CHAPTER 5

MESOMORPHISM OF 4,4'-di-n-PENTYLOXYAZOXYBENZENE

5.1 Introduction

p-Azoxyanisole (PAA) and its higher homologues constitute a classic series of liquid crystals which have received wide experimental and theoretical attention so far.[1] Extensive thermodynamic data on this series (hereafter abbreviated as C_n, where n is the number of carbon atoms in their alkyl end-chain) were first reported by Arnold[2] for the first twelve homologues, C_1 - C_{12}. Based on his and a few other investigations[3-9] it was hitherto considered that the lowest member of this series exhibiting an enantiotropic smectic - nematic transition (Sm - N) is C_7, the smectic phase in this case being of the C-type. C_6 is known to exhibit a monotropic smectic C phase.[10]

In this chapter we present evidence based on calorimetric, optical texture and infrared spectral studies which strongly indicate that 4,4'-di-n-pentyloxyazoxybenzene (C_5) exhibits a highly ordered enantiotropic smectic phase below its nematic phase. Hitherto, this phase, observed in the temperature range 341.5 K – 349.5 K on the heating cycle, was believed to be a solid phase. We also examine the nature of the molecular dynamics which might give rise to this mesophase.

5.2 Experimental

C_5 purchased from Eastman Kodak Co. was purified by column chromatography and then dried in vacuum. The nematic – isotropic (N – I) transition temperature was found to be 396.2 K. Calorimetric data were obtained with a Perkin-Elmer differential scanning calorimeter (Model DSC-2) at a scan rate of 5K/min. The phase transition temperatures were determined from both DSC and thermal microscopy and are accurate to within ±0.5 K. Infrared spectra in the different phases were obtained using a Leitz double-beam prism spectrometer with the sample sandwiched between two NaCl windows. Further experimental details are given in chapter 2.

5.3 Results and Discussion

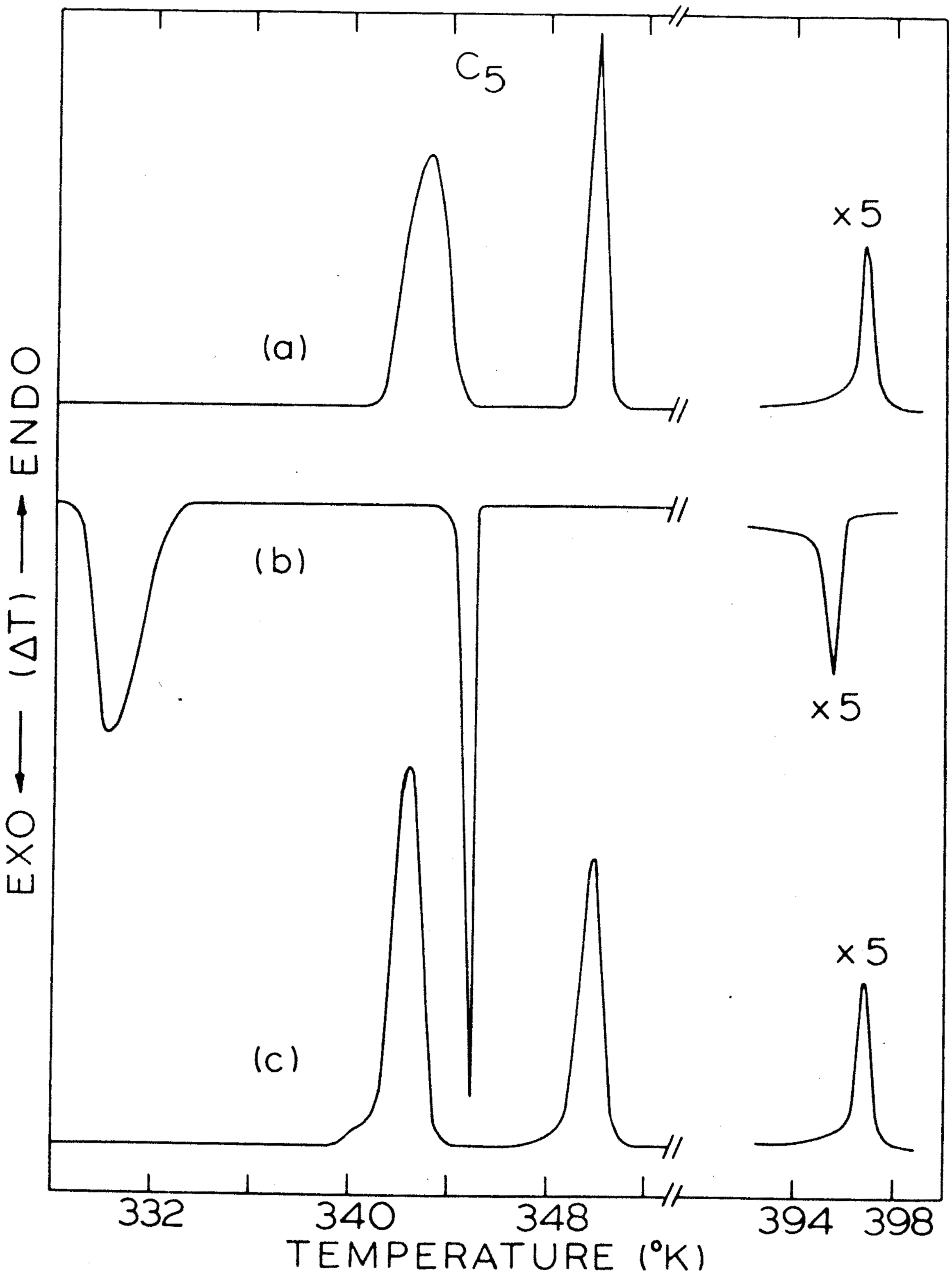
(a) Calorimetric study

Figure 5.1 shows the DSC results obtained during the heating, cooling and reheating cycles. The three endothermic transitions had been reported by Arnold[2] and Smith.[3] Our values of the enthalpy (ΔH) of all three transitions are in agreement with theirs to within $\pm 5\%$. It is significant that we see three and not just two exothermic peaks during the cooling cycle as well. The endothermic transition at 341.5 K has a large ΔH (22.2 kJ/mole). If this is a solid-solid transition as was presumed hitherto, the solid form stable at the higher temperature can be normally expected to supercool rather easily and exist as a metastable phase at room temperature for several hours or even days, before transforming completely to the stable solid phase. Such a slow transition would then be unobservable using a relatively <u>fast</u> technique as the DSC, both while cooling and upon immediate reheating of the sample. In figure 5.1e we observe the recurrence of the transition at 341.5 K upon immediate reheating as well.

For comparison, figures 5.2 and 5.3 show our DSC results on C_3 and C_4, two lower homologues of C_5 in the PAA series. They both exhibit strong solid-solid transitions at 378.5 K and 324.0 K, respectively. Their ΔH values are also large, being 21.7 and 12.5 kJ/mole, respectively. The higher temperature solid modifications supercool in both C_3 and C_4 and exist at room temperature for long periods, as long as a month in the case of C_4. The absence of the corresponding peaks in the reheating cycle clearly

FIGURE 5.1

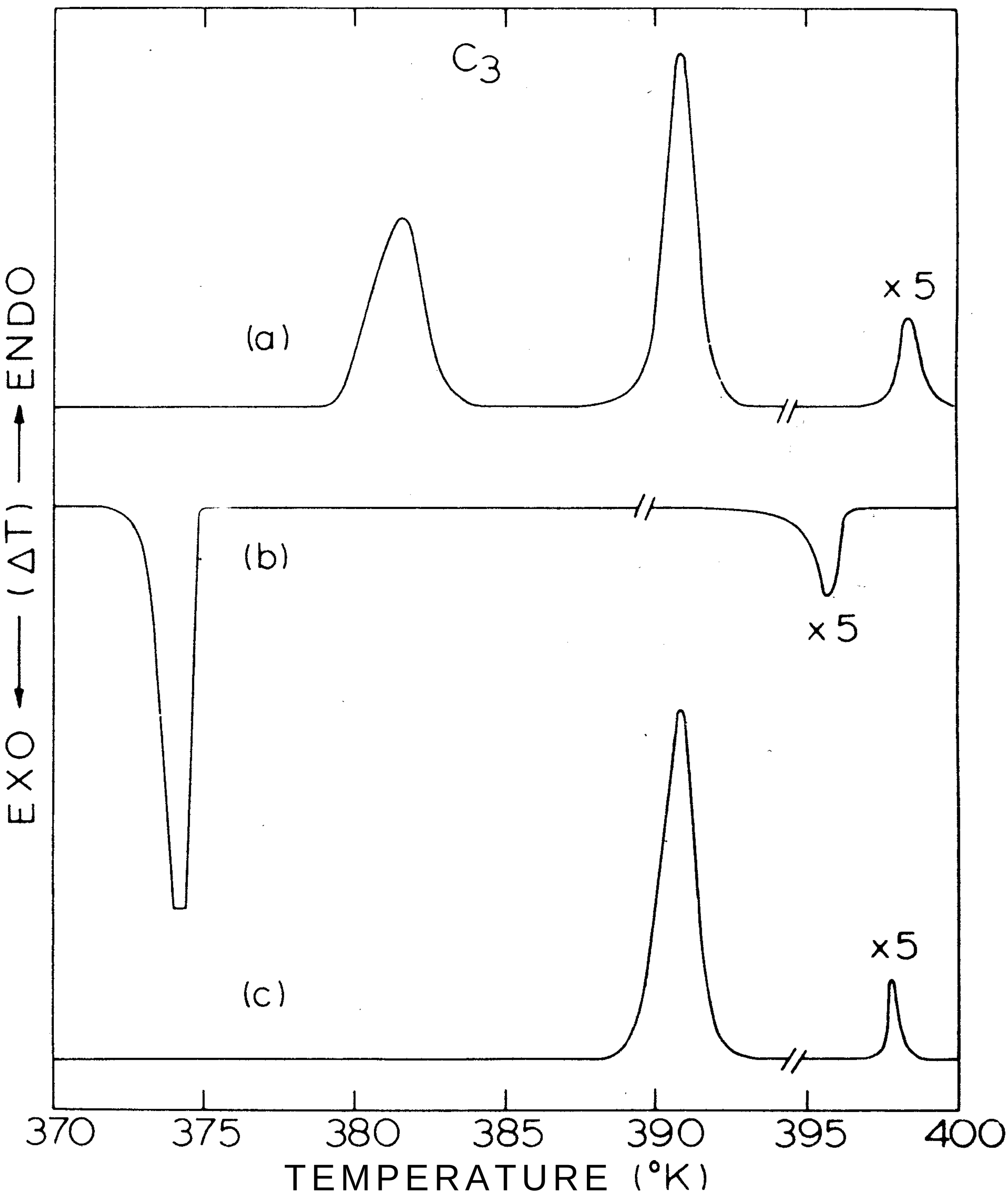
DSC curves of C_5 (p,p'-di-n-pentyloxy-azoxybenzene). (a),(b) and (c) correspond respectively to the heating, cooling and immediate reheating cycles. For the N-I transition, the vertical scale factor employed is five times more sensitive.



C5
(a)
(b)
(c)
x 5
x 5
x 5
EXO ← (ΔT) → ENDO
332
340
348
394
398
TEMPERATURE (°K)

FIGURE 5.2

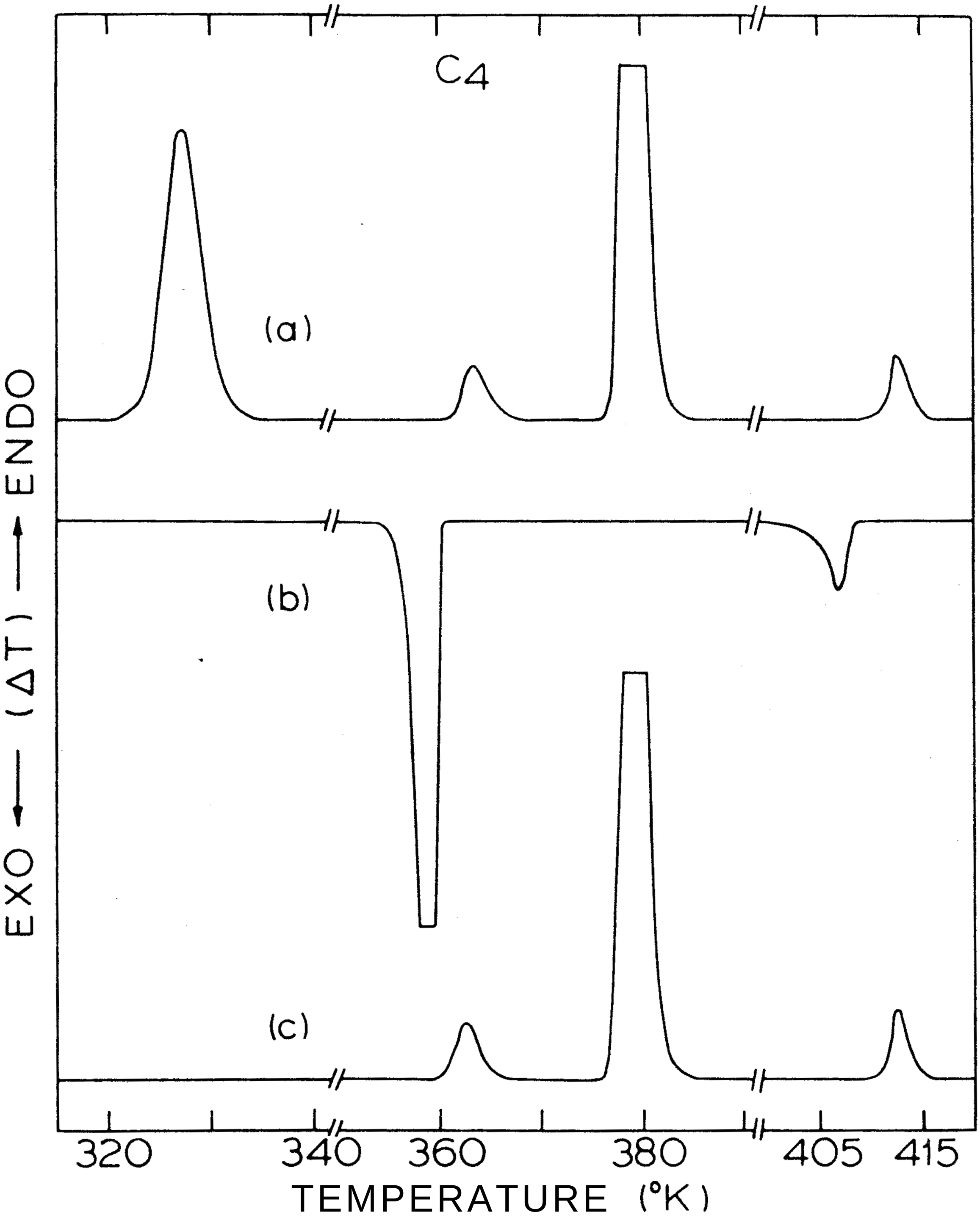
DSC curves of C_3 (p,p'-di-n-propyloxyazoxy-benzene). (a), (b) and (c) correspond respectively to the heating, cooling and immediate reheating cycles. For the N-I transition, the vertical scale factor employed is five times more sensitive.



C3
(a)
x 5
(b)
x 5
(c)
x 5
EXO ← (ΔT) → ENDO
370
375
380
385
390
395
400
TEMPERATURE (°K)

FIGURE 5.3

DSC curves of C_4 (p,p'-di-n-butyloxyazoxy-benzene). (a), (b) and (c) correspond respectively to the heating, cooling and immediate reheating cycles. The small endothermic peak at 360 K is due to a very weak solid-solid transition.



C4
(a)
(b)
(c)
EXO ⟵ (ΔT) ⟶ ENDO
320
340
360
380
405
415
TEMPERATURE (°K)

demonstrates this fact. (The small endothermic peak at ~ 360 K in the case of C_4 is due to a very weak solid-solid transition with an enthalpy comparable to that of the N-I transition. This is not seen in the cooling cycle but shows up in the reheating cycle.) CBOOA also exhibits a similar behaviour.[11]

The lowest temperature transition of C_5 could be detected by DSC during every cooling and reheating cycle. The transition temperature was also found to be the same on the first heating and the subsequent reheating cycles. This behaviour is in accord with the existence of a stable, enantiotropic phase in between the solid phases. The nature of this intermediate phase was ascertained through microscopic texture observations, as discussed below.

(b) Microscopic texture

Figure 5.4 shows the textures of the crystalline and the 'intermediate' phase discussed above, between crossed polarisers. The mosaic texture of the intermediate phase strongly suggests that it is a highly ordered smectic mesophase, similar to smectic B or H types.[12] This is also consistent with the relatively high enthalpy observed for the transition.

The texture of the mesophase was the same irrespective of whether it was obtained by heating the crystalline solid or by cooling the nematic phase. The latter observation excludes the possibility that the mosaic texture could be the result of strain cracks that may attend a solid-solid transition. A cover slip pressed over a thin sample of the mesophase could be displaced, but the viscosity in this phase was much greater than that in the nematic phase. Also, by pressing on the cover slip with a fine steel needle it was possible to observe a net reversible change in the mosaic texture. This is further evidence that the phase in question is not just a

FIGURE 5.4

Microscopic textures observed between crossed polarisers in the case of Q_5 (p,p'-di-n-pentyloxyazoxybenzene); X 250.

(a) solid phase at ~ 341 K

(b) smectic phase at ~ 345 K.

(a)

(b)

polymorphic modification of the solid phase.

An X-ray powder diffraction photograph showed that the mesophase exhibits several maxima in the low angle region. However, they were fewer and less intense than in the crystalline phase. This is in general accord with previous X-ray studies of other highly ordered mesophases.[13,14]

(c) Infrared spectra

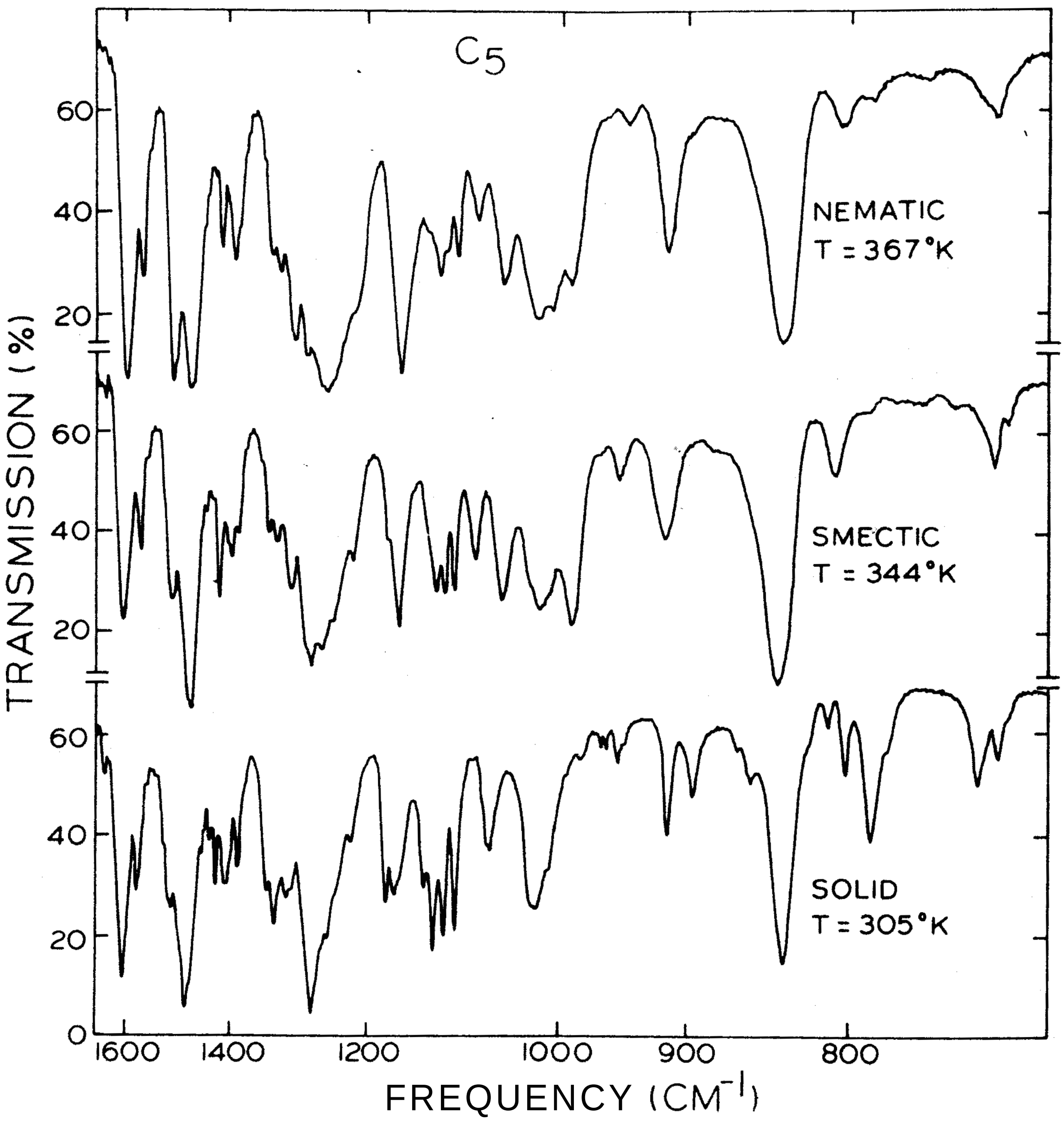
Figure 5.5 shows the infrared spectra of C_5 in the three different phases over the range 700 - 1600 cm^{-1} which covers the region of the internal modes. It is seen that, except for some changes in relative intensities, the spectra of the smectic and nematic phases are very similar to each other whereas significant differences are seen between the spectra of the solid and smectic/nematic phases. Several spectral features associated with the rocking, twisting and wagging modes of the $(CH_2)_5$ group and the aliphatic C - H stretching frequencies (in the range 700 - 1250 cm^{-1}) show differences between the solid and smectic phases. This would be expected[15] if new conformations of the polymethylene end-chain are allowed in the smectic phase as compared to the solid phase. The intramolecular changes associated with the end-chain of the molecule, as indicated by the observed changes in spectral features, appear to be a general feature of solid-mesophase transitions, especially when the molecules of the mesogen possess long, flexible end chains.[16]

Relative intensity changes are also observed between the solid and smectic phases in the two regions 1150 - 1200 cm^{-1} and 1550 - 1625 cm^{-1} which are associated with vibrations in the rigid central core of the liquid crystal molecule. They imply changes in the molecular dynamics of the rigid core at the solid-smectic transition.[17]

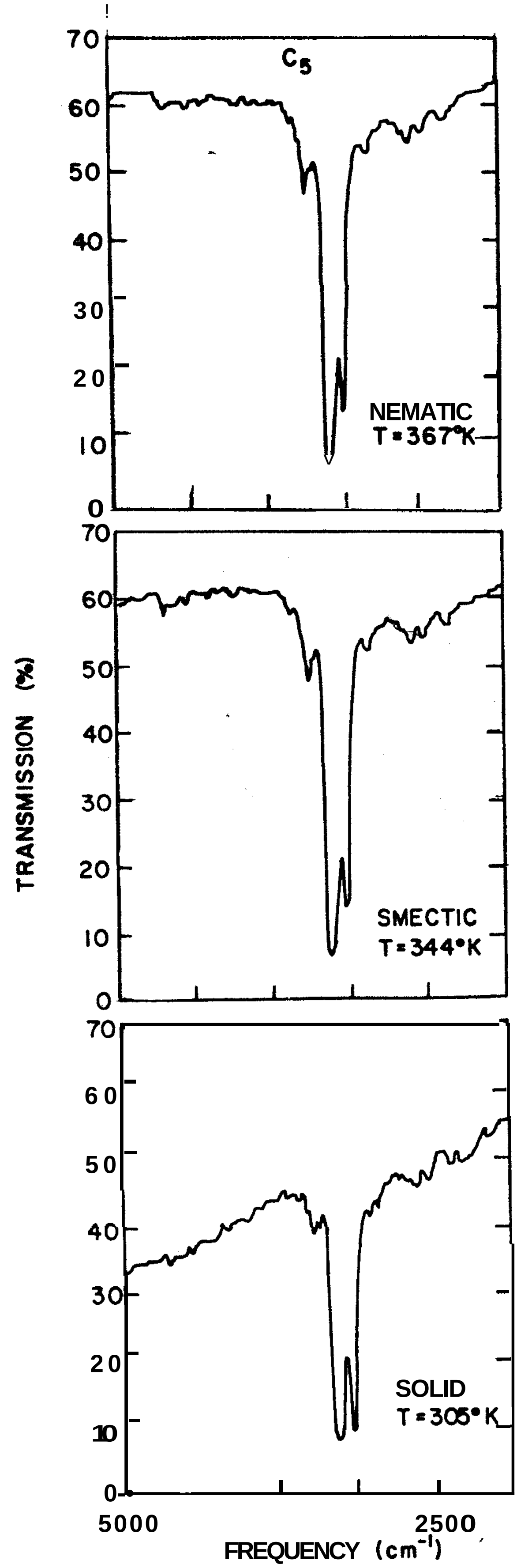
[redacted]going observations suggest the fluid-like of the molecular dynamics in the smectic phase identified here.

The infrared spectrum of the solid phase showed a pronounced baseline slope in the 3000 - 5000 cm^{-1} region (figure 5.6). This is a general feature of the infrared spectra of polycrystalline solid samples and is due to scattering by the crystallites in the short wavelength region. The slope disappeared in the two mesophases. Furthermore, the IR transmission in this spectral region was significantly higher than in the solid phase. These observations indicate the gross liquid-like feature of the mesophase in question.

High pressure studies of the PAA series[18] is also consistent with the assumption of a highly ordered smectic phase intermediate between the solid and nematic phases.



C5
NEMATIC
T = 367°K
SMECTIC
T = 344°K
SOLID
T = 305°K
TRANSMISSION (%)
FREQUENCY (CM⁻¹)
0
20
40
60
1600
1400
1200
1000
900
800


C5
NEMATIC
T=367°K
SMECTIC
T=344°K
SOLID
T=305°K
TRANSMISSION (%)
FREQUENCY (cm-1)
5000
2500
70
60
50
40
30
20
10
0

Based on our DSC and thermal microscopy data, the different transition temperatures (in K) of C_5 can be represented as follows:

$$\text{solid} \underset{333}{\overset{341.5}{\rightleftharpoons}} \begin{array}{c}\text{Highly}\\ \text{ordered}\\ \text{smectic}\end{array} \underset{345}{\overset{349.5}{\rightleftharpoons}} \text{nematic} \overset{396.2}{\longleftrightarrow} \text{isotropic.}$$

Compared to C_5, the ΔH values of the Sm-N transition in C_6 - C_{10} are all an order of magnitude smaller.[1,19] The smectic phase of all these higher homologues is of the less ordered C type; also it is only a monotropic transition in C_6.[10] In view of this, the occurrence of an enantiotropic, highly ordered smectic phase in C_5 points to a distinctly anomalous behaviour of this mesogen.

(d) <u>Thermodynamics of the solid-mesophase transition</u>

In the solid crystalline phase the alkyl end-chains of the C_5 molecules are expected to be in the fully extended, trans conformation.[5] From proton NMR studies[20,21] it is seen that the spectral second moment, $\overline{(\Delta H)^2}$ in the smectic phase of C_5 is comparable to that in the nematic phase, but much smaller than that in the crystalline phase. This indicates that considerable intramolecular motions are permitted in the smectic phase although these are quenched in the crystalline phase. On this basis, a closer scrutiny of the thermodynamic data suggests a plausible mechanism underlying the solid-smectic transition of C_5. The observed entropy of transition is $(7.8 \pm 0.4)R$, where R is the gas constant. Based on the NMR results, 19 nearly all [redacted] can be attributed to the liberation of degrees of freedom and the sum of the newly accessible molecular configurations is denoted by Ω, the total entropy would be given by $R \ln \Omega$. Thus Ω would be of the order of 2400. The only parts of the molecule which can give rise to such a large number of configurations are the flexible alkyl end-chains, where each C – C bond can exist in either the trans or two gauche states about the preceding C – C bond. Including the relative orientations of one end-chain with respect to the other, this leads to Ω values[22] in the range of $3^6 - 3^7$, the resultant entropy change being 6.6 – 7.7R. Although this is a qualitative estimate, it does serve to demonstrate that acquisition of configurational entropy by the two end-chains of the molecules can be a major contributory factor to the observed entropy of this transition. On this basis, the enthalpy of the transition per methylene group turns out to be ~ 2.4 kJ/mole. This value is also in agreement with that observed for other aliphatic 'chain melting' transitions.[23]

5.4 Conclusion

Calorimetric and optical texture studies supported by infrared spectra and NMR data reveal that the phase exhibited by 4,4'-di-n-pentyloxyazoxybenzene (C_5), in the temperature range 341.5 K - 349.5 K on the heating cycle, is a highly ordered enantiotropic smectic phase, hitherto believed to be a solid modification. This represents an anomalous behaviour as the next five homologues, C_6 - C_{10}, do not exhibit such a highly ordered smectic phase. It is shown that configurational melting of the alkyl end-chains of the molecules can largely account for the observed thermodynamic parameters of the solid-smectic transition of C_5. Further studies are required to determine the precise nature and type of the smectic phase exhibited by this mesogen.

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