CHAPTER VI

LIQUID CRYSTALS OF DISO-LIKE MOLECULES

6.1   Introduction

It has long been recognised that the distinctive feature of thermotropic liquid crystals formed by pure compounds is the rod-like or lath-like shape of the molecule. Brooks and Taylor[1] have found that, when the organic precursors to coke and graphite such as petroleum and coal tar pitches are subjected to severe thermal cracking, aromatic polymerisation occurs to build large, flat, polynuclear aromatic molecules. Zimmer and White[2] have also observed similar aromatic polymerisation to yield polynuclear aromatic molecules. According to their study, when the molecular weights approach 1500 around 450°C the molecules condense to form what has come to be known as the carbonaceous mesophase.[3] "This carbonaceous meso- phase thus appears to be a lamellar liquid crystal in which space is filled by plate like molecules which may vary in size and shape but tad to pack in parallel arrays."[2] Further the mesophase transformation occurs at high tempe- ratures, usually la the range of 400 to 500°C. Chemical studies[1] have indicated that the freshly formed mesophase consists of planar aromatic molecules ranging appreciably

in molecular weight but with typical values around 2000.

The carbonaceous mesophase displays the conventional characteristics of liquid crystals such as alignment of the molecular layers with a substrate surface or with a magnetic field. Also, the carbonaceous mesophase has only a transient existence in the temperature range in which its plastic properties are evident. As temperature is increased, the viscosity steadily rises as the reaction of aromatic polymerisation continue between the molecules in the layered configuration, eventually producing a hardened coke with the mesophase microstructure frozen in place. Thus, this mesophase transformation is an irreversible reaction that proceeds from the isotropic phase to the liquid crystal phase with increasing tempe-rature. Therefore, the carbonaceous mesophase is a liquid crystal consisting of plate-like complex molecules and which certainly cannot be regarded as single component liquid crystalline system.

## 6.2 Preparation of disc-like mesogens

With a view to exploring the possibility of obtain-ing thermotropic mesomorphism in relatively simple plate-like or more appropriately disc-like molecules in pure, single component systems, we prepared a number of benzene hexa-n-alkanoates. These were prepared following the

procedure of Neifert and Bartow.[4] Hexahydroxybenzene
was prepared by the reduction of 2,3,5,6-tetrahydroxy
1,4-benzoquinone following the method described by
Patiadi and Sager.[5] The esters were obtained by heating
six moles of the appropriate acid chloride with one mole
of hexahydroxybenzene. The sequence of reactions carried
out is shown (Chart X). Of the several benzene hexa-n-
alkanoates prepared, only a few exhibited thermotropic
mesophase. Nevertheless, this is the first observation
of such a behaviour in pure single component system. In
order to confirm the purity and structure sf these compounds,
^{13}C-NMR spectra of isotropic solutions of these were taken.
The spectra of two of these are shown in figures 6.1 and
6.2. The ^{13}C shieldings for all the carbons of four
benzene hexa-n-alkanoates are given in table 6.1.

Since this *first* observation,[6] similar disc-like
mesogens have been found by a group of French workers.[7]
They have synthesised several triphenylene hexa-n-ethers (I)
and triphenylene hexa-n-alkanoates (II) which exhibit
thermotropic mesomorphism.

The pure benzene hexa-n-alkanoates mixed with a
small quantity of benzene (up to about 10% w/w) also form
mesophases. These mesophases are somewhat more mobile
than the ones formed by the pure materials. They exhibit
fan-shaped textures and often form spherulites, some of

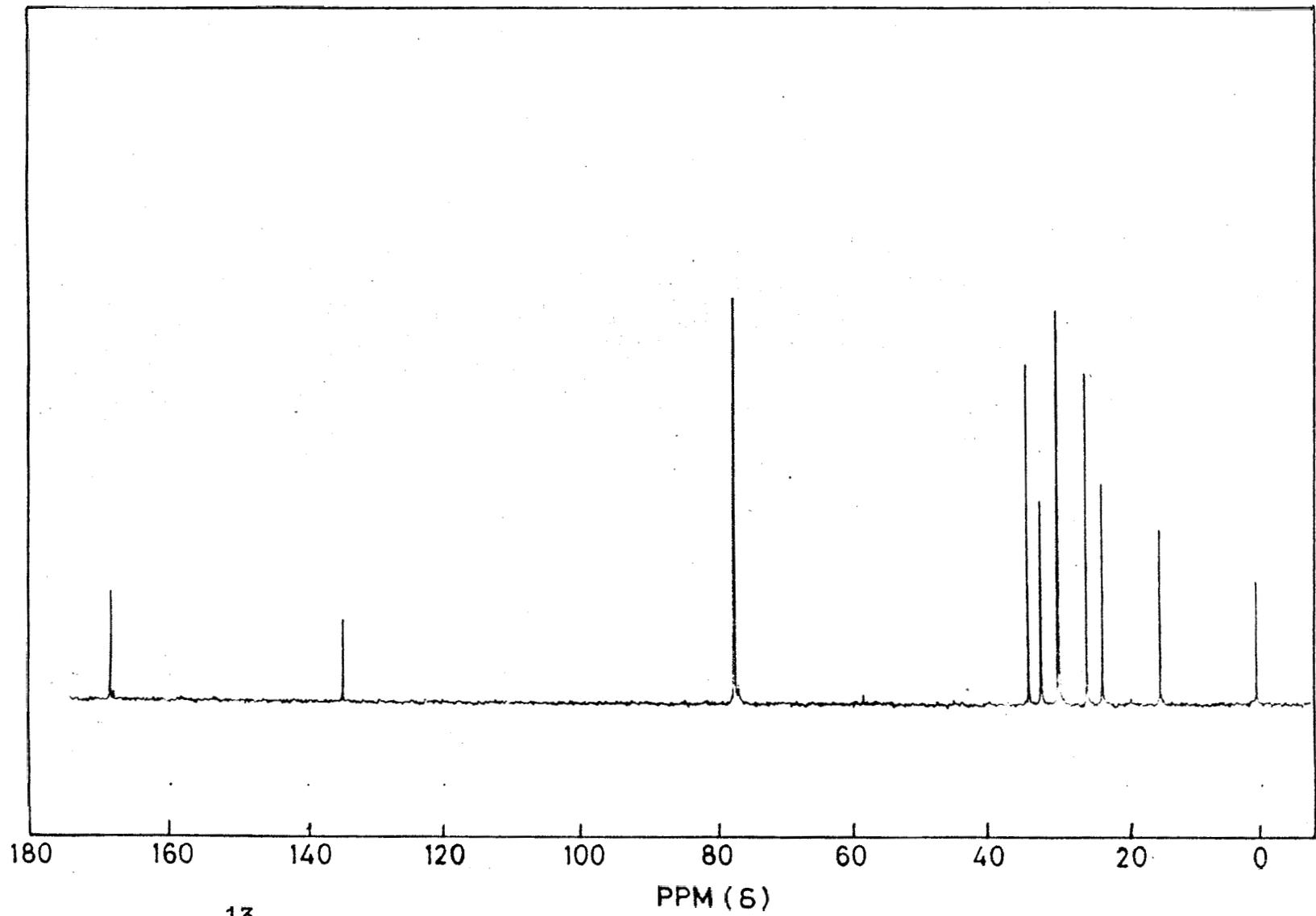# CHART X

HCl / SnCl$_2$

R.COCl / Δ
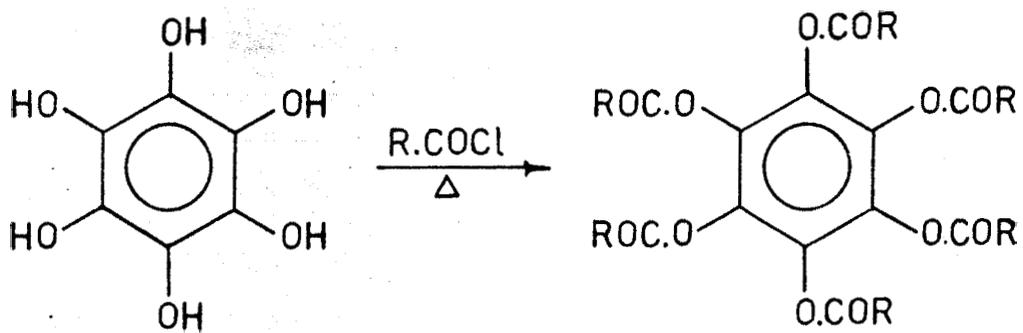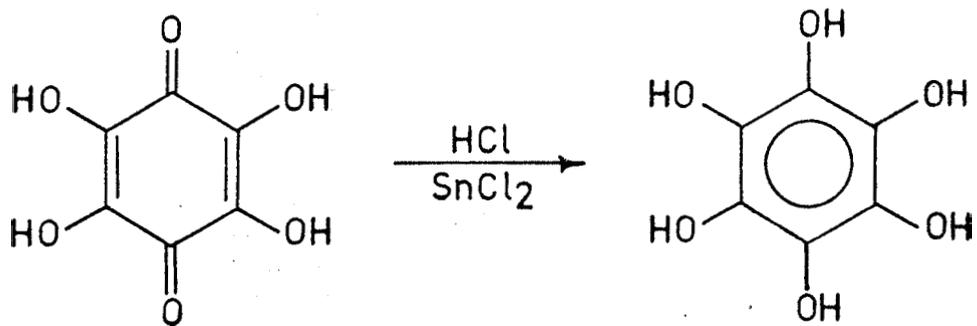
R = n-Alkyl

Figure 6.2: ^{13}C-NMR spectrum of an isotropic solution of benzene hexa-n-nonanoate in CDCl$_3$ with proton decoupling. Chemical shifts relative to TMS.

Table 6.1

Carbon-13 shieldings of some benzene hexa-n-alkanoates δ_C ppm from TMS

Compound	arC	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
Benzene hexa-n-hexanoate	134.7	168.73	33.63	31.28	24.58	22.32	13.85			
Benzene hexa-n-heptanoate	134.69	168.75	33.	31.49	28.83	24.89	22.50	13.98		
Benzene hexa-n-octanoate	134.72	168.75	33.72	31.70	29.16	28.98	24.95	22.67	14.03	
Benzene hexa-n-nonanoate	134.79	168.70	33.76	31.90	29.32	29.20	24.98	24.98	22.69	14.04
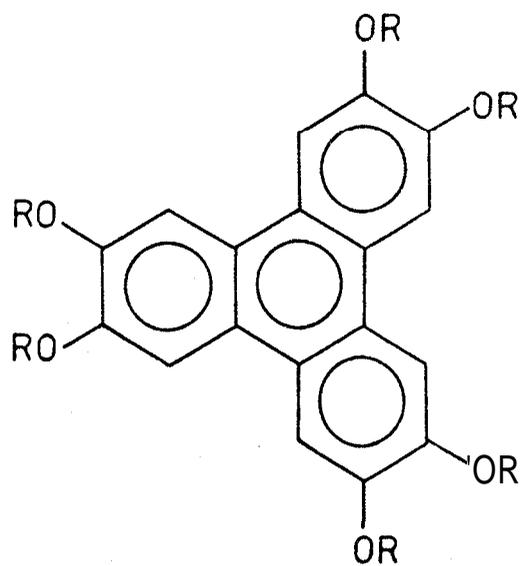
I
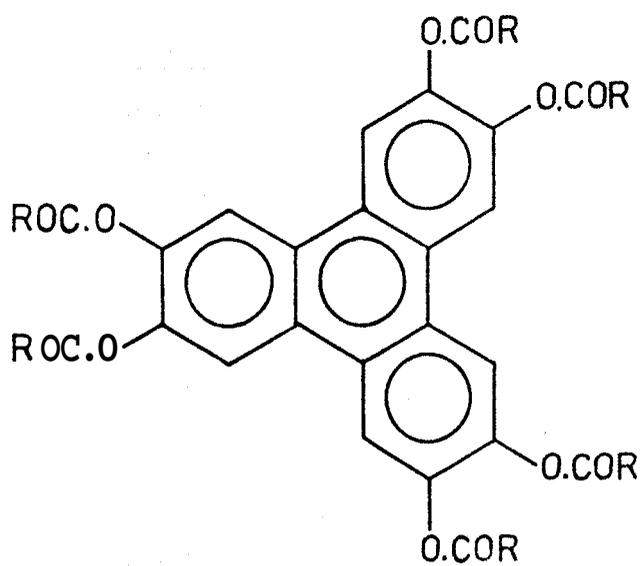
II

R = n-Alkyl

which show interesting growth spirals. X-ray study has shown that mesophase of the mixture is not as highly ordered as that of the pure compound. This is the first example of lyotropic mesomorphism for a disc-like mesophase.

6.3 Thermodynamic properties

After preliminary visual observation of a sample, mounted between a microscope slide and cover slip, as it cooled from the isotropic liquid, the transitions were studied by differential scanning calorimetry using a Perkin-Elmer model DSC2. Only three homologues, benzene hexa-n-heptanoate, benzene hexa-n-octanoate and benzene hexa-n-nonanoate show mesophases. The DSC curves for all the three of them are shown in figures 6.3, 6.4 and 6.5 respectively. The temperatures and heats of transition determined from the curves are given in table 6.2. As can be seen, in the heptanoate and octanoate derivatives there is supercooling of both the isotropic liquid and the mesophase. Supercooling of the isotropic liquid is not surprising in these cases, since the heat of the isotropic-mesophase transition is quite large. This is in contrast to the small heats of transition obtained during the nematic-isotropic and slightly higher values obtained during smectic-isotropic transition in conventional liquid crystals. This suggests a very highly ordered
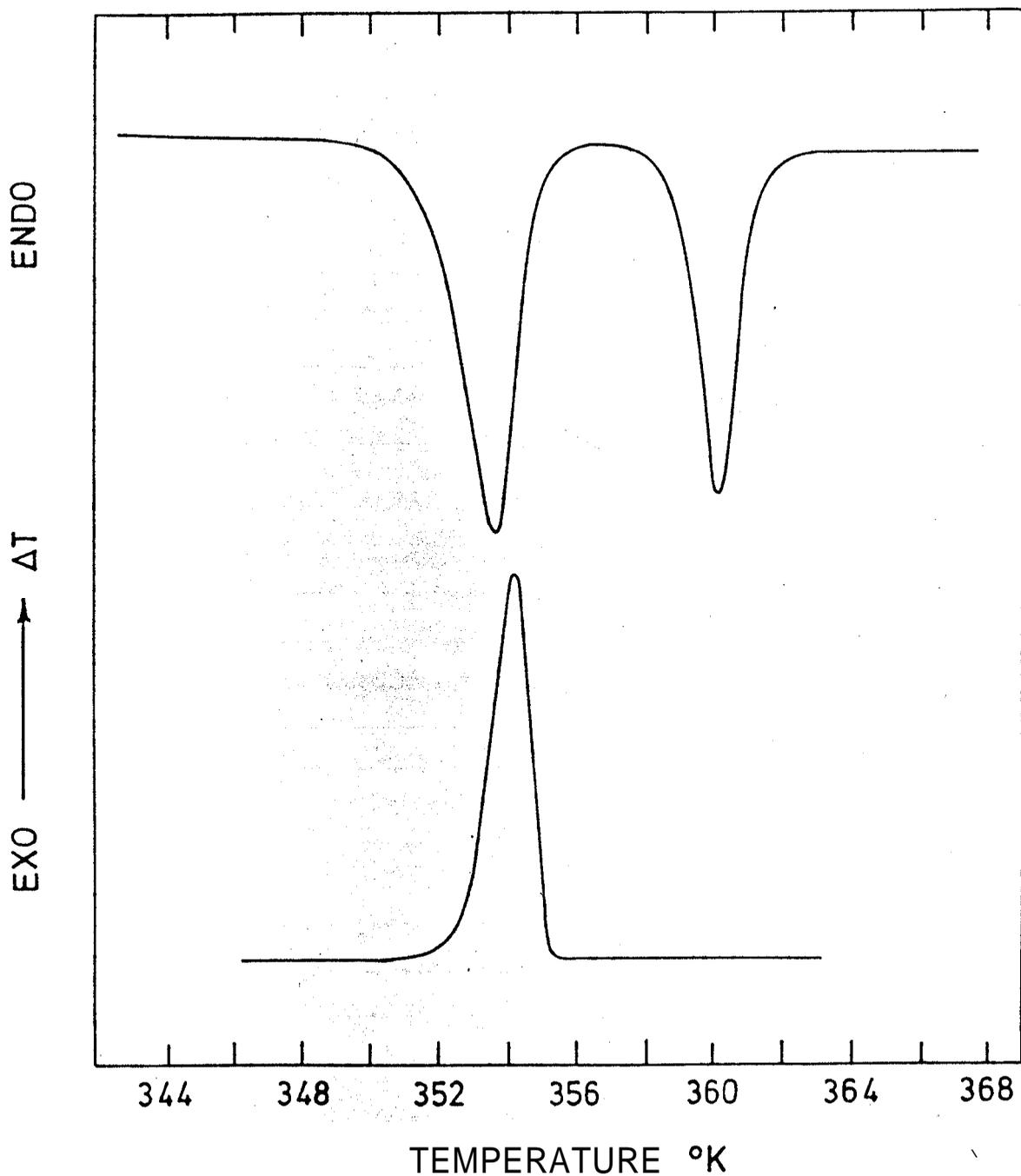
Fig. 6.3: Differential scanning claorimetric curves for benzene hexa-n-heptanoate.
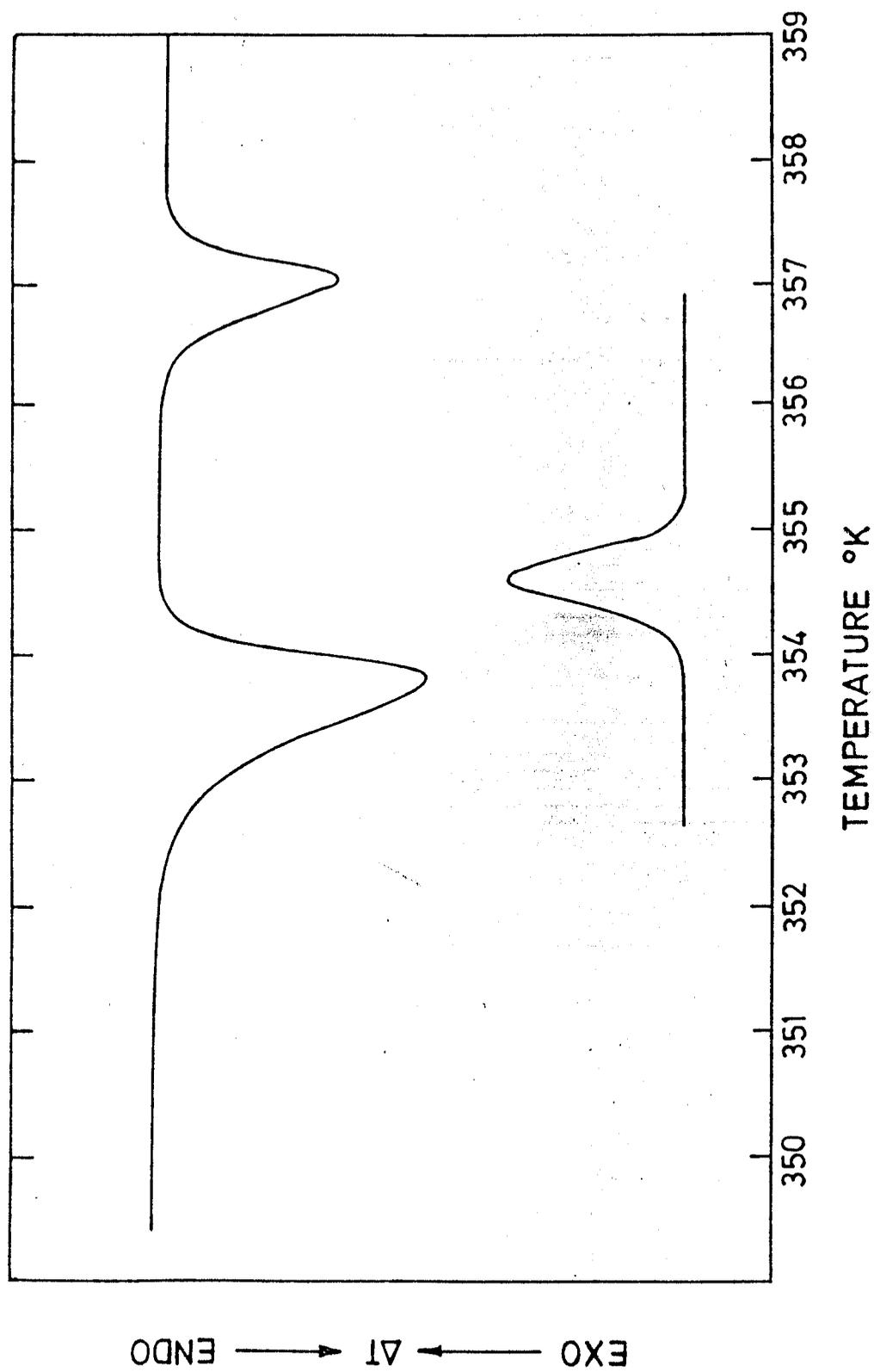
Fig. 6.4: Differential scanning calorimetric curves for benzene hexa-n-octanoate.

Axis labels:
- TEMPERATURE °K (horizontal axis, values 350 to 359)
- ENDO → ΔT ← EXO (vertical axis)

Table 6.2

Transition temperatures and heats of transition of
benzene hexa-n-alkanoates

Compound	Transition		Tempe-rature (°C)	Heat of transition Kcals/mole
Benzene hexa-n-pentanoate	crystal	isotropic	106	6.07
Benzene hexa-n-hexanoate	crystal II	crystal I	75.7	3.8
	crystal I	isotropic	94.5	7.9
Benzene hexa-n-heptanoate	crystal	mesophase	80.5	7.6
	mesophase	isotropic	86.1	5.3
	isotropic	mesophase	83.5	
Benzene hexa-n-octanoate	crystal	mesophase	79.8	10.7
	mesophase	isotropic	83.7	
	isotropic	mesophase	81.8	4.5
Benzene hexa-n-nonanoate	crystal	isotropic	80.5	16.7
	isotropic	mesophase	78.7	3.4
Benzene hexa-n-decanoate	crystal II	crystal I	58.5	10.4
	crystal I	isotropic	85.5	20.7

mesophase, probably smectic-like in character in the
disc-like molecules.

6.4 Optical textures of benzene hexa-n-alkanoates

The transitions could be seen very clearly through
the polarising microscope when the sample was cooled from
the isotropic phase. Typical textures obtained for these
compounds are illustrated in figures 6.6, 6.7 and 6.8.
Sometimes, the mesophase made its appearance as flower-
like particles (fig. 6.6), which on further cooling grew
in size and finally merged together to fill the entire
field of view (fig. 6.7). However, most often the meso-
phase adopted a 'broken-fan' texture similar to that of
smectic C (fig. 6.8), occasionally with striations running
across the fans as in smectics E and F.[8] Optical observa-
tions with the aid of a phase retardation plate confirmed
that the disc-like molecules are oriented with their long
molecular axes (i.e., the diameters of the discs) aligned
radially in the fan and their short axes (or the normals
to the discs) lying in the plane of the sample. Also,
like the smectic phases, the material is highly viscous.

The transition to the solid phase on cooling the
sample was also quite distinctly observable. However, the
change in texture attending the reverse transition, i.e.,
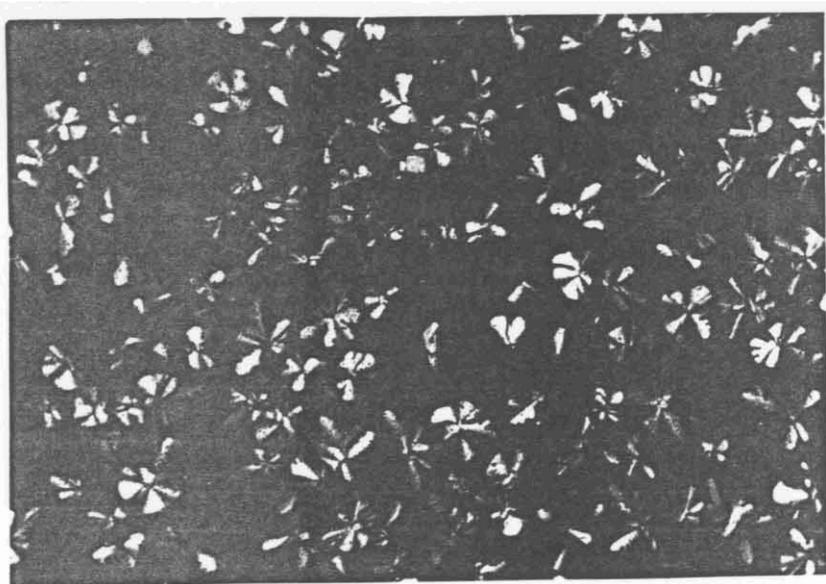when the solid transformed to the mesophase on heating was

Figure 6.6

The mesophase appearing as flower-like particles
on cooling the isotropic liquid

Figure 6.7

On further cooling, the particles grow and merge
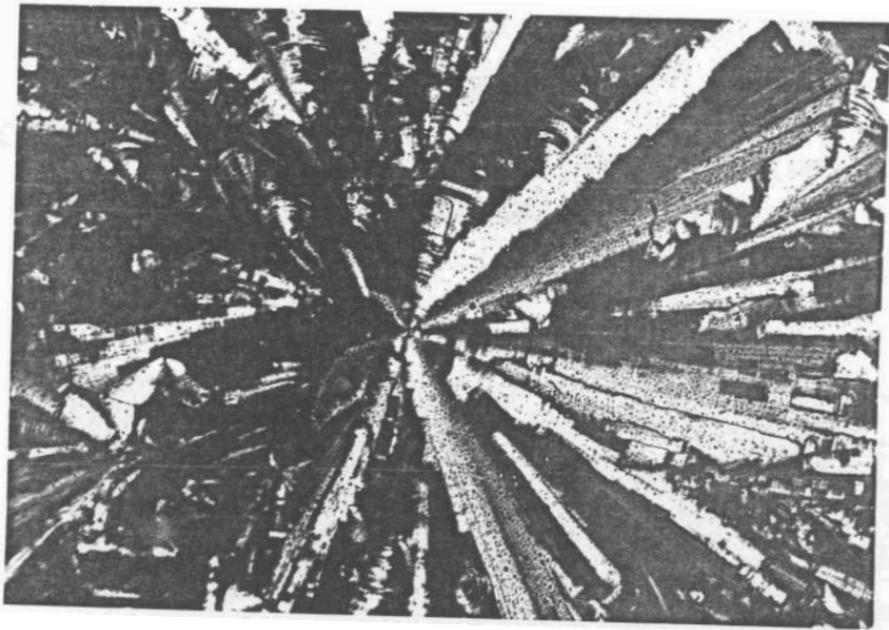together to fill the entire *field* of view.

Figure 6.8

Broken-fan texture of the mesophase.

so slight that it was practically undetectable, but the
DSC curves proved that the two compounds, heptanoate and
octanoate are in fact enantiotropic.

6.5   X-ray studies

X-ray studies[6] have indicated that the mesophase
la not a plastic crystal. A plastic crystalline phase is
obtained prior to melting of molecular solids, whose
constituent molecules have a globular shape.[9] Norbornylene
or [bicyclo(2.2.1)heptene-2], III and its homologues,
norbornane, IV, and norbornadiene, V, form a plastic
crystalline phase which has a hexagonal structure. They
generally possess a cubic crystal structure which is
usually face-centred. Based on our own X-ray diffraction
studies,[6] we have proposed a structure for the mesophase,
in which the discs are stacked one on top of the other in
columns, as shown in fig. 6.9, that constitute a hexagonal
arrangement, but the spacing between the discs in each
column is irregular. Moreover, by analogy with smectic A[10]
one may expect a structure consisting of liquid-like
columns to be readily deformed to give the radiating or
fan-like arrangement of molecules that is observed in the
optical textures.

Recently, Levelut[11] who obtained X-ray diffraction
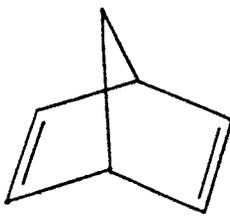patterns from the mesomorphic phase of two derivatives of
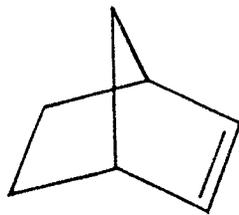
Norbornylene
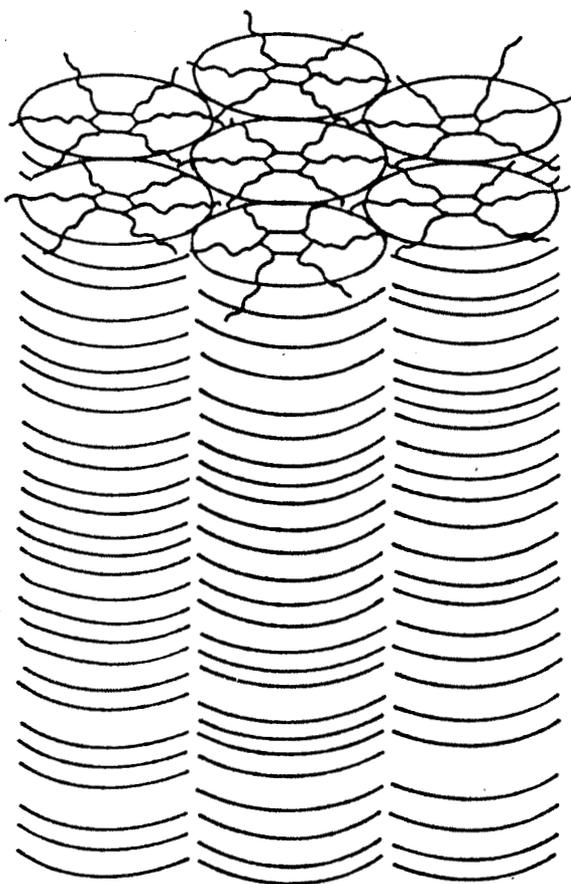
III
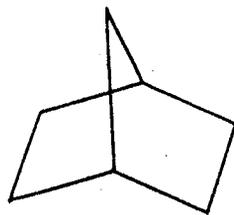
Norbornane

IV

Norbornadiene

V

Pig. 6.9

Schematic representation of the
structure of the mesophase. The
discs are spaced irregularly to
form liquid-like columns.

triphenylene hexa-n-ether (Structure I, $R = C_5H_{11}$ or C_7H_{15}) has confirmed the structure proposed by us; the molecules are stacked in columns and the columns form a regular array.

EXPERIMENTAL

Hexahydroxybenzene

?Ma was prepared following the procedure of
Fatiadi and Sager.[5] Thus, tetrahydroxybenzoquinone
(20.0 g, 0.116 mol) was added to a boiling solution of
stannous chloride dihydrate (200 g, 0.88 mol) in 2.4N
hydrochloric acid (400 ml) contained in a four litre
beaker. Concentrated hydrochloric acid (12N, 500 ml)
was added to the mixture and boiled with constant stirring.
The beaker was removed from the hot plate and concentrated
hydrochloric acid (12N, 1200 ml) was added and the solu-
tion cooled in a refrigerator overnight. The hexahydroxy-
benzene was collected on a sintered glass funnel. This
was recrystallised from a solution of 2.4N hydrochloric
acid (900 ml) and stannous chloride dihydrate (6.0 g)
using decolourising carbon (2.0 g). The white crystals
of hexahydroxybenzene were collected on a sintered glass
funnel under a blanket of nitrogen (15.2 g, 75%) m.p.
$>310°C$ (reported[5] yield 70-77%, m.p. $>310°C$).

Benzene hexa-n-heptanoate

This was prepared following the procedure of
Weifert and Bartow.[4] A mixture of hexahydroxybenzene
(0.348 g, 0.002 mol) and n-heptanoyl chloride (2.673 g,
0.018 mol) was heated in an oil bath at 150°C for six

hours and cooled. The mixture was dissolved in chloroform (100 ml) and washed with 10% aqueous sodium hydroxide solution (3 x 40 ml) and water (2 x 50 ml). The chloroform solution was dried over anhydrous sodium sulphate. Removal of solvent afforded a pale brown material which was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white material which was recrystallised from absolute ethyl alcohol to constant melting point (2.1 g, 88.5%) m.p. 80.5°C; ν_{max}^{nujol} 1770, 1465, 1370, 1216, 1042 and 725 cm^{-1}; δ (CDCl$_3$) 0.81 (t, 18H, 6xCH$_3$) 0.1-2.06 (m, 48H, methylenes) 2.41 (t, 12H, 6xO-C-CH$_2$-)

[Found: C, 68.21; H, 9.32% C$_{48}$H$_{78}$O$_{12}$ requires
C, 68.08; H, 9.21%].

The physical data of the cognate preparations of other benzene hexa-n-alkanoates are given below.

Benzene hexa-n-pentanoate

Yield 83%, m.p. 106°C; ν_{max}^{nujol} 1778, 1470, 1377, and 1220 cm^{-1}; δ (CDCl$_3$) 0.9 (t, 18H, 6xCH$_3$) 1.16-2.03 (m, 24H, methylenes) 2.41 (t, 12H, 6xOOCH$_2$)

[Found: C, 63.54; H, 7.82% C$_{36}$H$_{54}$O$_{12}$ requires
C, 63.71; H, 7.96%].

Benzene hexa-n-hexanoate

Yield 81%, m.p. 94.5°C; ν_{max}^{nujol} 1778, 1470, 1371 and 1018 cm^{-1}; a ($CDCl_3$) 0.93 (t, 18H, $6 \times CH_3$) 1.13-2.06 (m, 36H, methylenes) 2.43 (t, 12H, $6 \times CO.CH_2$)

[Found: C, 66.55; H, 8.90% $C_{42}H_{66}O_{12}$ requires
        C, 66.14; H, 8.72%].

Benzene hexa-n-octanoate

Yield, 83%, m.p. 79.8°C; ν_{max}^{nujol} 1778, 1470, 1376, 1210, 1135, 1005 and 724 cm^{-1}; δ ($CDCl_3$) 0.91 (t, 18H, $6 \times CH_3$) 1.1-2.0 (m, 60H, methylenes) 2.43 (t, 12H, $6 \times COCH_2$)

[Found: C, 69.51; H, 9.62% $C_{54}H_{90}O_{12}$ requires
        C, 69.67; H, 9.67%].

Benzene hexa-n-nonanoate

Yield 74%, m.p. 80.5°C; ν_{max}^{nujol} 1778, 1470, 1360, 1208, 1098 and 722 cm^{-1}; δ ($CDCl_3$) 0.91 (t, 18H, $6 \times CH_3$) 1.06-2.01 (m, 72H, methylenes) 2.43 (t, 12H, $6 \times COCH_2$)

[Found: C, 71.06; H, 10.43% $C_{60}H_{102}O_{12}$ requires
        C, 71.05; H, 10.05%].

Benzene hexa-n-decanoate

Yield 79%, m.p. 85.5°C; ν_{max}^{nujol} 1778, 1468, 1372,

1204, 1090, 1010 and 718 cm^{-1}; δ ($CDCl_3$) 0.9 (t, 18H,

6x$C\underline{H}_3$) 1.06-2.0 (m, 84H, methylenes) 2.4 (t, 12H, 6x$COC\underline{H}_2$)

[Found: C, 72.32; H, 10.21% $C_{66}H_{114}O_{12}$ requires

C, 72.13; H, 10.38%].

REFERENCES

1. J.D.Brooks and G.H.Taylor, Carbon. 3, 185 (1965).

2. J.E.Zimmer and J.L.White, Mol. Cryst. Liq. Cryst. 38, 177 (1977).

3. J.L.White, Progr. Solid State Chem. 2, 59 (1975).

4. I.E.Neifert and E. Bartow, J.Amer.Chem. Soc. 65, 1770 (1943).

5. A.J.Fatiadi and W.F.Sager, Org. Syn. Coll., Vol. V, 595 (1973).

6. S.Chandrasekhar, B.K.Sadashiva and K.A.Suresh, Pramana 2, 471 (1977).

7. (i) A. Beguin, J.Billard, J.C.Dubois, Nguyen Huu Tinh and A. Zann, J. Physique 40, C3-15 (1979).

   (ii) C. Destrade, M.C.Mondon and J. Malthete, J. Physique 40, C3-17 (1979).

8. H. Sackmann and D. Demus, Mol. Cryst. Liq. Cryst. 21 239 (1973).

9. R. Folland, D.A.Jackson and S.Rajagopal, Mol. Phys. 32, 1053 (1975).

10. S. Chandrasekhar, 'Liquid Crystals', Cambridge University Press, Cambridge (1977) p. 285.

11. A.M.Levelut, J. Physique 40, L-81 (1979).