$ in °C/kbar	$(T_{N-I})$ at 1 bar in °C
CCH <sub>2</sub>	35.7	47.1
CCH <sub>3</sub>	53.4	80.7
CCH <sub>4</sub>	45.8	79.1
CCH <sub>5</sub>	49.6	86.4



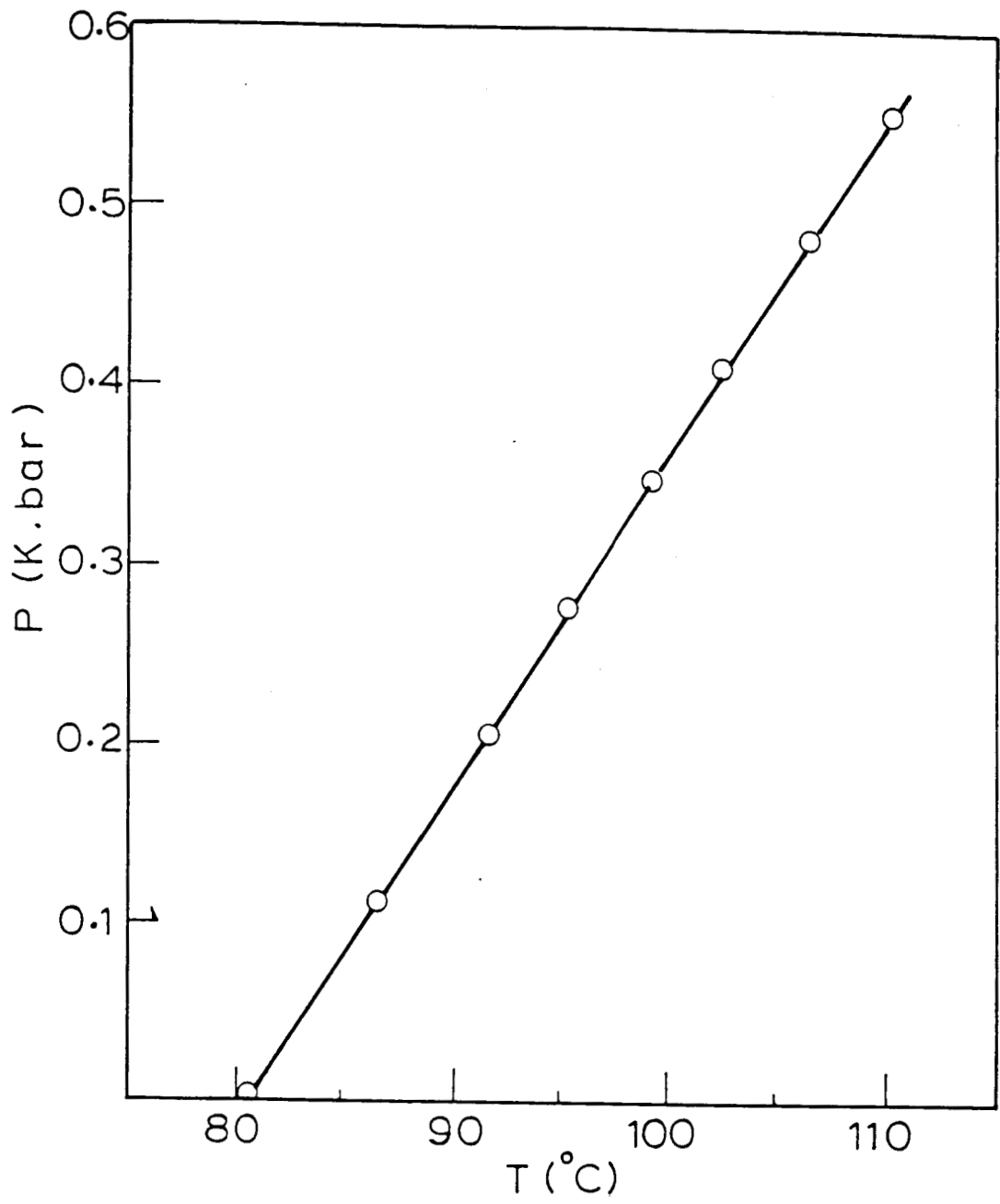


Figure 7.4

Pressure vs.  $T_{N-I}$  plot for  $CCH_3$ . (Also see legend of Fig. 7.3).

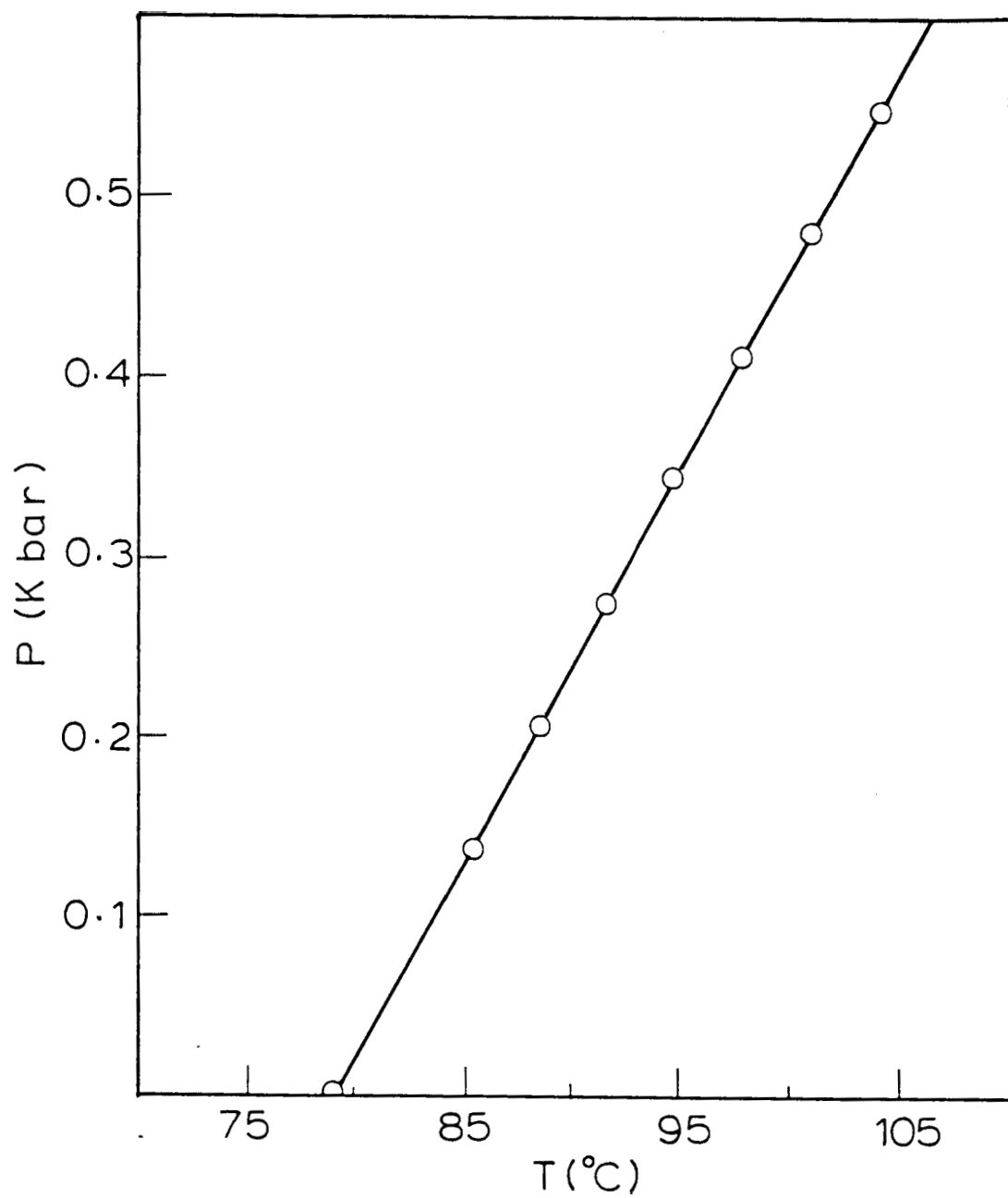


Figure 7.5

Pressure vs.  $T_{N-I}$  plot for  $CCH_4$ .  
(Also see Figure legend of 7.3)

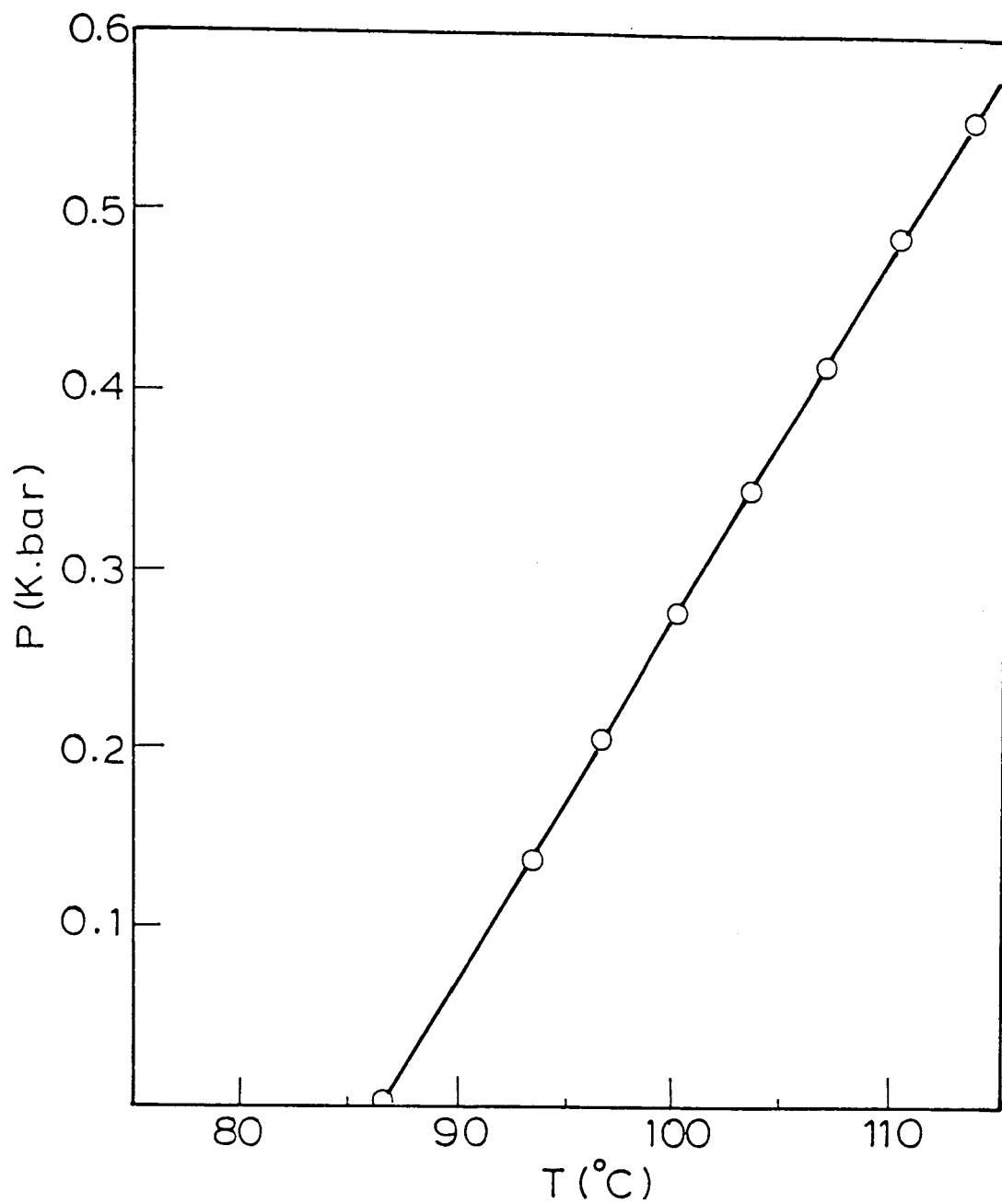


Figure 7.6

Pressure vs.  $T_{N-I}$  plot for  $CCH_5$ . (also see figure legend of 7.3)

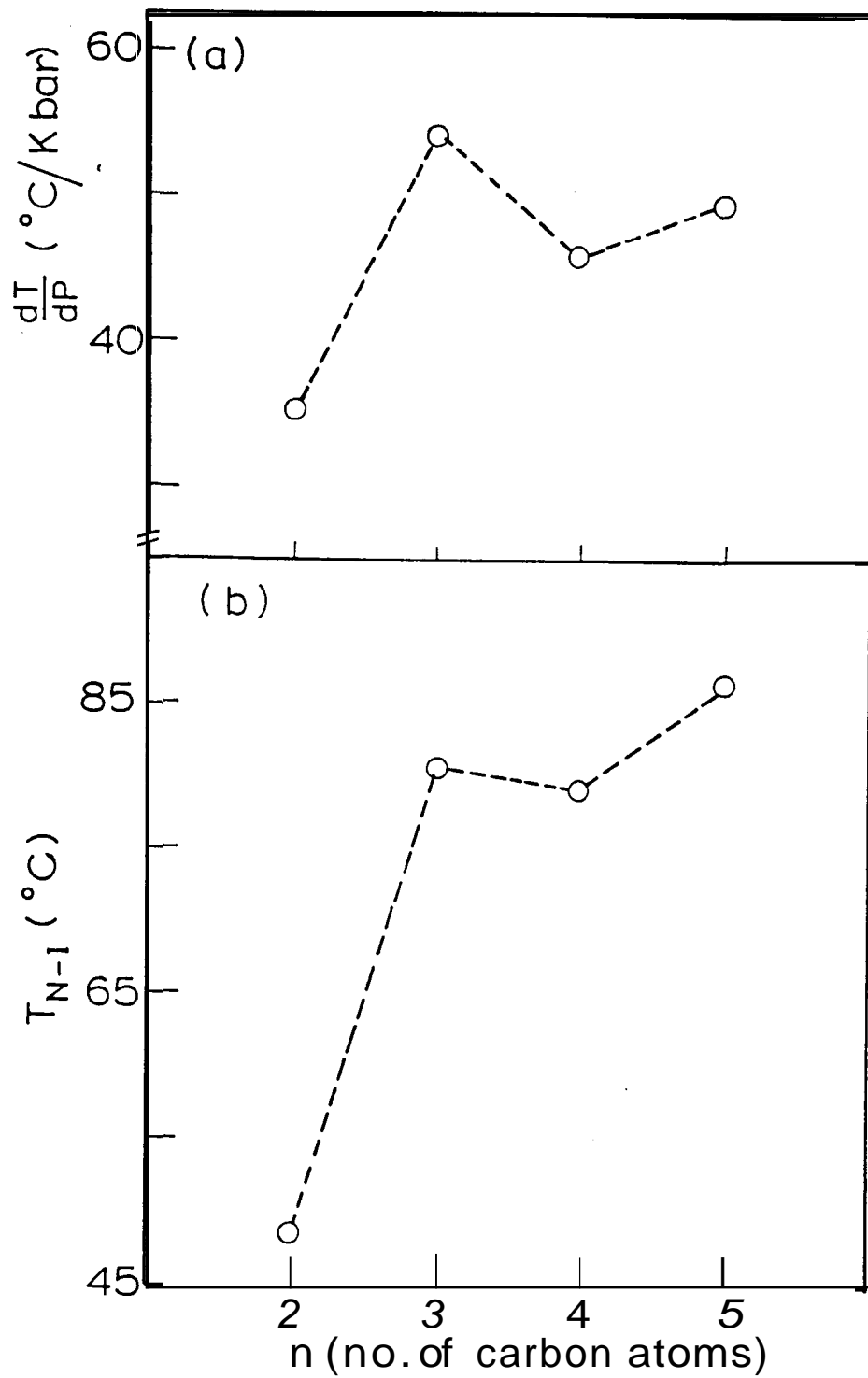


Figure 7.7

(a)  $(dT/dP)_{N-I}$  vs.  $n$  and (b)  $T_{N-I}$  vs.  $n$  plots for  $n = 2$  to 5 members of  $CCH_n$  series.

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