### <u>Chanter – III</u>

### HIGH PRESSURES STUDIES ON 4, 4 '-DI-N-ALKOCYAZOXYBENZENES

#### 1. Introduction:

Para azoxyanisole (PAA) and its higher homologues of the 4, 4 '-di-nalkoxyazoxybenezene series are perhaps the most widely studied of all the liquid crystalline materials. A variety of experimental techniques like calorimetry, (1) dielectric, (2) magnetic susceptibility, (3) volumetric (3,4) and infrared spectroscopy, (5) etc. have been employed to investigate the successive homologues of this series, in order to understand the effect of increasing chain length on the various physical properties. A number of high pressure studies have also been conducted, but virtually all of the them on PAA(6) only, although, there have been a few studies on PAP(7,8) the second homologue, and on 4, 4 '-di-n-heptyloxy-azoxybenzene, (9,10) the seventh member. We have carried out a systematic investigation of the effect of high pressure on the phase transitions in the first six homologues (C1 – C6) of this series. The results of these investigations are presented in this chapter.

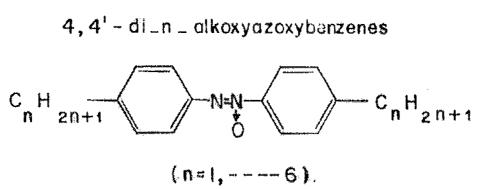
#### 2. <u>Experimental</u>

#### a) Compounds:

Compounds obtained from Eastman Kodak were recrystallised several times from npentane till the clearing points of the purified sample were constant. The molecular formula of these compounds are given in Figure 1. The transition temperatures at atmospheric pressure were determined using a polarizing microscope provided with a Nettler FP-52 hot stage and FP-5 temperatures control. These values are given in table I, and are found to be good agreement with those of Arnold (1). However, there are some difference between our data and those of Arnold for the C5 and C6 homologues. For C5 Arnold reported the S-N transition temperature as 75.5C. But, it has recently been shown by Prasad et al, (11) on the basis of differential scanning calorimetry (DSC), optical and X-ray studies that this compound exhibits a highly ordered but as yet unidentified smectic phase between the solid and the nematic phases. Our measurements are in accord with those of Prasad et al. As regards C6, Arnold found only a nematic phase (the smectic C phase was observed by him only for the C7 derivative and higher homologues). But it

## STRUCTURAL FORMULA

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was shown by Chow and Martire (12) that C6 exhibits a monotropic smectic C phase at atmospheric pressure; the monotropic smectic C-nematic transition temperature found by us agrees well with the values reported by these authors.

### b) Determination of transition temperatures as a function of pressure

The experiments were conducted using the 200 ton hydraulic press described in the previous chapter. Line pressure were measured to an accuracy of 0.2%, although the absolute pressure is reckoned to be accurate only to about 2% as described earlier. The variation in the cell pressures could be achieved to a resolution of 4% using relief values as described in section 1 of chapter II. The phase transition temperatures temperatures were determined using the DTA cell described at any pressure was determined by holding the pressure constant and varying the temperature slowly at about 2-3 per minute. The reproducibility of the transition temperature at any pressure is estimated to be 1.5C. All the DTA runs were taken during heating mode only (except in the case of C6) as there was large supercooling in the cooling mode.

The chemical purity and the stability of the compounds were ascertained, after each set of experiments by redetermining the transition temperatures at atmospheric pressure. Sometimes it was found, especially in cases when the compounds were heated beyond 150C for long periods of time, the N-I transition of the used sample was diminished by about 1 to 2 C. in such cases, the netire data were disregarded. We present here only those data, wherein it has been found that the transition temperatures at atmospheric pressure were identical before and after the experiments.

### 3. <u>Results and Discussions</u>

### A. Phase Diagram

### (a) <u>p-Azoxvanisole(C1)</u>:

The P-T diagram of the first homologue, viz., is given in fig.2 and the corresponding data are presented in table II. There have been eleven determinations of dT/dP for this compound, using different techniques and these have been listed in table III in the chronological order of their investigation along with the techniques used for each experiment. It is seen that of these eleven determinations, seven agree quite well, while the remaining four appear to be rather low. It should be mentioned that in atleast two of these instances, viz., Deloche et al. (13) and Tikhomirova et al,

(14) the values may have been affected by the contamination of the sample by the pressure transmitting media as the authors themselves have indicated. Our value of dT/dP for the S-N and N-I transitions evaluated from the initial slopes are 31.2C/kbar and 47.0 Clkbar respectively. These are in excellent agreement with the seven determinations discussed above (see table III)

## (b) <u>p-Azoxyphenetole (C2):</u>

The P-T diagram of PAP is given in fig. 3 and the data are given in table IV. The N-I transition could not be studied beyond 1 kbar, because at this pressure, the transition temperatures was already 215C approximately, and Teflon starts softening beyond this temperature. The S-N transition phase boundary was however studied up to **3** kbars. The S-N phase boundary in PAP is seen to curve more towards the pressure axis than in the case of PAA. Also, the increase in the nematic range with increase of pressure is roughly of the same order as that for PAA. So far there have been only three pressure studies on PAP. The dT/dP obtained from these investigations are listed in table V. Our values of dT/dP are 36.5 c/kbar are 49.5 c/kbar for the S-N and N-I transitions respectively. It is seen that our values are in good agreement with those obtained by the earlier investigators.

### (c) **<u>Propoxyazoxybenzene and butyoxyazoxybenzene (C3 and C4)</u>**:

The transition temperatures at different pressure for C3 and C4 are given in tables VI and VII respectively while their corresponding phase diagrams are given in figures 4 and 5. it is quite striking that in the case of C3, the increase in the range of the nematic phase with pressure is much less pronounced than in the case of either C1 or C2. the dT/dP for the S-N and N-I transitions are 34.5 C/kbar and 38.7 C/kbar. In the case of C4 the nematic range gets enhanced at a much faster rate with increase of pressure initially but appear to become constant beyond pressures of 2 kbars. The dT/dP for the two transitions for this compound are 24.2 C/kbar and 44.0 Clkbar respectively.

## (d) <u>Pentvloxvazoxvbenzene (C5):</u>

As discussed in the introduction, this compound exhibits a highly ordered and still unidentified smectic phase at atmospheric pressure. (11) We shall call this phase as SmX for convenience. The DSC traces taken with Perkin-Elmer DSC-@ for this

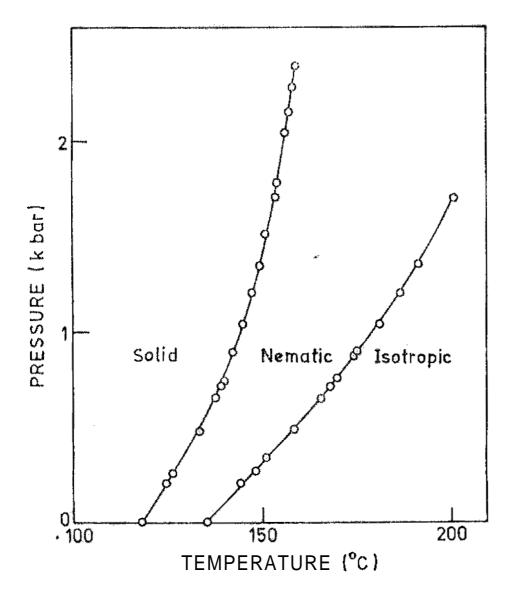


Figure 2: Phase diagram of p-asoxyanisole (PAA)

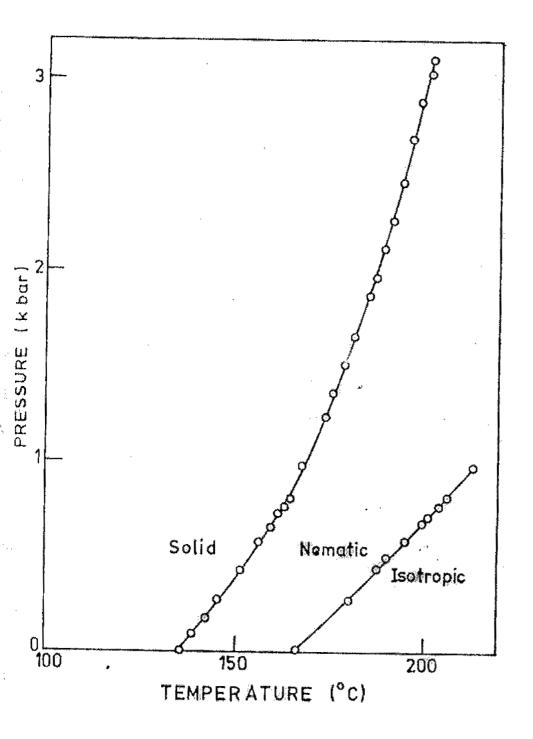


Figure 3: Phase diagram of p-asoxyphenetole (PAP)

compound are shown in fig.6. The heats of transistion (H) calculated from these traces turn out to be of comparable magnitudes for the S-SmX and SmX-N transitions (5.2 and 3.5 kcals/mole respectively.)

Figure 7a shows the raw DTA runs taken at 2.44 kbar. We notice from these runs that the relative heats of transitions of the S-SmX and SmX-N transitions appear to be comparable even at this pressure. At a pressure of 2.5 kbar, a new intermediate phase appears, in between the solid and SmX phases (Figure 7b). The heat H associated with the transition from the solid to this new pressure induced phase appears to be an order of magnitude smaller than that of either the S-SmX or SmX-N transistions. At 6.7 kbar, the SmX phase has completely disappeared and beyond this pressure only the new pressure induced phase exists (figure 7e)

The table VIII gives the transition temperatures at different pressures and Fig.\* shows the phase diagram. It is observer that the phase diagram has two triple points one at 2.45 0.02 kbar, 86 1.5C and the other at 6.7 0.02, 159 1.5 C.

The N-I phase boundary curves towards the pressure axis as is invariably the case with this transition. All the other phase boundaries in this compound curve towards the temperature axis. In this respect, the phase boundaries are reminiscent of those of columnar (or discotic) phases (see chapter VI) and of highly ordered smectics as reported by Spratte and Schneider for bis - (4'-n-alkoxybenylidene)-1, 4phenylinediamine. It therefore seems possible that the new pressure induced phase is another higher order smectic phase, although it can equally be a solid-solid transition. Optical high pressure texture studies are required to confirm the nature of this phase. Taking the slopes of the straight line portions of the P-T diagram at lower pressures, the dT/dP values for the various transitions have been calculated. The values are 7°.1 C/kbar, 9°.2 C/kbar and 32°.5 C/kbar for the S – Sm<sub>x</sub>, Sm<sub>x</sub>-N and N-I transitions  $\Delta$ spectively. Using the Clausius-Clapeyron equation and the experimental dT/dP values. the volume change  $\Delta V$  has been estimated which turn out to be 3.85 cm<sup>3</sup>/mole and 4.54 cm<sup>3</sup>/mole for the S-Sm<sub>X</sub> and Sm<sub>X</sub>-N transitions respectively. The dT/dP and the volume change

V are similar to those obtained for the disc like mesogens (see chapter VI) as well as for the higher order smectics studied by Spratte and Schneider. In view of this

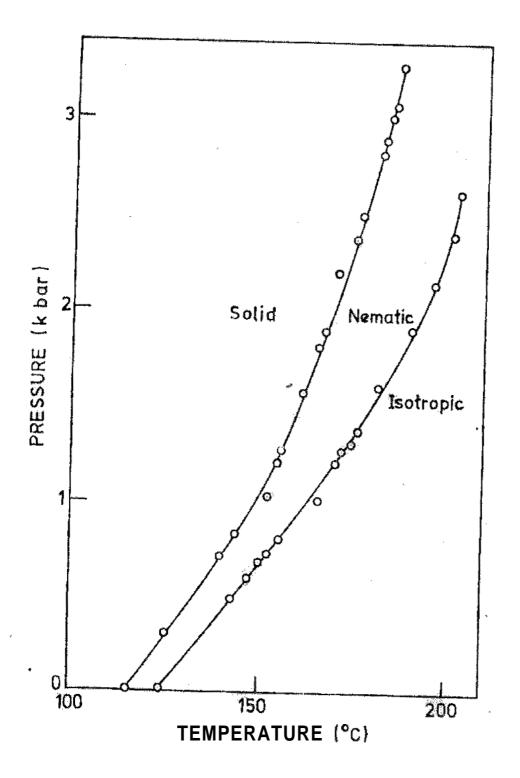


Figure 4: Phase diagram of 4,4'-di-n-propoxyazoxybenzene

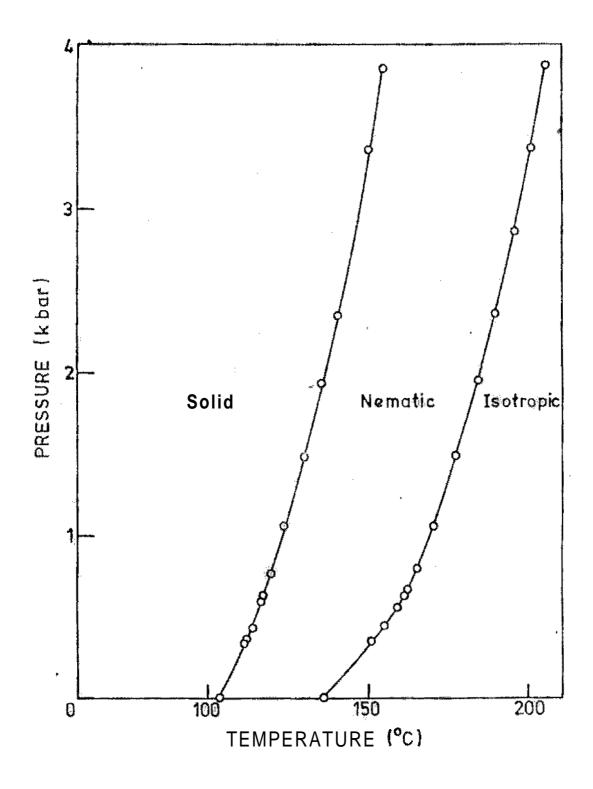


Figure 5: Phase diagram of 4,4'-di-n-butyloryazoxybenzene

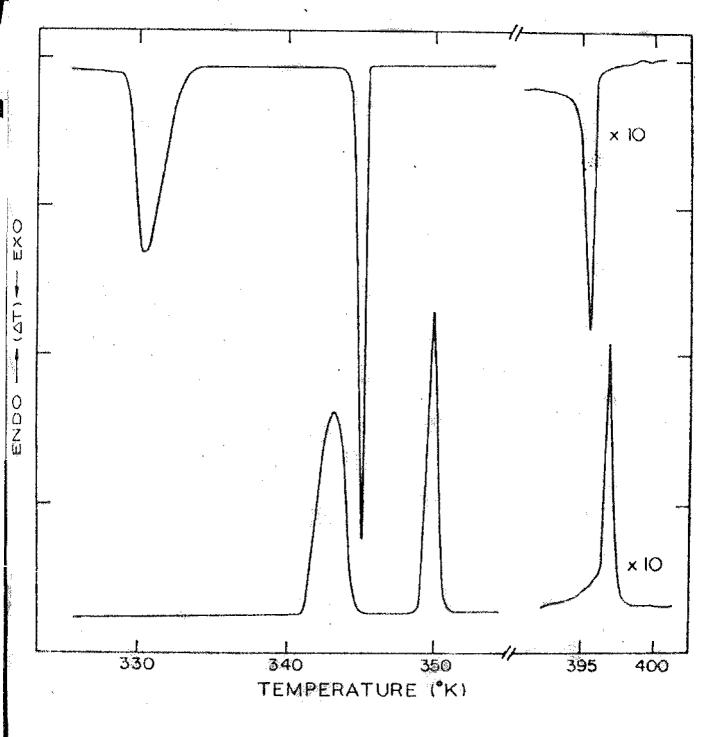
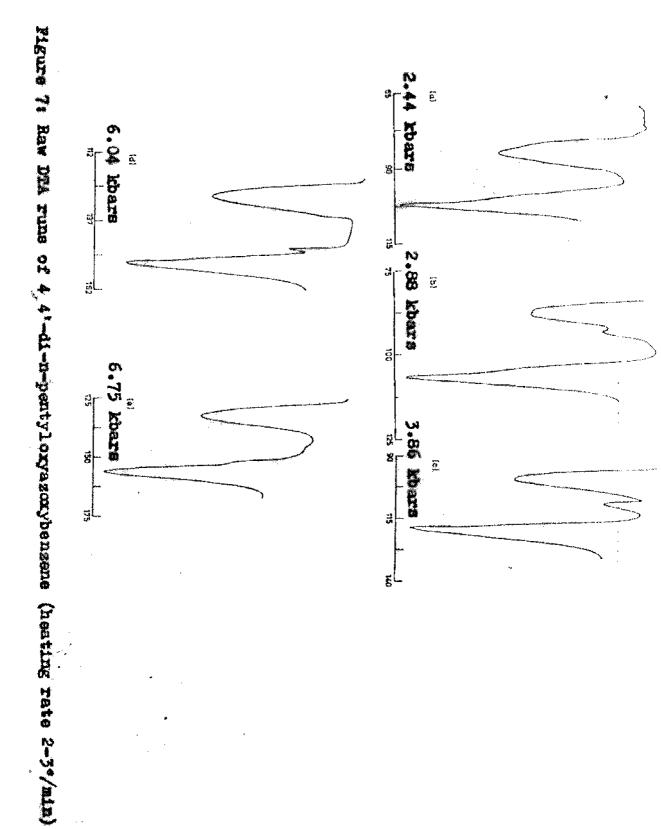
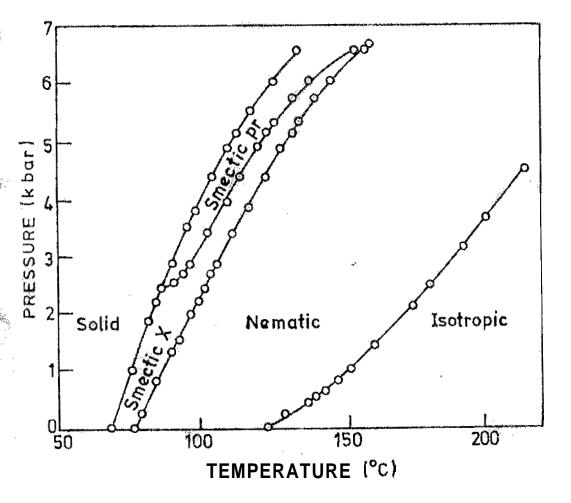
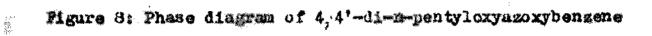


Figure 6: DSC traces of 4,4'-di-m-pentyloxyagoxybensene







V has been estimated which turn out to be 3.85 cm<sup>3</sup>/mole and 4.54 cm<sup>3</sup>imole for the S-Sm<sub>X</sub> and Sm<sub>X</sub>-N transitions respectively. The dT/dP and the volume change

V are similar to those obtained for the disc like **mesogens** (see chapter VI) as well as for the higher order smectics studied by Spratte and Schneider. In view of this evidence it would appear reasonable to infer that the behaviour is distinctly different from that of less ordered smectics or nematics. We shall be illustrating this point further when we present our results of the pressure studies on compounds exhibiting polymorphic smectic phases ( see chapter V).

(e) Hexyloxyazoxybenzene (C6) : As mentioned earlier, this compound shows a monotropic smectic C phase at atmospheric pressure, (whereas C7, 'the next higher homologue of this series exhibits an enantiotropic smectic C phase). Beyond pressures of 1.5 kbar, the monotropic smectic C phase becomes enantiotropic, appearing during the heating mode also, as can be seen directly from the raw DTA traces shown in figures 9a and 9b. The exact pressure at which the monotropicenantiotropic change in character of the transition could not be detected since it was not possible to resolve N-Sm<sub>C</sub> and Sm<sub>C</sub>-solid transitions during the cooling modes for pressures beyond 400 bars. However, a reasonably accurate interpolation of the Sm<sub>C</sub>-N phase boundary gives the S-Sm<sub>C</sub>-N triple point at  $1.25 \pm 0.02$  kbar,  $98.2 \pm 1.5$ C. As far as we are aware of this is the first observation of a monotropic smectic C becoming enantiotropic under pressure, although similar changes have been observed in the case of nematics by Shashidhar. It should also be mentioned that an opposite effect, viz., an enantiotropic to monotropic change in the character of a smectic A-nematic transition under pressure has been observed by Lin et al.

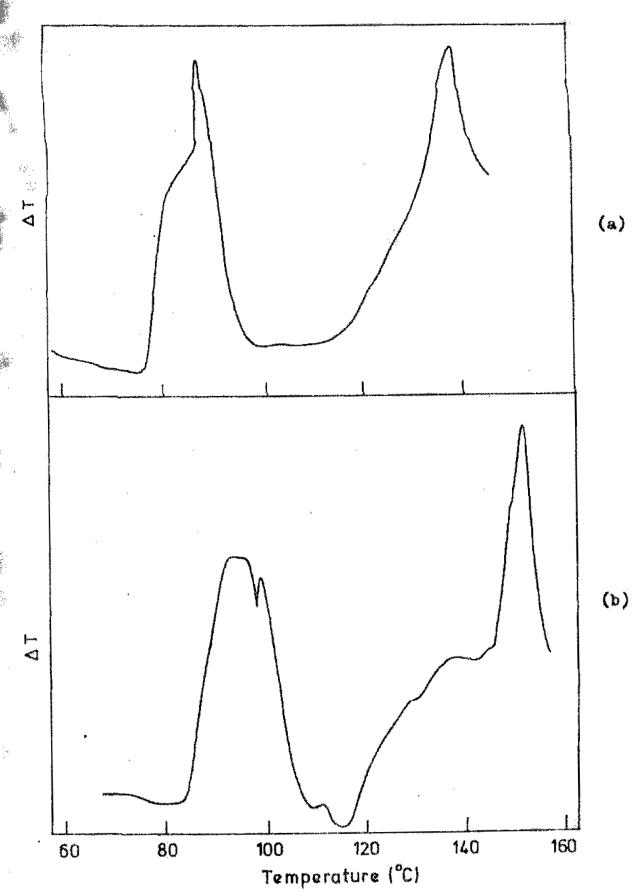


Figure 9: Raw DTA traces of 4 4'-di-n-hexyloxyazoxybenzene showing fa) solid-nematic and nematic-isotropic transitions, (b) the enantiotropic nature of the smectic C-nematia transition beyond 1.5 kbar.

The experimental data showing the transition temperatures at higher pressres are given in table IX and the phase diagram is given in figure 10. The dT/dP values obtained from the phase diagram are 14.4 Clkbar and 36.9 C/kbar for the S-Sm<sub>C</sub> and Sm<sub>C</sub>-N transitions respectively.

#### B. Behaviour of dT/dP for successive homologues

So far we have considered the dT/dP values obtained for individual compounds. We shall now see how dT/dP varies as the chain length is increased. Table X shows the dT/dP for the S-N as well as N-I transitions for the  $C_1 - C_6$  compounds of the series. These values are plotted in figures 11 and 12. It is seen that the dT/dP for the N-I transition shows an alteration with increasing carbon atoms in the alkoxy end chain, similar to the behaviour exhibited by  $T_{NI}$  at atmospheric pressure. It might be recalled here that a similar behaviour has been observed by Fayz and Kuss in all the five homologous series studied by them. As regards the S-N transition it is interesting to note that although dT/dP does not show an alternation, it does show a variation similar to the variation of  $T_{Sol-Nem}$  transition as the chain length is increased. This behaviour is in contrast with the behaviour observed in nCB ( chapter IV) wherein it is observed that dT/dP for S-N is almost the same, although the transition temperatures  $T_{SN}$  themselves at atmospheric pressure show an alternation. Considering the factor that even the alternation of T<sub>SN</sub> within

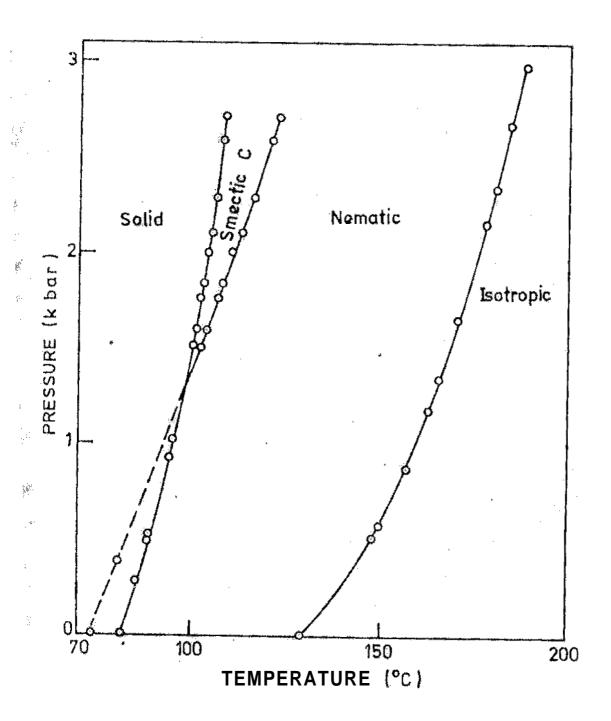


Figure 10: Phase diagram of 4,4'-di-n-hexyloxyasoxybenzene

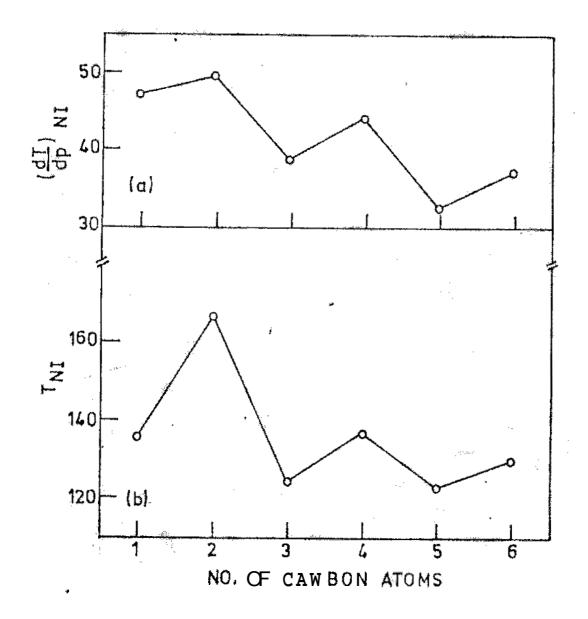
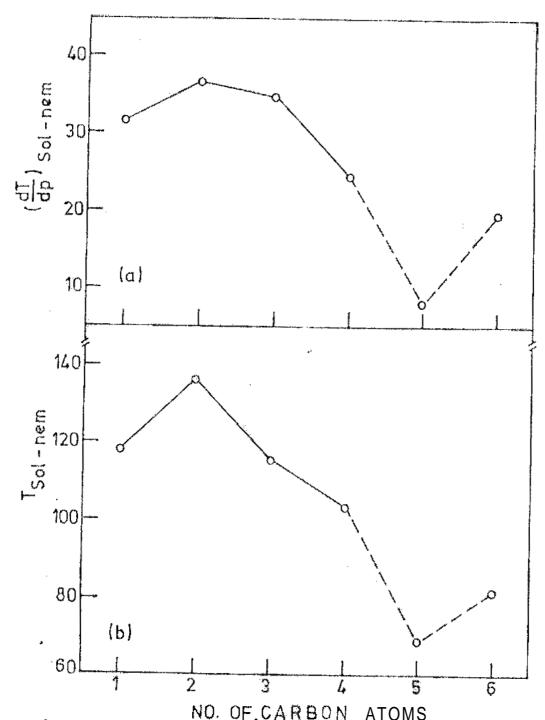
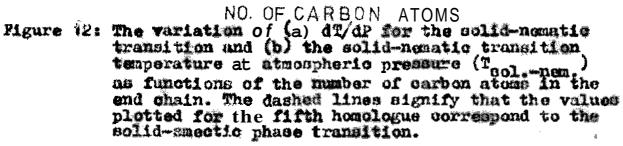


Figure 11: The variation of (a) dT/dP for the nematicisotropic transition and (b) the nematic-isotropic transition temperature at atmospheria pressure  $T_{NI}$  as functions of the number of carbon atoms in the end chain.





A homologous series is not well understood, it is rather difficult to understand this difference in behaviour. However, it may be mentioned that there is an essential difference between molecular arrangements in the alkoxyazoxybenzenes and the cyanobiphenyls; the cyanobiphenyls have a bilayer arrangement in which the polar heads are interdigitated. This bilayer arrangement is attributable to the strong dipole moment ( 5 debye ) associated with the cyano end group of the molecule. On the other hand, the molecules of the alkoxyazoxybenzene form a monolayer arrangement. This difference in molecular packing may conceivably account for the difference in behaviour of the S-N transition under pressure.

We shall now compare the experimentally obtained dT/dP values with those calculated from the Clausius-Clapeyron equation.

(I) <u>Solid-nematic transition</u>

( $\Delta V/V$ ) data are available for only first two members, viz., PAA and PAP. These studies are due to McLaughin et al and Bauer and Bernamont. Taking these values and AH values of Arnold, the dT/dP for the S-N transitions of PAA and PAP turn out to be 32.1 Clkbar and 36.6 Clkbar respectively (see table X).

### (ii) <u>Nematic – isotropic transition</u>

There have been many measurements of  $\Delta$  H. The most accurate data, however, are due to Arnold, obtained by adiabatic calorimetry, wherein, he has separated out the contribution due to pre-transition effects on  $\Delta$  H values. As regards  $\Delta$ V measurements, there have been two studies on by Linsert and the other by de Jeu and Claassen. These data agree with each other within few percent. Taking the mean of these determinations and the accurate  $\Delta$ H values of Arnold, dT/dP values are evaluated, which are also given in table X. The agreement between these values and the experimental values are seem to be extremely good, showing the validity of the Clausius0Clapeyron equation in all the cases studied.

#### C. Variation of Transition temperature with pressure

The variation of the transition temperatures with pressure can be expressed by the relation,

 $T_{\rm P} = T_{\rm O} + AP - BP^2,$ 

Where Tp and  $T_0$  are the transition temperatures at a pressure P and at atmospheric pressure respectively, A and B are empirical constants. A least square fit to each set of data points was carried out using a Hewlett Packard 9821 –A programmable calculator. The constants A and B evaluated in this manner are tabulated in table XI. It is seen that the behaviour of dT/dP is reflected in the magnitude of the constants.

#### **Application of Simon – Glatzel equation**

It was first shown by Feys and Kuss that the variation of both'the melting and clearing points with pressures can be adequately expressed by the equation of Kraut and Kennedy as modified by Simon-Glatzel. The equation used by Feyz and Kuss is

$$\frac{Pm}{a} = \frac{Tm}{To}^{c} - 1$$

where Tm and To are the transition temperatures at pressures Pm and atmospheric pressure respectively and a and c are empirical constants.

A least square fit to the set of experimental data points for each transition temperature point of each compound was carried out by using a PDP-11 computer. The fit was found to be reasonably satisfactory. The constants a and c evaluated in this manner are given in the table XII.

## <u>Table – I</u>

Transition temperatures (in °C) at atmospheric pressure of 4, 4'-di-nalkoxyazoxybenzenes(methoxy to hexyloxy)

Compound	Solid-Nematic (or smectic)	Smectic – Nematic	Nematic - Isotropic
C <sub>1</sub> (PAA)	118.0		135.0
$C_2$ (PAP)	136.0	·	166.0
$C_3$	115.0		124.0
C <sub>4</sub>	103.6		136.2
$C_5$	68.5	76.5	122.6
C <sub>6</sub>	81.3	74.0	129.1

This is a higher order and still unidentified smectic phase discovered very recently (Prasad, Venugopalan and Billiard).

() denotes a monotropic transition.

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## <u>Table – II</u>

Transition temperatures of PAA as a function of pressure

Pressure in kbars	Transition temperatures in C <sup>o</sup>				
r ressure in KDars	Solid – Nematic	Nematic – Isotropic			
0.207	124.0	144.0			
0.265	126.0	148.0			
0.345	129.5	150.5			
0.481	133.0	158.2			
0.655	137.0	165.5			
0.722	139.0	168.0			
0.754	140.0	170.0			
0.882		174.0			
0.899	142.0				
1.040	145.0	181.0			
1.200	147.5	186.5			
1.348	149.5	191.2			
1.514	151.0	196.0			
1.697	153.0	201.0			
1.784	154.0				
2.037	156.0				
2.165	157.0				
2.285	158.0				
2.395	159.0				

## <u>Table – III</u>

## dT/dP in °C/kbar for PAA

SI. No	Investigator	Solid- Nematic	Nematic – Isotropic	Technique Used
1	Hulett	32.0	48.0	Optical transmission
2	Puschin and Grebenschtschikow	25.6	39.5	Volumetric
3	Robberecht	32.0	48.0	Optical transmission
4	Deloche et al	24.5	27.0	NMR
5	McColl and Shih		46.3	NMR
6	Chandrashekharet al	32.0	47.0	DTA
7	Tikhomirova et al	23.2	31.3	DTA
8	Klement and Cohen	31.0	48.0	DTA
9	Baskakov et al		31.4	Volumetric
10	Spratte and Schneider	29.5	50.0	DTA
11	Stishov et al		45.9	Piezometric
12	Present work	31.2	47.0	DTA

# <u>Table – IV</u>

Transition temperatures of PAP as a function of pressure

D	Transition ten	nperatures in °C
Pressure in kbars	Solid – Nematic	Nematic – Isotropic
0.174	142.5	
0.184		168.5
0.209	145.5	
0.269		180.0
0.420	151.5	
0.431		187.5
0.490		190.0
0.569	156.0	
0.583		195.0
0.649	159.0	
0.662		199.5
0.702		201.5
0.720	161.0	
0.750	162.0	204.0
0.799	164.0	
0.808		206.8
0.969	167.0	213.0
1.281	173.5	
1.346	175.0	
1.496	178.5	
1.638	181.0	
1.860	185.0	

1.955	187.0
2.110	189.0
2.264	191.0
2.458	194.0
2.679	196.0
2.865	198.5
3.024	201.0
3.103	202.0

# <u>Table V</u>

## dT/dP in °C/kbar for PAP

SI. No	Investigator	Solid- Nematic	Nematic- Isotropic	Technique Used
1	Hulett	37.0	47.6	Optical transmission
2	Chandrashekhar et al	36.0	46.0	DTA
3	Spratte and Schneider	36.0	49.0	DTA
4	Present work	36.5	49.5	DTA

## <u>Table VI</u>

Transition temperatures of propoxyazoxybenzene as a function of pressure

Duccesso in the sec	Transition temperatures in <sup>o</sup> C			
Pressure in kbars	Solid – Nematic	Nematic – Isotropic		
0.296	126.0			
0.481		143.0		
0.587		147.0		
0.680		150.0		
0.706	140.0			
0.719		152.7		
0.796		155.5		
0.830	143.5			
1.002		165.5		
1.021	152.0			
1.196	154.0	==		
1.205		170.0		
1.264	156.0	171.5		
1.302		174.0		
1.365		176.0		
1.558	161.0			
1.593		182.0		
1.798	165.0			
1.876	167.0			
1.894		190.0		
2.132		196.0		

171.0	
175.0	
	200.5
176.0	
	202.0
181.5	
184.0	
185.0	
186.5	
	175.0  176.0  181.5 184.0 185.0

# <u>Table VII</u>

Transition temperatures of butyloxyazoxybenzene as a function of pressure

D	Transition temperatures in $^{\circ}\mathbf{C}$			
Pressure in kbars	Solid – Nematic	Nematic – Isotropic		
0.331	111.5	-		
0.344		151.0		
0.361	112.3	•		
0.433	114.0			
0.446		155.0		
0.561		159.0		
0.587	116.5			
0.640	117.5			
0.671		162.0		
0.772	119.5			
0.799		165.0		
1.063	123.5	170.0		
1.485	130.0	177.0		
1.933	135.0	<b></b>		
1.955	<b></b>	184.0		
2.353	140.0			
2.370		189.0		
2.847	145.0			
2.874		195.0		
3.350	149.5			
3.368		200.0		
3.853	154.0			
3.880		204.5		

# <u>Table VIII</u>

Transition temperatures of pentyloxyazoxybenzene as a function of pressure

Solid – S	Smectic X	Pressure induc	ed – Smectic X	Smectic X	- Nematic	Nematic -	-Isotropic
Pressure in kbars	Temp. in °C	Pressure in kbars	Temp. in ⁰C	Pressure in kbars	Temp. in ⁰C	Pressure in kbars	Temp. in <sup>o</sup> C
1.037	75.5			0.275	79.0	0.242	129.0
1.873	81.5			0.843	84.0	0.446	137.0
2.200	84.0			1.346	89.0	0.551	139.5
2.441	86.0			1.554	91.0	0.658	143.0
				2.008	96.0	0.861	147.5
				2.220	99.0	1.037	152.0
2.906	90.0	2.550	90.0	2.441	100.2	1.452	160.5
3.512	95.0	2.706	94.0	2.715	103.0	2.150	174.0
3.803	97.5	2.874	96.0	2.882	105.0	2.500	180.0
4.365	103.5	3.412	102.0	3.412	110.5	3.165	192.0
4.869	109.0	3.953	109.0	3.862	116.5	3.686	200.0
5.133	112.5	4.365	113.5	4.374	122.5	4.515	214.0
6.021	125.0	4.869	119.5	4.869	128.0		
6.564	133.5	5.142	122.5	5.142	131.5		
		5.734	132.0	5.319	134.0		
		6.038	137.0	5.734	139.5		
		6.577	153.5	6.052	145.0		
		0.696	159.0	6.577 .	157.0		
				6.696	159.0		

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# <u>Table IX</u>

Transition temperature of hexyloxyazoxybenzene as a function of pressure

Solid – nematic (or smectic C)		Smectic C-nematic		Nematic-iosotropic	
Pressure in	Temperatures	Pressure in	Temperatures	Pressure in	Temperatures
kbars	in C	kbars	in C	kbars	in C
0.278	86.0	0.384	(80.80)	0.516	148.0
0.466	88.5	1.505	102.5	0.580	149.5
0.516	89.0	1.602	103.5	0.873	156.8
0.925	94.0	1.761	106.5	1.168	162.0
1.020	95.0	1.841	108.5	1.345	165.0
1.505	100.0	2.000	110.0	1.655	170.2
1.602	101.0	2.097	112.5	2.147	177.5
1.761	102.0	2.290	115.5	2.335	180.2
1.841	103.0	2.582	120.5	2.670	184.2
2.000	104.0	2.706	122.5	2.971	188.0
2.097	105.0				
2.290	106.0				
2.582	107.2				
2.706	108.0				

## <u>Table X</u>

# dT/dP values for the successive homologues in C/kbar

		Ν	Nematic – isotropic		
Compound	Solid – nematic	Experimental	Calculated from Clausius -		
		Experimental	<b>Clapeyron equation</b>		
C1	31.2	47.0	48.5		
C2	36.5	49.5	50.5		
C3	34.5	38.7	39.1		
C4	24.2	44.0	43.4		
C5	7.1 (S – SmX)	32.5	. 34.0		
0	9.2 (SmX – N)				
C6	14.4	37.1	35.0		

## <u>Table XI</u>

# Constants A and B for alkoxyazoxybenzenes

Compound	Solid – nematic (or smectic)			Nematic – isotropic		
	Α	В	<b>RMS</b> error	Α	В	<b>RMS</b> error
C1	32.8	4.8	0.75	45.3	4.9	0.57
C2	36.5	5.1	1.15	50.7	4.7	2.20
C3	36.0	4.2	2.86	44.9	5.4	1.16
C4	21.1	2.2	1.12	36.1	5.0	0.34
C5	5.3	-0.7	0.65	28.7	2.0	0.67
C6	15.9	2.2	0.23	34.1	5.0	1.63

# <u>Constants of the Simon eauation for the compounds belonging to</u> <u>alkoxyazoxybenzenes series</u>

Table XII

Compounds	Transition	Cons	<b>RMS</b> value	
compounds		a	b	
C1	S-N	487.79	17.57	0.00751
	N-I	- 1.78	- 0.552	0.0171
C2	S-N	864.86	10.196	0.0160
C2	N-I	- 1172.63	- 12.099	0.0142
C3	S-N	940.60	8.893	0.00658
CS	N-I	1672.74	5.005	- 0.0194
C4	S-N	1390.22	10.66	- 0.01904
64	N-I	526.81	13.85	0.00805
	S-SmX	- 1.228	- 4.465	0.01006
C5	SmX-N	- 2.152	- 1.835	0.00383
	N-I	2324.60	5.269	0.00331
	S-SA	1203.68	15.88	0.0188
C6	SA-N	8362.94	2.15	- 0.0127
	N-I	758.15	11.75	- 0.00915

### **References:**

- 1. H. Arnold, Z.Phys. CHem. (Lei pzig), <u>226</u>, 146 (1964)
- 2. P. Rondelez and A. Mircea-ROussel, Mol. Cryst. Liquid Cryst., 28, 173 (1973)
- 3. W.H. de Jeu, and W.A.P. Claassen, J. Chem. Phys., <u>68</u>, 102 (1978)
- 4. F. Linsert, Master Thesis, University of Halle (1945)
- 5. S.N.Prasad and S. Venugopalan, J. Chem. Phys., 71 (12), 5293 (1979)
- 6. See for example Review on High Pressure Studies on Liquid Crystals, in Advances in Liquid Crystals, by S.Chandrasekhar and R.Shashidhar, 4, <u>83</u> (1979)
- 7. G.A.Hulett, Z.Phys. Chem., 28,629 (1899)
- 8. S. Chandrasekhar, S.Ramaseshan, A.S.Reshamwala, B.K.SAdashiva, R.Shashidhar and V.Surendranath, Proc. Int. Liquid Crystals Conf., Bangalore, Praman Suppl. <u>1</u> (1973)
- 9. R. Shashidhar and S. Chandrasekhar, J. Phys. (Paris), 36, C1-49 (1975).
- 10. P.H.Keyes, H.T.Weston, W.J.Lin and W.B.Daniels, J.Chem. Phys., 63, 5006 (1975)
- S.N.Prasad, S.Venugopalan and J.Billard, Mol. Cryst. Liquid Cryst. Lett., 49,271 (1979)
- 12. L.C.Chow and D.E.Martire, J.Phys. Chem., 73, 1127 (1969)
- 13. B.Deloche, BCabane and D. Jerome, Mol Cryst. Liquid Cryst., <u>15</u>, 197 (1971)
- N.A.Tikhomirova, L.K.Vistin and V.N.Nosov, Sov. Phys. Crystallogr. (Eng. transl.), <u>17</u>, 878 (1973); N.A.Tikhomirova and A.V.Ginzberg, Kristallografiya, <u>22</u>, 155 (1977)
- 15. N.A.Puschin and I.W.Grebenschtschikow, Z.Phys. Chem., 57,270 (1926)
- 16. J. Robberecht, Bull. Sov. Chim.Belg., 47, 597 (1938)
- 17. J.R.McColl and C.S.Shih, Phys. Rev. Lett., 29, 85 (1972)
- 18. W.Klement and L.H.Cohen, Mol. Cryst. Liquid Cryst., 27,359 (1979)
- V. Ya Baskakov, V.K.Semenchenko and N.A.Nedostup, Sov. Phys. Crystallogr., <u>19</u>, 112 (1974); V. Ya. Basakakov, V.K.Semenchenko and V.M.Byankin, Sov. Phys. JETP, 39,383 (1974)
- 20. W. Spratte and G.M.Schneider, Ber.Bunsenges. Phys. Chem., 80, 886 (1976)
- 21. S.M.Stishov, V.A.Ivanov and V.N.Kachinskii, JETP Lett. (Eng. transl.), 24, 297 (1977)
- 22. W. Spratte and G.M.Schneider, Mol. Cryst. Liq. Cryst., 51, 101 (1979)
- 23. R. Shashidhar, Mol. Cryst. Liq. Cryst., <u>43</u>, 71 (1977)
- 24. W.J.Lin, P.H.Keyes and W.B.Daniels, Phys. Lett., <u>A49</u>, 453 (1974)
- 25. P.E.Cladis, R.K.Bogardues, W.B.Daniels and G.N.Taylor, Phys. Rev. Lett., <u>39</u>, 720 (1977)
- 26. P.E.Cladis, R.K.Bogardues and D.Aadsen, Phys. Rev., A18, 2292 (1978)
- 27. M. Feyz and E.Kuss, Ber. Bunsenges. Phys. Chem., 78, 834 (1974)
- 28. E. McLaughlin, A.Shakespeare and A.R.Ubbelohde, Trans. Faraday Soc., 60, 25 (1964)
- 29. E. Bauer and J. Bernamont, J.Phys. Radium, 7, 19 (1936)
- 30. E.A.Kraut and G.C.Kennedy, Phys. Rev. Lett., 16,608 (1960)
- 31. F.E.Simon and G.Glatzel, Z.Anorg. Allg. Chem., 178,309 (1929)