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## Liquid Crystals

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### Phase Transition and Structural Investigations in 50.5, 50.6 and 50.7

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## Phase transition and structural investigations in 5O.5, 5O.6 and 5O.7

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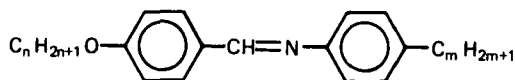
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(Received 4 January; 1988; accepted 25 May 1988)

We report X-ray diffraction, density, ultrasonic velocity and refractive index studies in the *N*(*p*-*n*-pentyloxy benzylidene) *p*-*n*-alkylaniline compounds, viz. 5O.5, 5O.6 and 5O.7. The nematic-smectic A (NA) transition is found to be weak first order in 5O.6 while it is second order in 5O.5 and 5O.7. The salient features observed are cybotactic clusters in the nematic phase in all the compounds, molecular tilt which was inferred due to the end alkyl chains tilt causing orientational disorder (smaller orientational order parameters 's' than expected) in smectic A phase, smectic F phase and large tilt angle variation in smectic C phase in a small temperature range in 5O.5. The observed results are discussed in the light of available data in other *nO.m* compounds.

### 1. Introduction

The investigation of a physical parameter in a homologous series of compounds is particularly useful in order to understand the relation between the molecular structure and the polymorphic properties of liquid crystals. One interesting series in the *N*(*p*-*n*-alkoxy benzylidene) *p*-*n*-alkylanilines, popularly known as *nO.m* series [1-3], is *N*(*p*-*n*-pentyloxy benzylidene) *p*-*n*-alkylanilines. The *nO.m* compounds have the molecular formula



when *n* and *m* represent the number of carbon atoms in alkoxy and alkyl chains respectively. The lower homologue 5O.2 shows the nematic and the smectic G phases, while the higher homologues show the nematic, smectic A and smectic B phases (5O.10 [4] and 5O.12 [5]). The intermediate compound 5O.6 exhibits the phase sequence NACBFG which has the most extensive polymorphism of an individual compound reported [3] so far in *nO.m* series. In view of this and the interesting results observed in the other homologues, viz. 5O.8, 5O.10 and 5O.12, we carried out the experimental investigations by various techniques leading to the information regarding structural properties and other characteristics of the mesophases, and the order of the phase transitions. In the present work the structural properties and the order of the phase transitions as obtained by thermal microscopy. X-ray diffraction, density, ultrasonic velocity and refractive index studies are presented.

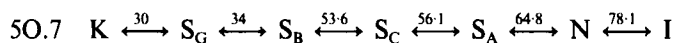
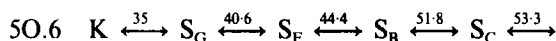
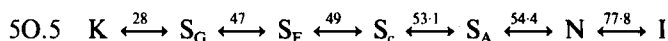
## 2. Experimental details

The compounds 5O.5, 5O.6 and 5O.7 were prepared following a method described elsewhere [6]. The thermal microscopy was carried out using a Hertel and Reuss, Superpan II Polarizing microscope with an attached heating block. The X-ray diffraction experiments were carried out using Ni filtered  $\text{CuK}\alpha$  radiation and a Laue camera. Samples were contained in Lindemann glass capillaries of 0.5–1 mm diameter held perpendicular to the incident X-ray beam. Aligned samples were obtained by slowly recycling the sample through the nematic–smectic A transition in the presence of magnetic field of strength 1.6 kG. The temperature stability in these experiments was  $\pm 0.25^\circ\text{C}$ . The density and ultrasonic velocity experimental details are reported earlier [6]. The ultrasonic velocity was measured by an interferometric technique, frequency 2 MHz, using the ultrasonic interferometer UF 101, N.P.L., India. The cell was modified to make the reflector and transducer more parallel with a minimum spacing of 0.4 cm.

## 3. Results and discussion

### 3.1. Thermal microscopy

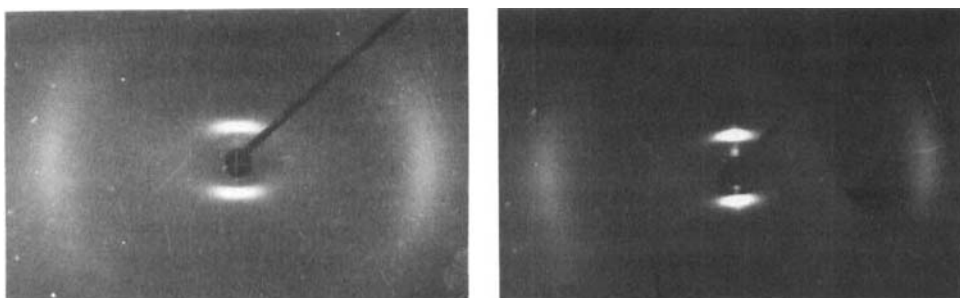
The phase sequence and the transition temperatures ( $^\circ\text{C}$ ) of 5O.5, 5O.6 and 5O.7 observed from thermal microscopy studies are



Smith and Gardlund [1] suggested that the unidentified phase between  $\text{S}_C$  and  $\text{S}_G$  may be  $\text{S}_F$  in 5O.5. However, Wiegeleben *et al.* [2] reported the unidentified phase as smectic B. We observed a chequered board fan texture for about  $2^\circ\text{C}$  below  $\text{S}_C$  in this unidentified phase. This texture is reminiscent of the  $\text{S}_F$  phase. The miscibility studies with standard TBPA (Terephthalylidene bis-*p-n*-pentylaniline), 9O.4 (*N*(*p-n*-nonyloxy benzylidene) *p-n*-butyl aniline) and 7O.6 (*N*(*p-n*-heptyloxy benzylidene) *p-n*-hexyl aniline) confirmed [7] this phase as smectic F. The other observed phases and the phase transition temperatures are in agreement with literature data [2].

### 3.2. X-ray diffraction

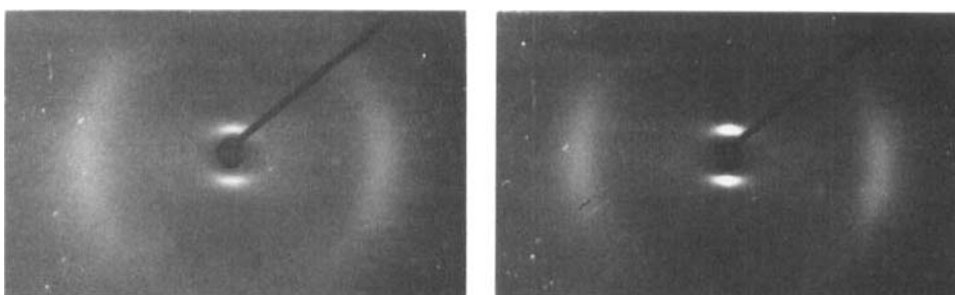
The X-ray diffraction photographs of 5O.5, 5O.6 and 5O.7 are displayed in figures 1 to 3 respectively. The direction of the nematic director  $\mathbf{n}$  is perpendicular to the line joining the maxima of outer diffuse reflections. The intensity of the inner maxima in nematic phase continuously grows with decreasing temperature in all three compounds. This characterises the formation of cybotactic layered clusters in the nematic phase. Earlier reports [8] established that X-ray diffraction photographs of classical nematic phase show that the outer and inner maxima possess almost identical intensities. However, in the cybotactic nematic phase the intensity of inner maxima is greater than the intensity of the outer maxima. The formation of the cybotactic clusters which were observed earlier in the nematic phase at 5O.8 and 5O.10 are reported as pretransitional effects. [9].



(a)

(b)

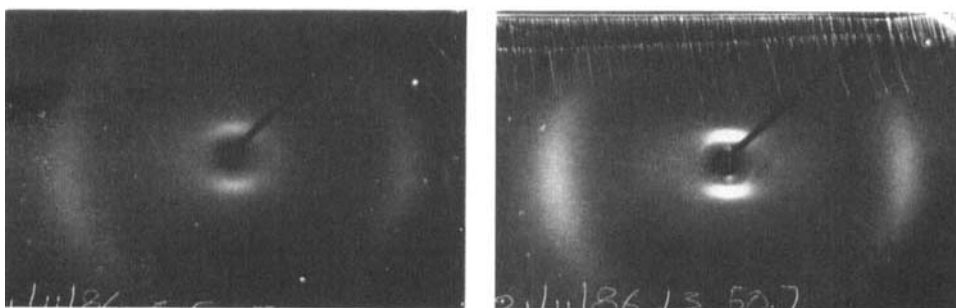
Figure 1. (a) Nematic of 5O.5 at 74°C. (b) Nematic of 5O.5 at 54.75°C.



(a)

(b)

Figure 2. (a) Nematic of 5O.6 at 71.75°C. (b) Nematic of 5O.6 at 62.5°C.



(a)

(b)

Figure 3. (a) Nematic of 5O.7 at 75.75°C. (b) Nematic of 5O.7 at 66°C.

The average intermolecular spacing ( $D$ ) and the layer thickness ( $d$ ) are calculated following the relations used by de Vries [10]

$$1.117\lambda = 2D \sin \theta$$

$$\lambda = 2d \sin \theta$$

where  $\lambda(1.54 \text{ \AA})$  is the wavelength of the X-ray beam and  $\theta$  is the angle of diffraction. The variation of average intermolecular spacing ( $D$ ) obtained from outer maxima with temperature is shown in figure 4 for the three compounds. Solid lines represent

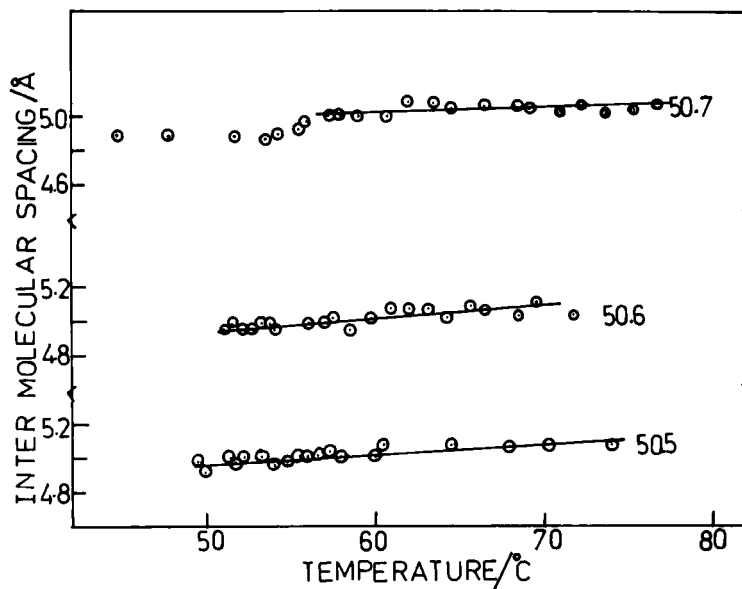


Figure 4. Variation of average intermolecular spacing ( $D$ ) with temperature in 50.5, 50.6 and 50.7.

the least square fit of the data. The intermolecular spacings are found to be  $5.027 \pm 0.07 \text{ \AA}$ ;  $5.026 \pm 0.06 \text{ \AA}$  and  $4.970 \pm 0.13 \text{ \AA}$  for 50.5, 50.6 and 50.7 respectively. It is apparent that the intermolecular spacing is fairly constant as the chain length increases in a homologous series. This indicates that the intermolecular spacing mainly depends on the cross-section of the rigid portion and is fairly independent of the length of the molecule. The intermolecular spacing decreases slightly with decreasing temperature leading to the close packing of the molecules. The temperature dependence of the intermolecular spacing was discussed by de Vries [11, 12].

The variation of the layer thickness with temperature of the three compounds is shown in figure 5. The estimated length of 50.5 molecule from bond angles and bond lengths, in its fully stretched form, is  $25.9 \text{ \AA}$ . The experimental molecular length of smectic A phase is  $25 \text{ \AA}$  and this fact indicates a tilted nature in the molecules in this phase. It reflects the aliphatic chain spreading which in turn needs a larger molecular area yielding a smaller value of the orientational order parameter than the predicted value for an orthogonal nature in the molecules. Thus this difference in molecular length is attributed to the orientational disorder of the molecules. Also, the thermal vibrations of the flexible part of the molecule, i.e. end chain part of the aliphatic segments, at high temperatures cause a decrease in the layer spacing. A small but noticeable increase in layer spacing with decreasing temperature is observed in N and  $S_A$  phases, while it decreases substantially in the  $S_C$  phase. On further lowering the temperature, the layer spacing decreased in the phase below the  $S_C$  phase which was reported to be  $S_B$  phase [2]. However, in this phase the layer spacing never reached a value close to the layer spacing observed in smectic A phase. The tilt angle estimated from the layer spacings in this phase is found to be  $25^\circ$ . The conoscopic studies indicated a biaxial character while the thermal microscopy and miscibility studies [7] confirmed this tilted phase as smectic F. Thus the X-ray studies inferred this phase as

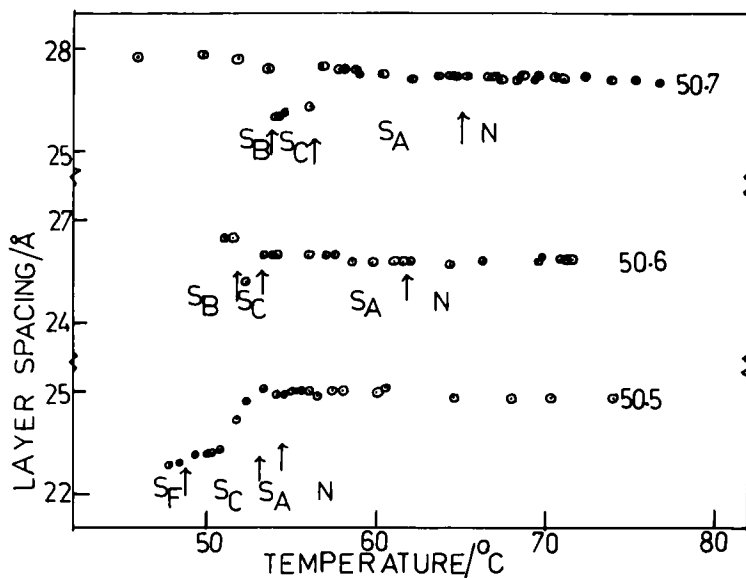


Figure 5. Variation of layer thickness ( $d$ ) with temperature in 50.5, 50.6 and 50.7.

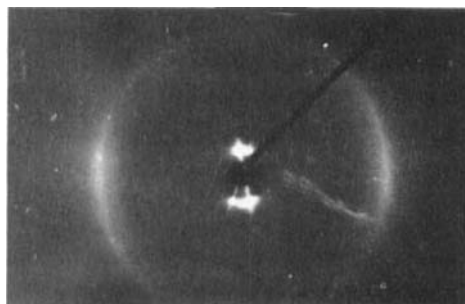


Figure 6. Smectic F of 50.5.

a tilted phase which is in disagreement with reported smectic B phase [2]. An X-ray diffraction photograph in  $S_F$  phase is displayed in figure 6.

Furthermore, the tilt angle in smectic C phase is found to vary from  $0^\circ$  to  $23.6^\circ$  in a phase range of  $4^\circ\text{C}$ . This is analogous to the tilt angle variation of  $0^\circ$  to  $11.4^\circ$  in a temperature range of  $1.2^\circ\text{C}$  of  $S_C$  phase in 70.4 evaluated from E.S.R. studies [13].

In 50.6 and 50.7 the layer thickness increases slightly with decreasing temperature in the nematic and smectic A phases and decreases in  $S_C$  phase. However, the layer thickness in  $S_B$  phase is comparable to that in  $S_A$  phase. Because of the experimental limitations in the temperature control, the variation of tilt angle in the narrow temperature range of  $1.5^\circ\text{C}$  in 50.6 and  $2.6^\circ\text{C}$  in 50.7 could not be carried out. The observed tilt angles estimated, from the available data in  $S_C$  phase are  $14^\circ$  in 50.6 and  $17^\circ$  in 50.7 are found to be higher than the reported values in compounds exhibiting similar narrow  $S_C$  ranges [13].

### 3.3. Density, ultrasonic velocity and refractive index studies

The variation of density, thermal expansion coefficient,  $\alpha = (1/M_v)(dM_v/dt)$ , and ultrasonic velocity  $V$  with temperature are shown in figures 7 to 9, 10 to 12 and

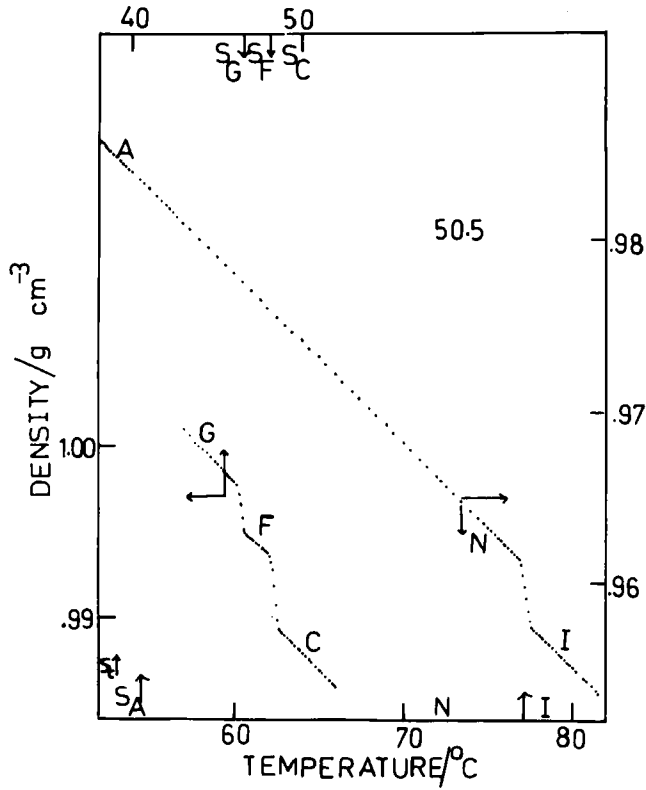


Figure 7. Variation of density with temperature in 50.5.

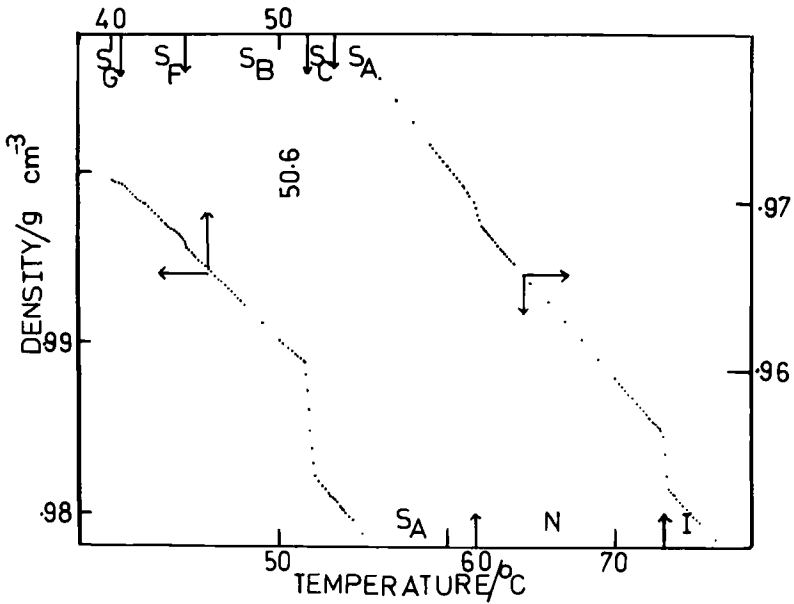


Figure 8. Variation of density with temperature in 50.6.

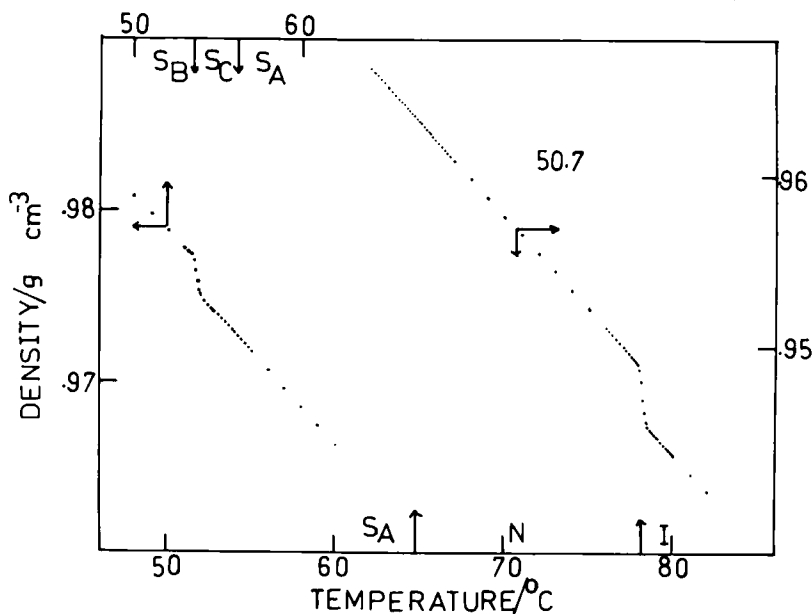


Figure 9. Variation of density with temperature in 50.7.

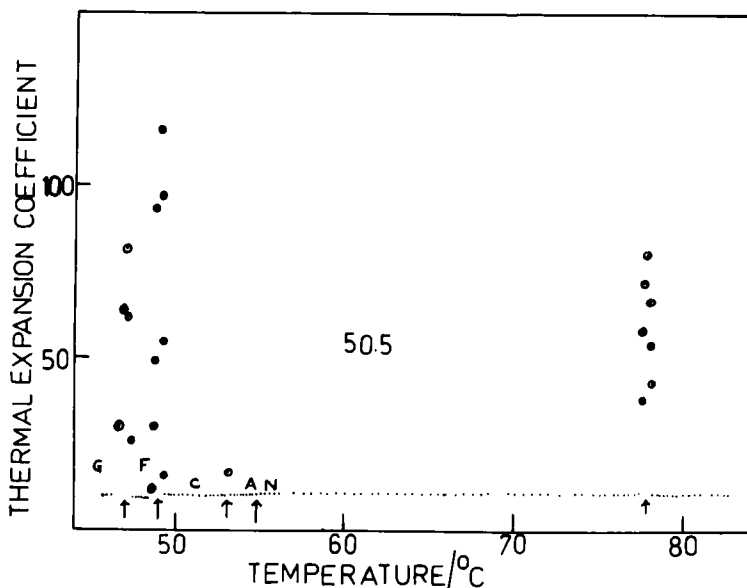


Figure 10. Variation thermal expansion coefficient ( $\alpha$ ) with temperature in 50.5.

13 to 15 for 50.5, 50.6 and 50.7 compounds respectively. The variation of refractive index with temperature is shown in figures 12 and 13 for 50.6 and 50.6 respectively. The density and ultrasonic velocity increases with decreasing temperature, except in the vicinity of transitions.

The isotropic-nematic transition is indicated by a sudden jump ( $\Delta\rho/\rho = 0.3$  per cent in 50.5;  $\Delta\rho/\rho = 0.30$  per cent in 50.6 and  $\Delta\rho/\rho = 0.33$  per cent in 50.7) in all the three compounds. The discontinuities in densities and peaks in thermal expansion



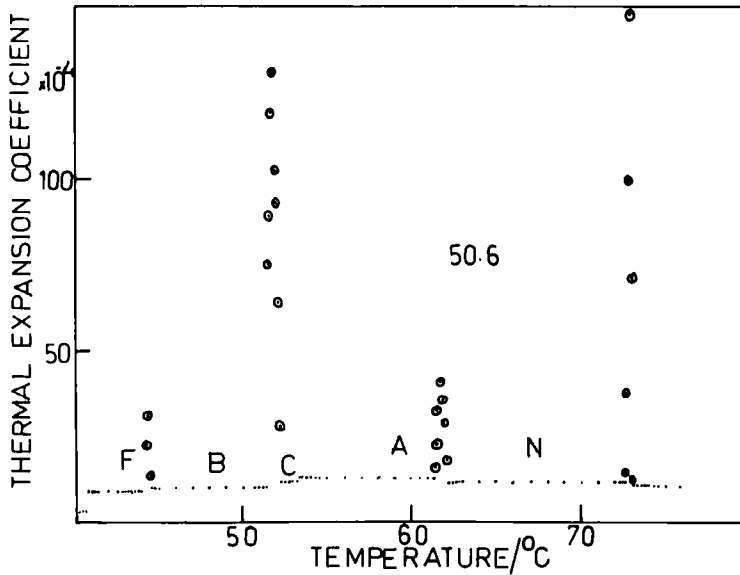


Figure 11. Variation of thermal expansion coefficient ( $\alpha$ ) with temperature in 50.6.

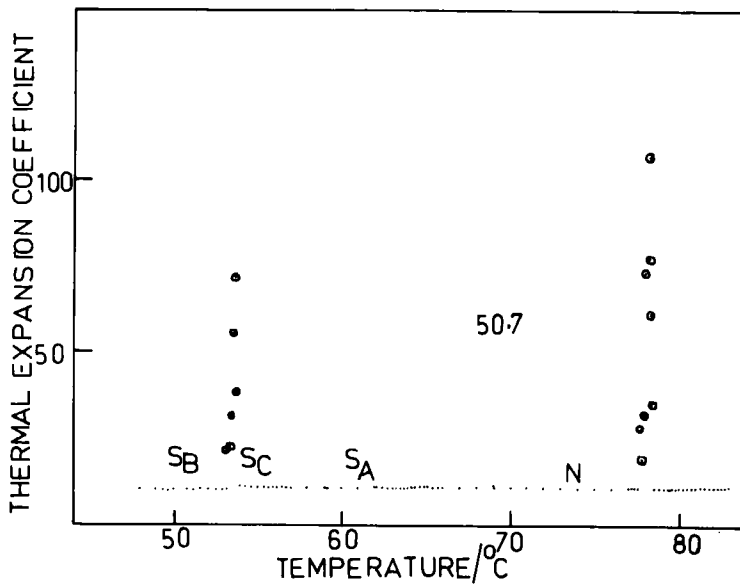


Figure 12. Variation of thermal expansion coefficient ( $\alpha$ ) with temperature in 50.7.

coefficients at the IN transition indicate it to be a first order transition. In the isotropic phase the ultrasonic velocity linearly increases with decreasing temperature. In the vicinity of the phase transition, the velocity suddenly decreases with decreasing temperature in the isotropic phase and then increases with decreasing temperature in the nematic phase. Such an anomalous decrease in ultrasonic velocity is observed across this transition and this is  $\Delta V/V = 2.91$  per cent in 50.5;  $\Delta V/V = 2.3$  per cent in 50.6 and  $\Delta V/V = 2.71$  per cent in 50.7 in comparison with normal observed linear temperature dependence, while the breadth of the anomalous behaviour is

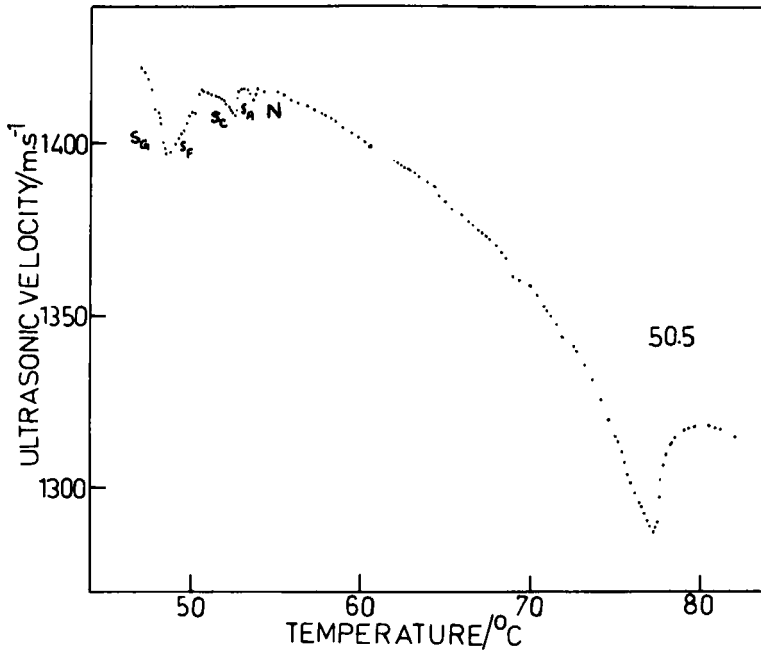


Figure 13. Variation of ultrasonic velocity with temperature in 50.5.

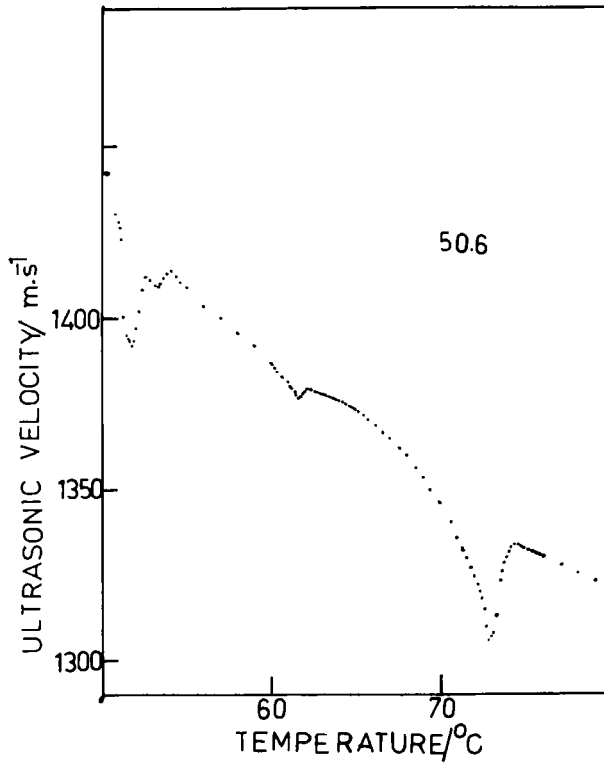


Figure 14. Variation of ultrasonic velocity with temperature in 50.6.

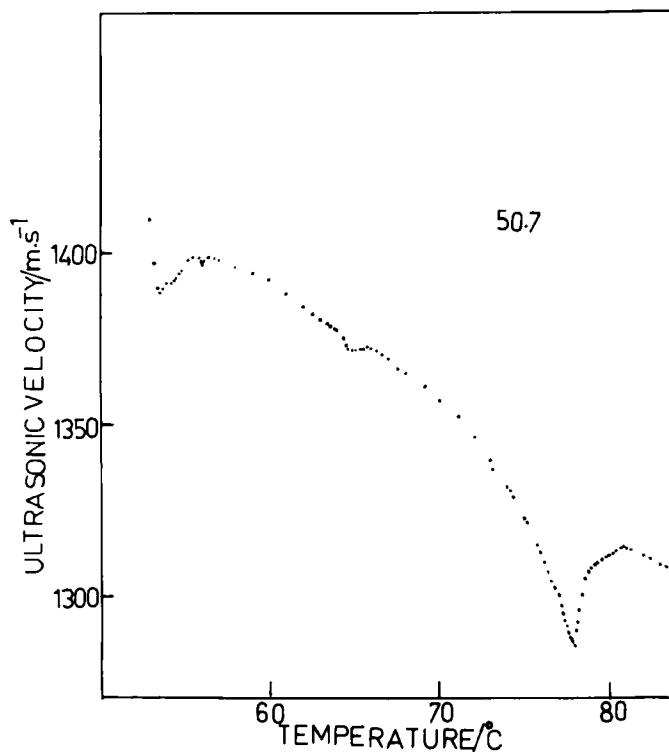


Figure 15. Variation of ultrasonic velocity with temperature in 50.7.

2.8°C in 50.5, 1.4°C in 50.6 and 2.8°C in 50.7. The large breadth of anomalous behaviour in velocity may result from the pretransitional effects present at the I–N transition. A study of velocity change with temperature gives information about the changes accompanying the molecular interactions. The anomalous behaviour in ultrasonic velocity at the I–N transition results from a disordered molecular arrangement in the isotropic phase to an ordered molecular arrangement in the nematic phase, complements the first order transition observed by density measurements in these compounds. The pressure dependence of transition temperatures are estimated using Clausius–Clapeyron equation  $dT_i/dp = T_i \cdot \Delta M_v / \Delta H$  where  $T_i$  is the transition temperature,  $M_v$  is the molar volume change and  $\Delta H$  is the latent heat associated with the transition. The estimated pressure dependence of transition temperatures for I–N transition of 50.5, 50.6 and 50.7 are presented in table 1. The  $dT_i/dp$  value obtained for 50.5 is slightly higher, while the values for 50.6 and 50.7 are found to be in agreement with literature values [14] of other compounds. However,  $dT_i/dp$  value of I–N transition is in disagreement with that of the reported value of Shashidhar *et al.* ( $dT_i/dp = 20.6 \text{ K/k bar}$ ) in 50.6 by P–T studies [15]. The refractive index measurements (figures 16, 17) complement the observed nature of the transition, i.e. refractive indices  $n_e$  and  $n_o$  are continuous for 50.5 while they are distinctly discontinuous in 50.6 across NA transition when studied as a function of temperature.

The nematic–smectic A (NA) transition is of particular importance, because conflicting reports appeared regarding the order of the transition [14] and its dependence on certain physical parameters, viz. nematic and smectic A thermal ranges, the McMillan parameter defining the ratio of transition temperatures  $T_{NA}/T_{NI}$  where  $T_{NA}$

Table 1. The estimated pressure dependence of isotropic-nematic transition temperature of some *nO.m* compounds.

| Name of the compound   | Abbreviated name | $dT_i/dp$ K/kbar |
|--|------------------|------------------|
| <i>N</i> ( <i>p-n</i> -butyloxy benzylidene)<br><i>p-n</i> -octylaniline   | 40.8             | 23.3             |
| <i>N</i> ( <i>p-n</i> -pentyloxy benzylidene)<br><i>p-n</i> -ethylaniline  | 50.2             | 21.4             |
| <i>N</i> ( <i>p-n</i> -pentyloxy benzylidene)<br><i>p-n</i> -pentylaniline | 50.5             | 36.5             |
| <i>N</i> ( <i>p-n</i> -pentyloxy benzylidene)<br><i>p-n</i> -hexylaniline  | 50.6             | 33.0             |
| <i>N</i> ( <i>p-n</i> -pentyloxy benzylidene)<br><i>p-n</i> -heptylaniline | 50.7             | 29.2             |
| <i>N</i> ( <i>p-n</i> -pentyloxy benzylidene)<br><i>p-n</i> -octylaniline  | 50.8             | 26.3             |
| <i>N</i> ( <i>p-n</i> -hexyloxy benzylidene)<br><i>p-n</i> -ethylaniline   | 60.2             | 26.4             |
| <i>N</i> ( <i>p-n</i> -heptyloxy benzylidene)<br><i>p-n</i> -butylaniline  | 70.4             | 22.5             |
| <i>N</i> ( <i>p-n</i> -heptyloxy benzylidene)<br><i>p-n</i> -pentylaniline | 70.5             | 28.4             |

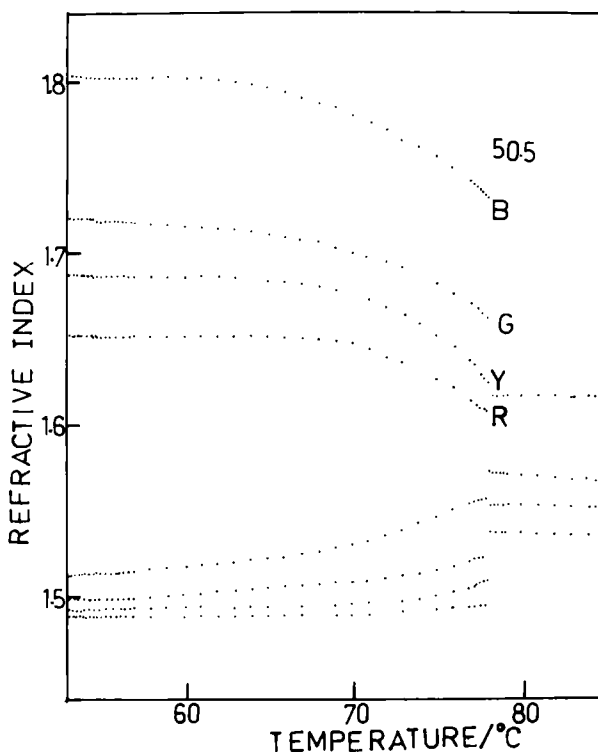


Figure 16. Variation of refractive index with temperature in 50.5.

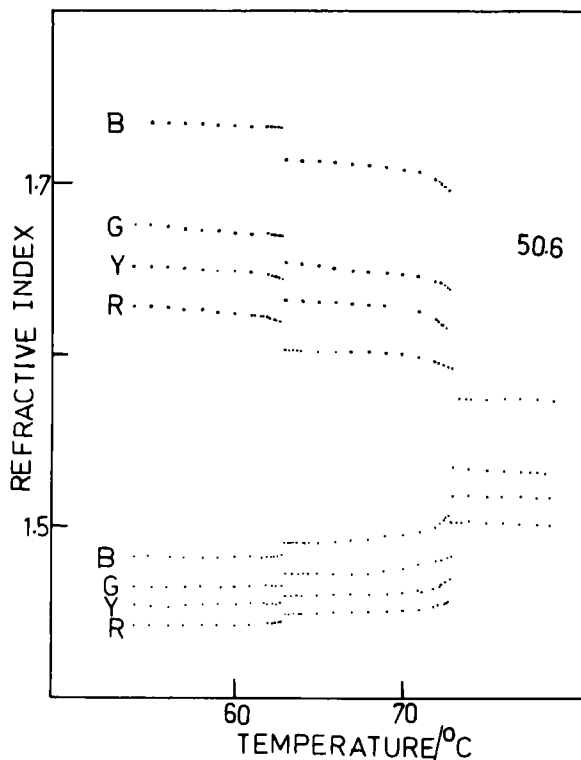


Figure 17. Variation of refractive index with temperature in 50.6.

and  $T_{NI}$  are the nematic–smectic A and nematic–isotropic transition temperatures respectively and the smectic A layer spacing to molecular length ratios. Earlier theoretical predictions [18–24] which inferred a tricritical point separating the first and second order transitions at  $T_{NA}/T_{NI} = 0.87$ , suffers from not considering the pre-transitional enthalpy. Experimental observations in binary mixtures reported [25–28] a TCP around 0.978. In the compounds 50.5, 50.6 and 50.7 possessing the  $T_{NA}/T_{NI}$  values of 0.933, 0.968 and 0.962 respectively, a small jump in density across the NA transition is observed only in 50.6 ( $\Delta\rho/\rho = 0.1$  percent), whereas no discontinuity is observed across the NA transition in 50.5 and 50.7, in spite of the repeated runs and at different rates of cooling (0.3°C per hour to 1.5°C per hour). The NA transition is visible to the naked eye, i.e. a change from opaque nematic to translucent  $S_A$  phase of the substance in the bulb. A small jump in density and a peak in thermal expansion coefficient in 50.6 indicate the NA transition to be a weak first order which is in agreement with the reported dilatometric studies by Thiriet *et al.* [29]. A continuous density change across the NA transition in 50.5 and 50.7 indicate it to be a second order transition. The other homologues of the same series which also exhibit NA transition, have shown a questionably weak first order and second order phase transitions respectively. In 50.6, the pressure dependence of the transition temperature  $dT_i/dp = 13.1$  K/k bar is in agreement with the reported [15] data of  $dT_i/dp = 14$  K/k bar from P–T studies.

From the experimental results of  $nO.m$  compounds, it is observed that the alkoxy chain length plays a predominant role on the nematic range and for the characterization of NA transition (first or second order) irrespective of alkyl chain length. It can

be clearly seen from the reported literature that the 40.m series exhibits only second order transitions, while all compounds reported in 60.m and 70.m homologous series exhibit first order NA transitions. No such conclusions can be made regarding 50.m series. The compounds 50.4, 50.5 and 50.10 exhibit a second order NA transition. Compounds with odd methylene group number in the alkyl chain always show a wider nematic range than do the even numbered compounds, thus exhibiting an odd-even effect; while no such effect with the change of alkoxy chain length is observed, instead the nematic range decreases steeply with the increase of alkoxy chain length. It is interesting to note that the compounds 50.6 and 60.5 (the difference between the two compounds being the interchange of end chain) with slightly different ( $T_{NA}/T_{NI}$ ) values and of comparable nematic range show a weak first order and a first order NA transition respectively. Furthermore in the 50.m homologous series a second order NA transition was observed in 50.10, which exhibits a nematic thermal range comparable to that of compounds in the 60.m series, viz. 60.4 and 60.5. One possible explanation given from the density studies is that the end aliphatic chain can overlap in long molecules like 40.8, 50.8 and 50.10, thereby occupying comparatively smaller volume than their all trans configuration requirement. Experiments on 70.7 and 60.8 by a.c. calorimetry [31] and density studies [32] contradict the above explanation. These two compounds show a strong first order NA transition.

The NA transition in 50.5 is signalled by a small dip in ultrasonic velocity (2 m/s) at the end of a flattened region in the nematic phase, while ultrasonic velocity variation has exhibited a broad dip at the NA transition in 50.7. In 50.6 the transition is observed by a dip ( $\Delta V/V = 0.76$  per cent) in ultrasonic velocity. The observed results indicate the transition in 50.5, 50.6 and 50.7 complementing the density measurements at the NA transition. Further, the refractive index studies also complement the observed NA transition in 50.5 and 50.6.

Pretransitional effects are observed on both sides of the transition but predominantly on the nematic side in all the three compounds in both density and ultrasonic velocity measurements. The formation of cybotactic clusters in the nematic phase just above the NA transition, which were clearly observed in X-ray diffraction studies may explain the pretransitional effects. Also the formation of smectic like ordering in nematic phase itself may be the reason for the second order or weak first order NA transition. The ratios  $N = h_2/h_1$  where  $h_1$  and  $h_2$  are the heights of the D.S.C. transition peaks obtained with two temperature scanning rates: one ( $h_2$ ) being twice the other ( $h_1$ ) keeping the weight of the compound constant. The ratio  $N$  is  $1 \leq N \leq \sqrt{2}$  for an isothermal first order transition and equals 2 for a second order transition [33]. Our results are in good agreement with the reported values of  $N$  (1.53 for 50.6 and  $2.00 \pm 0.05$  for 50.7) [34] predicting the weak first order and second order NA transition in 50.6 and 50.7 respectively.

The smectic C phase which resembles smectic A phase possesses molecular tilt. The  $S_A-S_C$  phase transition (AC) is inferred by a continuous change in density across the transition in all the three compounds. However, no enthalpy change is reported at this transition except in 50.5 ( $\Delta H = 260$  J/mol). The  $\Delta H$  value in 50.5 across the AC transition, which is an interesting point for discussion, apparently suggested a first order AC transition. The true latent heat, which should be related to a purely first order transition, in a realistic way is different from the heat of the transition which may also include, besides a latent heat, the pretransitional effects. Hence, the  $\Delta H$  across AC transition is probably due to a large pretransitional effects effecting the

molecular arrangement in the transformation. Furthermore, this small enthalpy in 5O.5 may also result from the effective narrow region of  $S_A$  phase of  $1.3^\circ\text{C}$ . Thus the AC transition in 5O.5 probably suggested the vicinity of an NAC tricritical point. Analogous observation of small enthalpies at the phase transitions following narrow high temperature phases are reported in literature [35]. In 5O.6 and 5O.7 the  $S_A$  range is  $8.4^\circ\text{C}$  and  $8.7^\circ\text{C}$  respectively and heat of transition is not observed at AC transition is second order. The observed data inferred that the AC transition is second order in these compounds. The transition is indicated by a dip in ultrasonic velocity ( $6\text{ ms}^{-1}$  in 5O.5,  $5\text{ ms}^{-1}$  in 5O.6 and  $2\text{ ms}^{-1}$  in 5O.7) at the transition in all the three compounds.

The smectic C–smectic F transition (CF), which is observed in 5O.5 is an example of disordered tilted structure to ordered tilted structure transition and is inferred by a large jump in density ( $\Delta\rho/\rho = 0.39$  per cent). Thermal expansion coefficient shows a peak at the transition. The smaller value of thermal expansion coefficient in  $S_F$  phase than in  $S_C$  phase suggests a closer packing of molecules leading to rigidity in  $S_F$  phase. The transition from  $S_C$  phase, possessing one dimensional translational order of tilted molecules with disordered centres of mass positions and fluid layers, to  $S_F$  phase, possessing molecules packed in layers with pseudo hexagonal packing with two dimensional structure regarding the positional order and long axes tilted (tilt directed towards an edge of hexagon) with respect to the layer planes, i.e. uncorrelated layers but with long range bond orientational order, is expected to be a first order transition.

The observed jump in density and a peak in thermal expansion coefficient indeed suggest a first order CF transition. The estimated pressure dependence of transition temperature in 5O.5 ( $dT_i/dp = 42.5\text{ K/k bar}$ ) is in agreement with the estimated value at CF transition in terephthalydene bis-*p-n*-octylaniline, TBOA ( $dT_i/dp = 43\text{ K/k bar}$ ) [36]. An anomalous decrease in ultrasonic velocity ( $\Delta V/V = 1.8$  per cent) per cent at the transition complements the observed phase transition.

Both 5O.6 and 5O.7 exhibit the  $S_C$ – $S_B$  transition (CB) and is inferred by a large jump in density across the transition. The observed density jumps are  $\Delta\rho/\rho = 0.62$  per cent in 5O.6 and  $\Delta\rho/\rho = 0.5$  per cent in 5O.7 across the CB transition. The peak in thermal expansion coefficient and the observed jumps across the CB transition inferred it to be a first order transition in both the compounds. The pressure dependence of transition temperature, estimated from Clausius–Clayperon equation is presented in table 2, along with the literature values. The estimated value of

Table 2. The estimated pressure dependence of smectic C–smectic B transition temperature of some compounds.

| Name of the compound  | Abbreviated name | $dT_i/dp$ K/kbar | Reference    |
|---|------------------|------------------|--------------|
| <i>N</i> ( <i>p-n</i> -pentyloxy benzylidene <i>p-n</i> -hexylaniline   | 5O.6             | 33.7             | Present work |
| <i>N</i> ( <i>p-n</i> -pentyloxy benzylidene) <i>p-n</i> -heptylaniline | 5O.7             | 32.6             | Present work |
| <i>N</i> ( <i>p-n</i> -heptyloxy benzylidene) <i>p-n</i> -pentylaniline | 7O.5             | 35.8             | [14]         |
| <i>N</i> ( <i>p-n</i> -heptyloxy benzylidene) <i>p-n</i> -ocylaniline   | 7O.8             | 42.4             | [16]         |
| 4,4'-di- <i>n</i> -octadecyloxybenzene                                  |                  | 34.1             | [17]         |
| <i>n</i> -amyl, 4(4- <i>n</i> -dodecyloxy benzylidene) aminocinnamate   |                  | 35.1             | [17]         |

$dT_i/dp = 33.7 \text{ K/k bar}$  for 5O.6 is in disagreement with the reported value [15] of  $dT_i/dp = 14 \text{ K/k bar}$ . The ultrasonic velocity dips ( $\Delta V/V = 1$  per cent) both in 5O.6 and 5O.7 complement the observed transition.

The  $S_B-S_F$  transition (BF) is encountered only in 5O.6. This transition is inferred by a very small jump in density ( $\Delta\rho/\rho = 0.03$  per cent) across the transition. Goodby *et al.* [3] reported an enthalpy change of  $150 \text{ J/mol}$ . Hence, the transition may be a weak first order or a second order one.

### 3.4. Structural data of 5O.m series ( $m = 6, 7, 8$ and $10$ )

The variation of molar volume  $M_v$ , molecular area  $S$  and layer spacing  $d$  as a function of the length of the aliphatic chain, at a temperature  $T = 60^\circ\text{C}$  in the  $S_A$  phase is illustrated in figures 18 (a), (b) and (c) respectively. It appears that the layer spacing is a linear function of chain length,  $m$ ; by applying the equation

$$d(m, T) = d_a(T) + (m + 1) dp(T),$$

where  $d(m, T)$  stands for the layer spacing of the  $m$ th term of the series,  $d_a(m, T)$  and  $dp(T)$  for the aromatic sublayer thickness and for the methylene group thickness respectively. ( $m + 1$ ) was used instead of  $m$  in order to take into account the contribution of the  $\text{CH}_2$  group belonging to the terminal  $\text{CH}_3$  group. From the data of the figure 18 the following values are obtained for

$$d_a(60^\circ\text{C}) = 18.5 \text{ \AA} \text{ and } dp(60^\circ\text{C}) = 1.27 \text{ \AA},$$

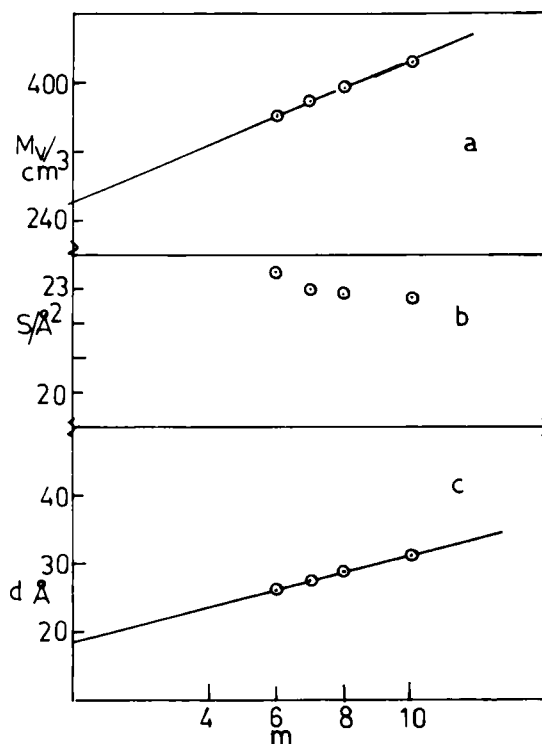


Figure 18. Variation of Molar volume ( $M_v$ ), molecular area ( $s$ ) and layer spacing ( $d$ ) as a function of chain length ( $m$ ) in 5O.m series in  $S_A$  phase at  $60^\circ\text{C}$ .



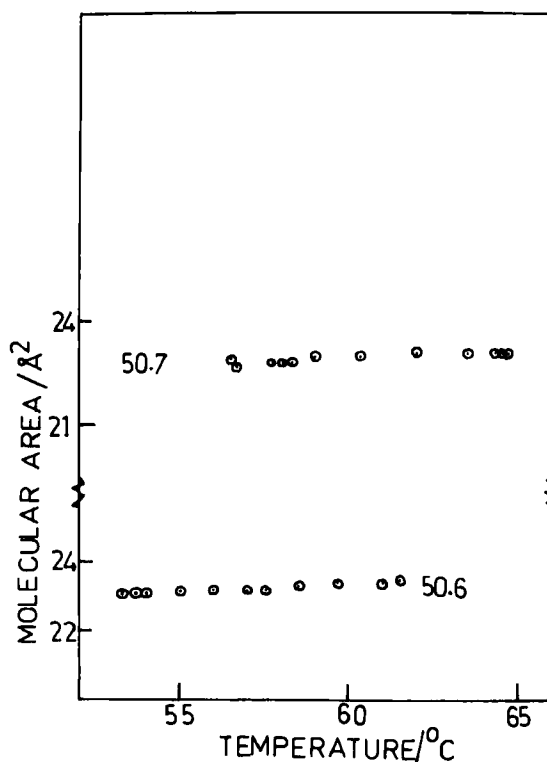


Figure 19. Variation of molecular area ( $s$ ) with temperature in  $S_A$  phase of 50.6 and 50.7.

where  $C_5H_{11}O-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-$  represents the  $d_a$ , the aromatic sublayer thickness.

An important physical quantity that can be derived by both dilatometric and X-ray diffraction data is the molecular area,  $s$ . This quantity which was successfully used in reported investigations of soaps and liquid crystal molecular structures [37, 38] is defined as the surface occupied by one molecule in the plane of layers.

In a lamellar system, when the molecules are rigid rods and arranged in a single layer then  $s$  is very easy to calculate using the relation  $s = M_v/N \cdot d$ , where  $M_v$  is the molar volume,  $N$  is Avogadro's number and  $d$  is the layer spacing. Figure 19 represents the temperature dependence of  $s$  for the compounds 50.6 and 50.7 in  $S_A$  phase, as obtained from the dilatometric and X-ray diffraction data. From the figure 19, it is apparent that  $s$  increases very slightly with increasing temperature, in both the compounds, in the thermal range of the  $S_A$  phase. A small variation of  $s$ , which is about  $4 \times 10^{-3} \text{ \AA}^2$  between  $53.3^\circ\text{C}$  and  $61.5^\circ\text{C}$  for 50.6 and  $7 \times 10^{-3} \text{ \AA}^2$  between  $56.5^\circ\text{C}$  and  $64.7^\circ\text{C}$  for 50.7, shows that the molecular area is practically constant, in the  $S_A$  phase, therefore apparently indicating no change in the internal structure of the  $S_A$  layers in the whole temperature range.

#### 4. Structural model for the $S_A$ phase

The important observation reported above is the value  $dp(T) = 1.27 \text{ \AA}$  for the methylene group thickness which is exactly in agreement with the increment of one

methylene group for a crystalline paraffin in its most stretched configuration (1.27 Å). Moreover, it is important to emphasize that the layer spacing is smaller than the length of the molecule calculated from the atomic model.

|                         | 50.5 | 50.6 | 50.7 | 50.8 | 50.10 |
|-------------------------|------|------|------|------|-------|
| $l_{\text{expt}}$ in Å  | 25.0 | 25.9 | 27.3 | 28.6 | 30.9  |
| $l_{\text{theor}}$ in Å | 25.9 | 26.6 | 28.1 | 28.7 | 30.8  |

These two observations suggest a monolayer arrangement of the molecules inside the smectic layers, with some tilt of the molecules which is attributed to the orientational disorder of the molecules. The average tilt angle of the aromatic cores results in a more pronounced spreading of the aliphatic chains in the interface.

The aromatic sublayer thickness  $d_{\text{ar}}$  can be deduced from the experimental values of  $M_{\text{v}}$ ,  $M_{\text{v(aromt)}}$  and  $d$  through the relation

$$M_{\text{v}}/M_{\text{v(aromt)}} = d/d_{\text{ar}}$$

The values of  $d_{\text{ar}}$  are calculated for 50.6, 50.7, 50.8 and 50.10 at 60°C is shown in figure 20.  $d_{\text{ar}}$  is roughly the same for all  $m$ . Only a slight increase as a function of  $m$  ( $d_{\text{ar}} = 18.86 \text{ Å}$  for 50.6 and  $d_{\text{ar}} = 19.34 \text{ Å}$  for 50.10) is observed. These experimental values of  $d_{\text{ar}}$  are higher than the length of the aromatic core of the molecule calculated from the atomic model (16.8 Å).

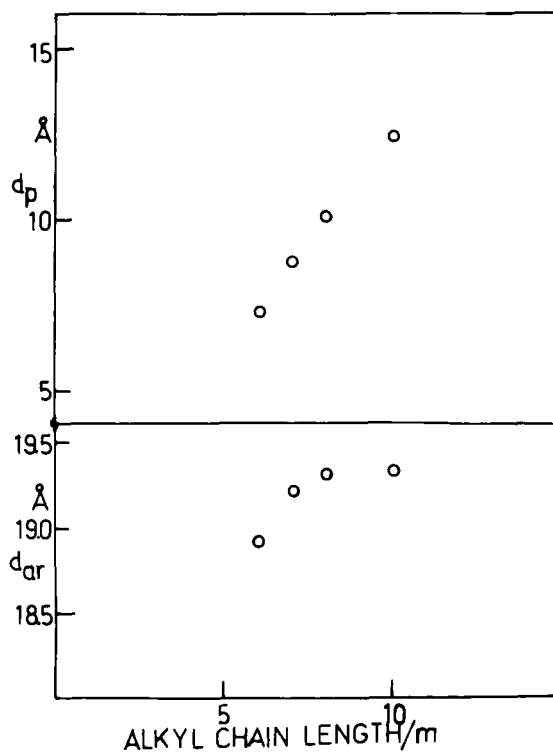


Figure 20. Variation of aromatic sublayer thickness ( $d_{\text{ar}}$ ) and aliphatic sublayer thickness ( $d_{\text{p}}$ ) with aliphatic chain length ( $m$ ).

The behaviour of  $d_{ar}$  as a function of  $m$  has to be related to that of  $s$  as a function of  $m$ . The molecular area,  $s$ , decreases as the number of carbon atoms in the aliphatic chain increases and is shown in the figure 18 (b). This indicates that the aromatic cores are slightly tilted on an average when  $m$  is small. As  $m$  increases, the average tilt angle of rigid cores decrease, thereby indicating the decrease in orientational disorder of the molecules.

As  $m$  increases, the values of  $d_{ar}$  tend to be the same in 5O.7, 5O.8 and 5O.10 (19.20 Å, 19.30 Å and 19.34 Å respectively). As we know that the aromatic cores are oriented quasi normal to the plane of the layers; this result shows that there remains still an average tilt angle of the aromatic cores, even when the aliphatic chain is long.

The aliphatic sublayer thickness  $dp$  can be calculated using the relation

$$dp = d - d_a$$

The aliphatic sublayer thickness  $dp$  variation with  $m$  is shown in figure 20. The increment per methylene unit in aliphatic sublayer thickness is 1.11 Å. When compared with the increment of  $d$  per CH<sub>2</sub> group  $dp(T) = 1.4$  Å, it implies the spreading of the aliphatic chains thereby indicating the orientation of aromatic cores quasi-normal to the plane of the layers. Thus it is clear that the average tilt angle of the aromatic core decreases as a function of  $m$ .

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