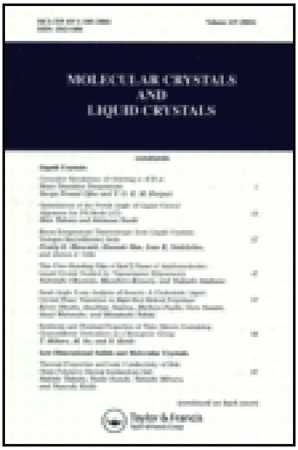

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Phase Transitions in a Discotic Liquid Crystal from ^{13}C NMR

M. Bose [a] & S. Sanyal [a]
[a] Bose Institute, Calcutta, 700 009, India

Version of record first published: 22 Sep 2006.

To cite this article: M. Bose & S. Sanyal (1990): Phase Transitions in a Discotic Liquid Crystal from ^{13}C NMR, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 185:1, 115-130

To link to this article: http://dx.doi.org/10.1080/00268949008038495

Mol. Cryst. Liq. Cryst., 1990, Vol. 185, pp. 115–130
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Phase Transitions in a Discotic Liquid Crystal from ^{13}C NMR

M. BOSE and S. SANYAL
Bose Institute, Calcutta 700 009, INDIA

(*Received October 16, 1989; in final form February 23, 1990*)

^{13}C CPMAS NMR spectra of benzene-hexa-*n*-heptanoate $C_6(OCOC_6H_{13})_6$ have been studied from 150–360 K. Three broad regions corresponding to C═O, aromatic carbon and the alkyl chain (with splittings due to solid state effects) show dramatic variations with temperature, paralleling the configurational and conformational changes and pinpoints the onset of successive group motions in the paraffinic chains. The NMR results are interpreted in terms of a rigid non-planar asymmetric short (C—)H. .O contact, the so-called hydrogen-bonded gauche structure involving $CH_2(2)$ and C═O within a chain between 150–207 K. At 227 K, the CH_3 group is free to rotate but breaks up the intramolecular (C—H) . . .O 'bond' to give a more symmetric structure with the onset of $CH_2(2)$ motion, corresponding to the first-order phase transition observed at 230 K from dTA. Finally at 287 K, an intermolecular (C—)H . . . O 'bond' between $CH_2(6)$ of one molecule and a C═O group of an adjacent molecule stabilizes the columnar structure and leads to a virtually planar molecule (only carbonyl oxygens lying out of the plane) with onset of $CH_2(3)$ motion. This 'hydrogen-bonded' structure is stable throughout the solid phase and the 'bond' is broken only in the mesophase. $CH_2(4)$ motion is evident at 336 K from fine structure in the spectrum. Around 347–348 K, a strong pre-transitional effect viz., aromatic singlet abruptly gives a triplet along with $CH_2(5)$ motion. At 352 K, the aromatic signal is lost in the noise and solid state splittings tend to disappear. At the mesophase (353 K), only narrow lines from alkyl chains are observed with onset of $CH_2(6)$ motion. Interestingly, though shifts of the groups do not change from meso to isotropic phase, line intensities and widths reveal that the part gauche conformer changes to an extended trans conformation, whereupon the isotropic phase is reached at 359 K. In general, the groups are more deshielded in the solid state due to intermolecular interaction effects as compared to that in the isotropic phase.

INTRODUCTION

Since the discovery of discotic liquid crystals by Chandrasekhar *et al.*[1] they have attracted considerable attention. These discotics differ in many aspects from classical rod like mesogens. It is now well recognised[2,3] that apart from the central rigid core (generally aromatic), a dense paraffinic crown with at least six paraffinic chains is necessary for the manifestation of the discotic (columnar) mesophase. Generally, normal aliphatic chains with at least six carbon atoms must be bound to the central aromatic part by either an ether or an ester linkage. Sorai *et al.*[4–6] as early as 1981 have shown that one of the characteristic features of discotic benzene-hexa-n-alkanoates is a rich solid polymorphism, in addition to the liquid crystalline mesophase. ^{2}H NMR[7] as well as ^{1}H and ^{13}C NMR[8,9] studies have been performed in several discotics in order to investigate molecular order and dynamics in the mesophase. More recently, a proton decoupled ^{13}C MAS spectra of the discotic benzene-hexa-*n*-octanoate[10] (BH8) in the isotropic (353 K), liquid crystalline (349 K) and solid (287 K) phases have indicated differences in the structure in the three different phases.

From thermodynamic studies of the homologous benzene-hexa-*n*-alkanoates (Figure 1), Sorai *et al.*[4–6] showed that the solid-solid phase transitions were accompanied by a large amount of transition entropy (58.90 JK^{-1} mol^{-1}) which is 65% of that of the melting entropy (91.08 JK^{-1}) in case of benzene-hexa-*n*-heptanoate (BH7)[5]. Three large endothermic peaks at 230.5 K (solid-solid), 354.7 K (solid-meso) and 359.8 K (meso-isotropic) corresponding to three first-order phase-transitions were observed in a heating run by DTA. The corresponding phase-transitions from heat capacity measurements were at 230.81, 353.79 and 359.28 K respectively.

Sorai *et al.*[4–6] also found that the IR and far IR spectra of benzene-hexa-*n*-alkanoates including that of BH7 were remarkably dependent on temperature. With increasing temperature, there was a smearing effect of the intramolecular vibration modes (in the range of 1500–400 cm^{-1}), mainly arising from the paraffinic chains and a reduction in the number of IR active bands. These results appear to

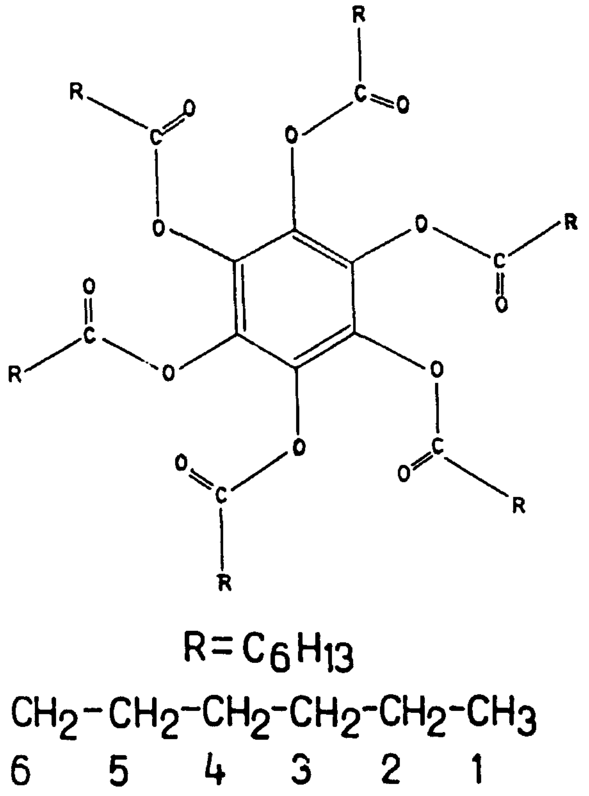

FIGURE 1 Structure of Benzene-hexa-*n*-heptanoate (BH7).

confirm the rich polymorphism observed in heat capacity studies. Drastic changes were observed in the last solid-solid phase transition. However, the IR spectra of the meso and isotropic phases are very similar, which led them to postulate that short-range order effects in the mesophase also persist in the isotropic phase. They regarded the sequential phase-transition in the solid state, as successive phase-transitions involving increased conformational disorder in the paraffinic moities (chains) attained through gauche trans type kinking and suggested that the conformational melting progresses from the periphery of the molecule into it's inside, each time a phase transition takes place.

Though heat capacity and IR studies have unfolded several aspects of the successive phase transitions, being macroprobes, they are unable to throw light on the detailed structural aspects of these transitions. As such, there is the need for a microstructural probe. As a matter of fact, Sorai *et al.*[4] had stated that their model of successive phase-transitions is speculative and NMR or X-ray analysis is needed to test it. X-ray studies over this temperature range would be a Herculean task. In this respect, ^{13}C NMR appears to be an ideal probe, as it is technically feasible to obtain a high-resolution spectra in the solid state at different temperatures for proper comparison with data in the meso and isotropic phases.

Thus in the present work, a very detailed CPMAS (cross polarization-magic angle spinning) ^{13}C NMR study of Chandrasekhar's classic discotic benzene-hexa-*n*-heptanoate was carried out from 150–361 K in an attempt to correlate the solid-solid, solid-meso and meso-isotropic phase transitions with the onset of various types of motion and structural changes in the molecule. It may be pointed out that MAS with high power proton decoupling was unable to produce a high-resolution spectrum of benzene-hexa-*n*-octanoate[10] in the solid state.

EXPERIMENTAL

The ^{13}C CPMAS spectra were recorded on a Bruker CXP-300 NMR Spectrometer in a magnetic field of 7.0463 T and a frequency of 75.46 MHz, equipped with MAS accessories and a B-VT 1000 Temperature Controller. The driving gas was dry nitrogen and the rotation rates were between 2.5 and 4 KHz. 'Single' polarization contacts with contact times of 5 ms were employed using the flip back sequence. Recycle time between acquisitions were 5 s. The acquisition time was 50 ms at a sweep width of 31.125 KHz. Spectra in the solid phase was obtained by accumulating 50 transients, the mesophase with 100 transients and the isotropic phase with 150–500 transients. Temperature was varied from 150–360 K, in steps of 20 K from 150–327 K and at intervals of 1K from 327 K onwards to 361 K.

With the onset of the mesophase, the rigid lattice gave away to a more disordered two dimensional columnar phase, wherein CPMAS became more and more ineffective. Thus at 352 K, the ring carbon line disappeared and at 353 K, both C=O and ring carbon lines vanished. As such, high power proton decoupled ^{13}C spectra were recorded from 352 to 361 K with a much lower spinning speed (of the order of 1 KHz) in which case C=O and ring carbon atom lines reappeared and alkyl chain ^{13}C lines became more intense.

All shifts reported are with respect to TMS as external reference.

STRUCTURE AND CONFORMATION

In the absence of X-ray structural data on BH7 at room and low temperatures, one cannot directly correlate the observed ^{13}C NMR spectra with structural changes in the solid phase. However, it is now well recognised that NMR spectra itself may be employed to throw light on the conformational[11–14] changes in the solid state with rise in temperature leading to phase transitions.

Though the mesophase of BH7 is now established to have a columnar structure in which the discs are arranged one on top of another in an irregular fashion[1] maintaining the hexagonal symmetry, the situation may be quite different in the crystalline state, particularly at low temperatures. In general, the solid has a minimum energy close packed structure, wherein the hexagonal symmetry may be disturbed. Further, it is known that the paraffinic chains may not lie in the plane of the aromatic core. X-ray diffraction study has revealed that for triphenylene esters,[15] the six ester chains are alternatively situated up and down the triphenylene core plane and molecules are associated in pairs. More recently, Heiney *et al.*[3] have shown from X-ray studies that the discotic hexa (hexylthio)triphenylene has a monoclinic structure in the crystalline phase with a fundamental spacing which equals that in the D_{ho} phase. Further, experiments indicate the preferred tendency of alternate hexyl tails to tilt up and down the aromatic core to avoid steric repulsion. Thermal motion of the alkyl chain is also present in the solid state. The tilting of the alkyl chains breaks the reflection symmetry of the molecule.

However, for BH7 to have a compact structure with ester chains up and down, one has to have a gauche configuration of the ester chain and study of models reveals that an intramolecular interaction between $CH_2(2)$ and the polar C=O within a folded chain (if it may be considered as hydrogen-bond like) will stabilize an almost planar ring structure of the ester chain either above or below the core (Figure 2a). The adjacent molecule can then just pack in with the ring chain in the vacant sites and this would lead to a compact structure in the lowest temperature phase, where the molecule with all the ester chains are completely frozen. At higher temperatures, where the chains are not frozen, the situation may be different. The subject of hydrogen bond involving a carbon viz., (C—)H . . . O has been a controversial subject but during the last ten years experimental as well as theoretical evidence for a (C—)H . . . O bond has been forthcoming.[16,17]

Short (C—)H . . . O intermolecular contacts observed by neutron diffraction[16] have been shown to be the effect of electrostatic stabilization over Van der Waals repulsive forces. However, for intramolecular contacts, geometrical and steric considerations become more important and so the intramolecular bond is expected to be weaker than the intermolecular 'hydrogen bond'.

The so-called weak intramolecular 'hydrogen bond' between $CH_2(2)$ and C=O in BH7 is likely to be broken but intermolecular 'hydrogen bond' between C=O group of one chain and $CH_2(6)$ of another chain in an adjacent molecule would stabilize the columnar structure but permit conformational melting of the CH_2 groups in the chains. However, for the solid even in this case, the chains would prefer to have a part gauche conformation (Figure 2b) with respect to the core, though they need not be up and down about the core. The —O—, carbon of C=O

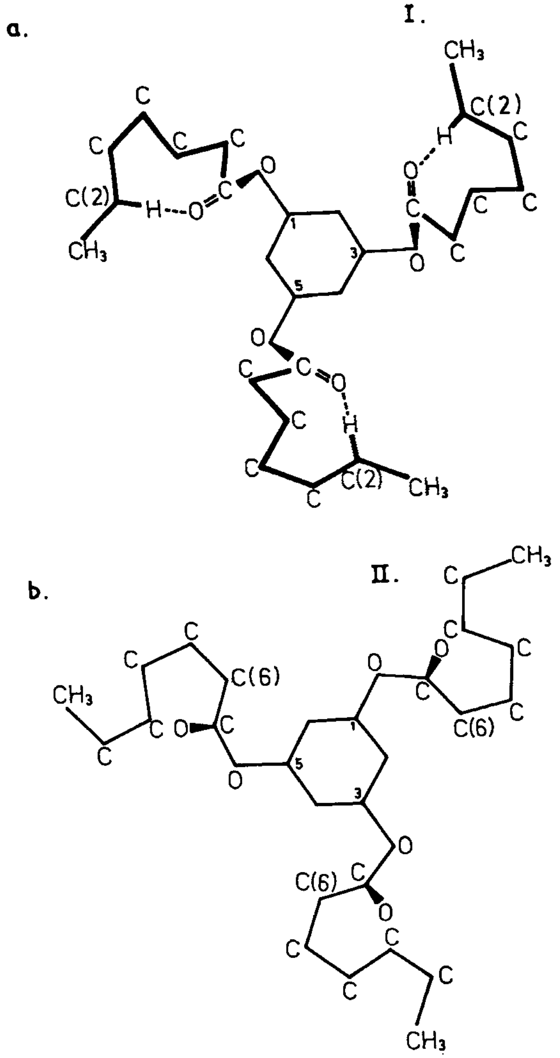

FIGURE 2 Structural models of BH7 (a) intramolecular 'hydrogen bond' I (b) intermolecular 'hydrogen bond' II.

and CH_2 groups may be almost in the plane of the core but of the carbonyl oxygens, three may be above and three below the aromatic core, thus permitting strong interaction between successive disc-like molecules within the column. The C=O groups would then display a trigonal symmetry. This configuration takes care of the $(\text{—}\ddot{O}\text{—}\overset{\overset{\ddot{O}}{\|}}{C})$ lone pair-lone pair repulsion of $\text{—}\ddot{O}\text{—}$ and $\overset{\overset{O}{\|}}{C}$ groups. This would ensure a compact stable structure within the column with freedom of rotation of the remaining CH_2 groups of the paraffinic chains. Possibly only at the mesophase, the intermolecular 'hydrogen bond' involving $CH_2(6)$ is broken, permitting free movement within the column. Finally in the mesophase, the columnar structure gives away and a more random distribution of the discotics with translational motion occurs in the isotropic phase. An attempt to correlate the NMR spectra with the above model is made below:

CPMAS ^{13}C SPECTRA IN THE SOLID STATE

Additional line splittings not observed in solution spectra[18] arise from conformational and crystallographic effects in the solid state. In this case, the different conformers may be locked in position, creating different chemical environments for nominally equivalent carbon atoms leading to line splittings.[11-14] The crystallographic effect[14] arises from the existence of non-congruent molecules in the unit cell resulting in additional line splittings which can be very large and of the same order or larger than that of conformational effects.

^{13}C NMR spectra in the solid, mesophase and isotropic phases of BH7 exhibit dramatic changes in the multiplicity and relative intensities of the resonances of the different carbon atoms particularly near the phase transition temperatures (Tables I–III, Figures 3–5). Three broad regions corresponding to $C{=}O$, aromatic carbon and the alkyl chain (R) exhibit a triplet, doublet and 11 lines with CH_3 triplet respectively at 150 K, corresponding to a completely rigid lattice (cf. singlets for $C{=}O$ and aromatic carbon and 6 lines from C_6H_{13} in solution spectra[18]). The results are in harmony with a non-planar asymmetric short C—H . . . O contact between $CH_2(2)$ and $C{=}O$ (structure I of Figure 2) between 150–207 K. The aromatic doublet clearly points to the fact that the hexad symmetry is lost from (a) tilting of the core due to close packing (b) asymmetry of alkyl chains and/or $C{=}O$ groups (c) asymmetric pairing of the two molecules of BH7. Further if the magnetic field lies along the C_2 axis of the core, four of the carbon atoms would be different from the remaining two, in consonance with the observed intensity of 2:1. Structure I with $C{=}O$ groups above and below the aromatic core gives rise to different chemical shifts, further split by the intramolecular 'hydrogen bond'. In the lower homologue benzene-hexa-*n*-hexanoate (BH_6), IR studies reveal a splitting of $C{=}O$ stretching bond[4] at 1775 cm^{-1} indicating that $C{=}O$ groups are non-equivalent at low temperatures (Phase IV). Similar splittings are also observed in the alkyl spectra but instead of 10 lines from five CH_2 groups only 8 lines are observed due to overlap of C(2) and C(3) as also C(4) and C(5). Further, the small splittings of the CH_3, $C{=}O$ and aromatic carbon reflect conformational effects of this highly symmetric molecule. Crystallographic effects, if present would have been much larger viz., ~3 ppm for CH_3 etc.[19].

At 207 K, restricted rotation[20] of CH_3 group is revealed in the doublet, which becomes free to rotate (singlet) at 227 K (Figure 4). This breaks up the intramolecular C—H . . . O 'bond' to give a more symmetric structure ($C{=}O$ doublet, benzene singlet and 9 lines from C_6H_{13}) with the onset of $CH_2(2)$ motion, corresponding to the first-order phase transition observed at 230 K from DTA.[5] Finally at 287 K, the $C{=}O$ triplet reappears, R gives 11 lines but the aromatic carbon

TABLE I

Structure and motion in $C_6(OCOC_6H_{13})_6$ from ^{13}C CPMAS spectra

T/K	C=O		C_6H_{13}	CH_3	Structure	Motion
150	Triplet	Doublet	11	Triplet	'H-bonded' (Intramolecular)	Rigid
207	Triplet	Unresolved Doublet	10	Doublet	'H-bonded' (Intramolecular)	Restricted rot. of C(1)
227	Doublet	Singlet (S)	9	Singlet	Symm. changes. H-bond breaks	(PT)†, C(2) motion, free rot. of C(1)
287	Triplet	Singlet	11	Singlet	'H-bonded' (Intermolecular)	C(3) motion
336	Triplet	Singlet	10	Singlet	'H-bonded' (Intermolecular)	C(4) motion
347–348	Triplet (T)	Triplet Unresolved	10	Doublet	Symmetry changes	C(5) motion, hindered rot. of C(1)
352	Unresolved Doublet (D)	Lost in noise	7	Doublet		Pre-transition
353	Vanishes	Vanishes	7 C(6) Weak D	Singlet (Weak)	Intermolecular 'H-bond' breaks	Mesophase, C(6) restr. motion, free rot. of CH_3
354			7 C(3) Doublet	Singlet (Intense)		Faster rot. of CH_3 C(2) free, C(3) rigid
358			6 I* of C(3) increases & C(4) decreases	Singlet Intense		C(3)-free motion C(4)-restr. motion
359			6	Singlet Intense		Isotropic phase

*I Intensity
†PT—Phase transition

TABLE II

^{13}C chemical shifts (in ppm) of carbonyl group and aromatic carbons at different temperatures

Temp	C=O	⌬	Temp.	C=O	⌬
150K	171.74 170.81 169.24	135.13 134.24	336K	171.00 169.64 168.86	135.95
177K	171.64 170.70 169.15	135.33 134.33	337K	171.04 169.73	136.05
207K	171.45 170.70 169.00	135.48	338K	171.05 169.78 168.89	136.03
227K	171.20 169.27	135.58	347K	171.06 169.65 168.90	136.70 136.07 135.37
247K	171.08 169.44	135.71	349K	171.10 169.64 168.93	136.23 135.68
267K	171.26 169.46	135.86	350K	169.67 169.07	136.10
287K	171.24 170.49 169.46	135.87	351K	169.69 169.19	136.06
307K	171.17 170.17 169.24	135.95	352K	169.65	almost vanishes
			352K (o.d.)*	169.43 168.37	135.14
327K	171.05 169.87	136.01	353K (o.d.)	167.45	134.27
335K	170.99 169.67	136.01	354K–361K (o.d.)	167.44–167.42	134.27–134.26

*o.d.—only decoupled.

singlet remains unchanged, indicating the formation of an intermolecular C—H . . . O 'bond' (structure II of Figure 2). This bond between $CH_2(6)$ of one molecule and C=O of an adjacent molecule stabilizes the columnar structure and leads to a virtually planar but asymmetric part gauche conformation of the paraffinic chains with respect to the core with onset of $CH_2(3)$ motion. This 'hydrogen bonded' structure appears to persist up to the mesophase as CPMAS is most effective for $CH_2(6)$ from 267–349 K.

After 329 K, intensity of CH_3 tends to decrease but at 335–336 K it suddenly increases but again decreases at 337 K. This change at 336 K is possibly related to $CH_2(4)$ group motion which makes it's effect felt not only on the C=O group, where one gets a well resolved triplet but also on the aromatic carbon which tend to broaden and become slightly more shielded (Table II). At 347–348 K, the

TABLE III

Chemical shifts of ^{13}C lines from C_6H_{13} group at different temperatures

Temp. (K)	Shift in ppm					
	C(6)	C(5)	C(4)	C(3)	C(2)	C(1)
150	35.68,34.79	33.14,31.48	29.08	27.07,25.53,23.27		16.54,15.92,15.44
177	35.85,34.81	33.22,31.52	30.51,29.34	27.06,25.88,23.22		16.55,15.94,15.39
207	35.50,34.98	33.44,31.53	29.53	26.83,25.58,23.24		16.34,15.33
227	34.79	33.38,31.58	29.71,28.68	25.22	23.57	15.25
247	34.79	33.48,31.31	29.84,28.53	25.81,24.94,23.52		15.25
267	34.74,33.43	31.81,29.93	28.69,28.12	25.89,24.70,23.55		15.30
287	34.57,33.36	30.81,29.94	28.74,27.81	25.92,25.20	24.48,23.54	15.29
307	34.37,33.21	30.59,29.88	28.76,27.35	25.89,25.17	24.46,23.51	15.19
327	34.44,33.11	30.49,29.85	28.74,26.98	25.85,25.23	24.05	15.12
335	34.26,32.98	30.36,29.74	28.68,26.80	25.78,25.16	23.89	14.97
336	34.35,33.01	30.39,29.77	28.69,26.83	25.83,25.16	23.89	15.01
345	34.38,32.94	30.33,29.78	28.68,26.69	25.75,25.14	23.82	14.97
348	34.43,33.05	30.41,29.81	28.84,26.78	25.85,25.12	23.94	15.12,14.50
349	34.46,33.05	30.43,29.88	28.88,26.81	25.84,25.08	23.92	15.12,14.60
350	34.49,33.11	30.44,29.88	29.07,26.81	25.10	23.91	15.14,14.59
351	34.03,33.17	32.42,30.72	29.11,26.89	25.13	24.02,23.01	15.16,14.41
352	33.32	32.55	29.31	25.23	23.42	15.33,14.77
353	32.74,31.94	31.11	27.91	23.85	21.86	13.18
354	32.75	30.96	27.86	24.21,23.79	21.83	13.14
355	—	30.97	27.87	23.78	21.83	13.14
356	32.90	31.00	27.90	23.34	21.84	13.15
357	32.56	31.06	27.93	23.84	21.84	13.15
358	32.57	30.97	28.04	24.06	21.84	13.10
359	32.64	30.88	28.02	24.08	21.71	12.97
360	32.72	30.92	28.06	24.07	21.74	12.98

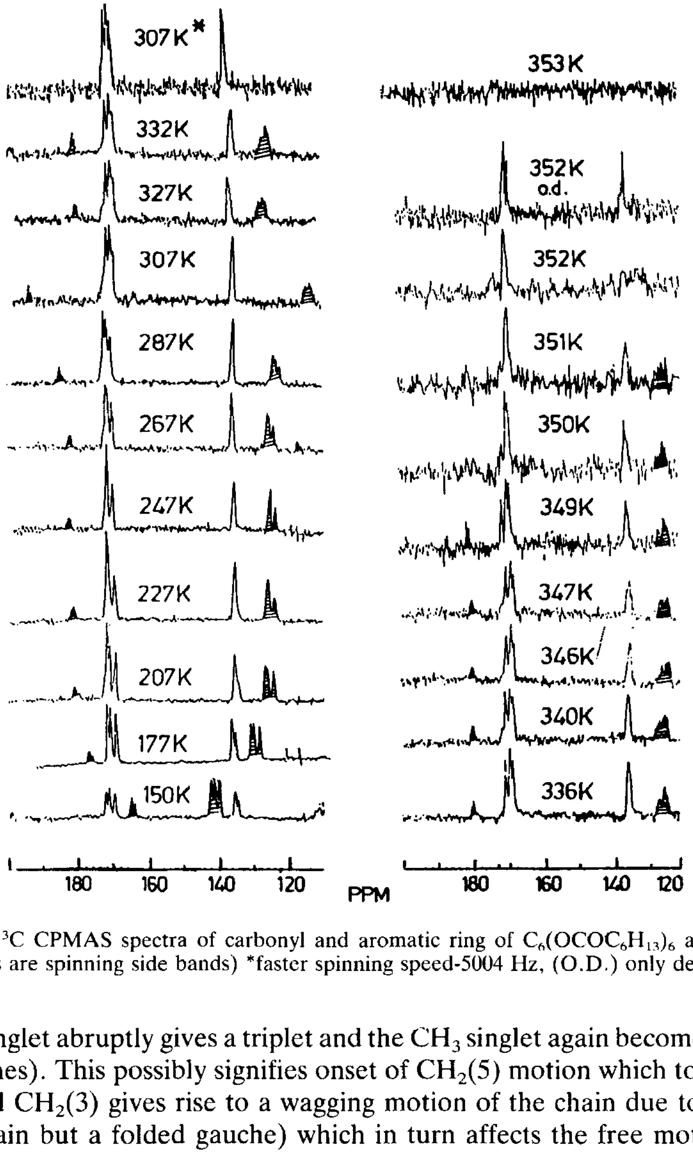

FIGURE 3 ^{13}C CPMAS spectra of carbonyl and aromatic ring of $C_6(OCOC_6H_{13})_6$ at 75.46 MHz. (hatched areas are spinning side bands) *faster spinning speed-5004 Hz, (O.D.) only decoupled.

aromatic singlet abruptly gives a triplet and the CH_3 singlet again becomes a doublet (R = 11 lines). This possibly signifies onset of $CH_2(5)$ motion which together with $CH_2(4)$ and $CH_2(3)$ gives rise to a wagging motion of the chain due to kinks (not a linear chain but a folded gauche) which in turn affects the free motion of CH_3 and also lowers the symmetry of the aromatic core in addition to any tilting of the same. At 351 K, the C=O and the aromatic carbon becomes an unresolved doublet, whereas for C_6H_{13}, resolution of the 11 lines progressively deteriorates.

PRETRANSITION

At 352 K, the aromatic carbon signal is lost in the noise and solid state splittings tend to disappear viz., C=O (unresolved doublet) and C_6H_{13} (7 lines). Interestingly, in the CH_3 doublet, the higher ppm (σ = 15.42) line is more intense from

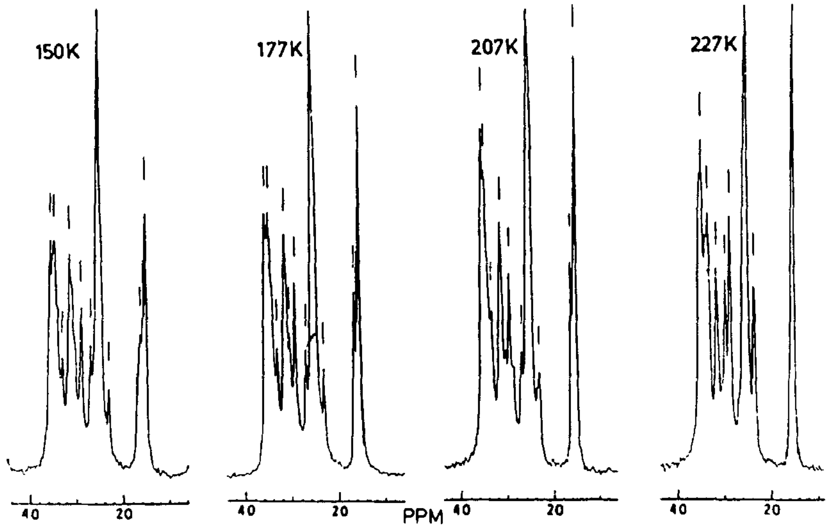

FIGURE 4 ^{13}C CPMAS spectra of the onset of CH_3 group rotation in the rigid chain C_6H_{13}.

347–351 K but at 352 K, the lower ppm signal becomes more intense (Figure 5a), indicating a change in the nature of the potential barrier.[20] As the core aromatic carbons are at large distances from the hydrogen in the aliphatic chains, CPMAS becomes rather ineffective, leading to vanishing of this signal, while C=O which has CH_2 groups in it's proximity is still observed. Thus at 352 K, BH7 presents the picture of a highly disordered solid.

MESOPHASE SPECTRA

That the mesophase is attained within a degree at 353 K is manifest from the sharp lines of the aliphatic chains and the collapse of the CH_3 (Figure 5a) doublet in the CPMAS spectrum due to fluidity of this phase. Of the seven lines from C_6H_{13}, five are singlets of which C(1,2,4,5) are narrow while that from C(3) is rather wide. C(6) gives a very weak doublet. C(4,5) are much more intense than C(2,3), while $CH_3(1)$ is less than half in intensity as compared to C(4,5). In the mesophase, the molecules (discs) have two dimensional order and is free to move in the third dimension in the column. CP effects are thus further reduced and both C=O and ring carbon atom signals vanish, as all intramolecular, intracolumnar or intercolumnar spin transfers are affected by this motion. However, for the proton decoupled (O.D.) spectrum, sharp intense singlets reappear for C=O and aromatic ring carbon atoms, while for C_6H_{13} a narrow seven line spectrum is observed. The appearance of the $CH_2(3)$ doublet (Figure 5b) in the mesophase at 354 K (CPMAS) may be explained as follows: as the intermolecular bonds are broken, the C(3)—C(4)—C(5)—C(6) group which was gauche to C=O (Structure II) tend to assume an extended trans configuration for free rotation. In this rearrangement,

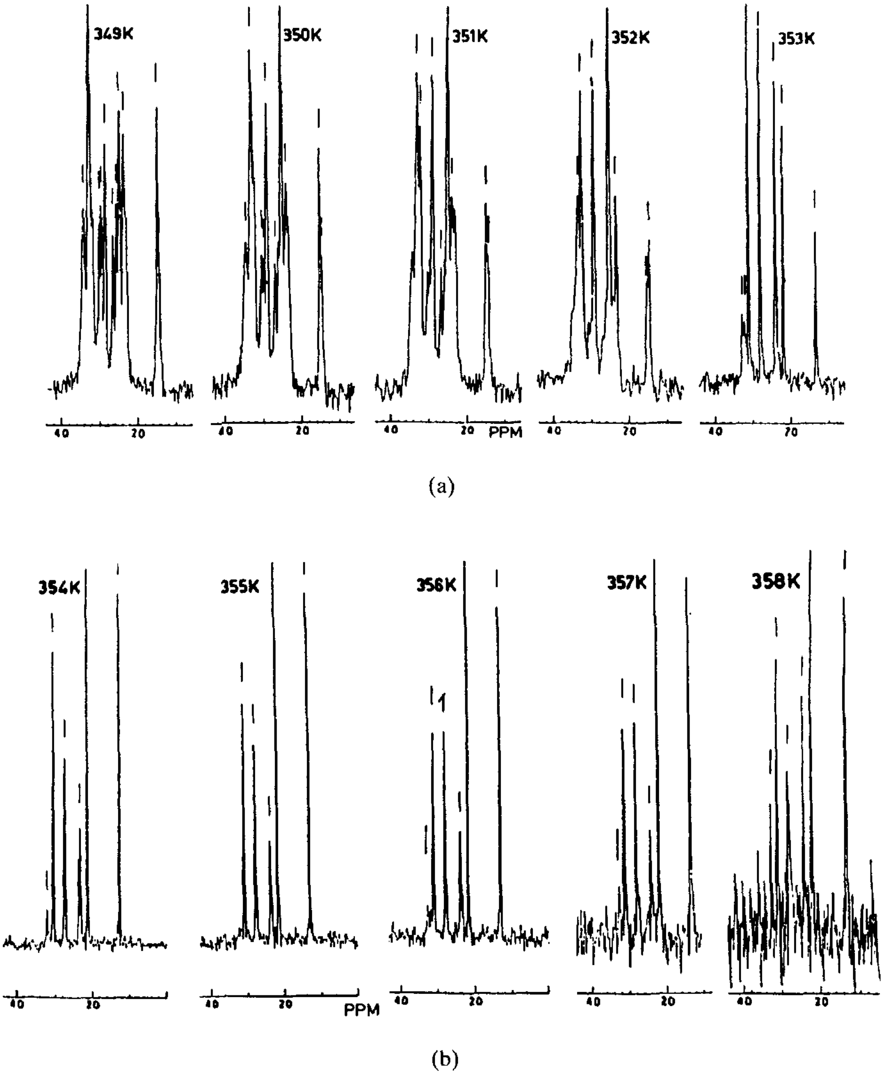

FIGURE 5 ^{13}C CPMAS spectra of C_6H_{13} (a) crystalline to mesophase (b) within mesophase.

the $CH_2(3)$ group acts as a hinge about which $CH_3(1)-CH_2(2)$ rotate. Thus this $CH_2(3)$ acts as a rigid group. This is shown up in the $CH_2(3)$ splitting at 354 K, which still exhibits a seven line spectrum. The free $CH_3(1)$ and $CH_2(2)$ give intense singlets, while a weak doublet is observed for $CH_2(3)$ and not so intense singlets for C(4) and C(5), while C(6) is a very weak singlet.

A sharp change occurs in the spectrum at 355 K, when the seven lines from C_6H_{13} reduce to five lines from C(1–5), while C(6) is lost in the noise and C(3) doublet collapses to a singlet. At 356 K, six lines are observed as C(6) just reappears above the noise but interestingly C(3) remains unchanged in intensity, indicating that it is still not free to rotate. At 357 K, CPMAS becomes still more ineffective and the spectrum is obtained only at a higher gain. However at 358 K, C(3) increases in intensity while that of C(4) decreases abruptly. Apparently C(3) becomes free at this temperature at the expense of C(4), which becomes more rigid. Strangely at 359 K, intensity of C(2) decreases to less than half, C(3) increases somewhat, while 4 and 6 increase but 5 decreases. It appears that at the start of the mesophase at the molecular level, 1 and 2 become free but 3 becomes rigid, whereas midway through the mesophase 4, 5 become free due to segmental motion. Later 3 becomes free but again affects the motion of 1, 2 and 4. Finally, the chain completely unfolds into an extended trans conformation as the isotropic phase is reached (above 359 K), when only the extended chain is free to move as a whole. Thus in O.D. at 359 K all the six lines are quite intense. At 360 K in CPMAS, intensity of all the lines increases (only at a higher gain), though CH_3 singlet is the most intense. Thus one has virtually free motion in the isotropic phase.

CHEMICAL SHIFTS

As expected, the changes in chemical shifts reveal structural and conformational changes, as also the dynamics of the system. Thus for the first order phase change at 227 K, the C=O triplet gives a doublet, aromatic carbon doublet a singlet and subtle changes occur in C_6H_{13} (Table II & III). Thus CH_3 and C(6) doublets changed to more shielded singlets, but C(4) singlet goes over to a doublet and the three overlapping lines from C(2) and C(3) give separate single lines for C(2) and C(3), corresponding to the break-up of Structure I and onset of C(2) motion. The large deshielding at 150 K (~4.3 ppm) of C=O as compared to the isotropic phase parallels that observed in p alkoxy benzoic acids (~5 ppm)[14] from hydrogen bonding. Thus this shift also supports the intramolecular 'hydrogen bonded' Structure I. The same subtle changes occur when Structure II is being formed at 267–287 K. Thus C(6) singlet again reverts to a doublet and C(2) and C(3) give doublets. At 336 K, C(4) motion marginally affects the CH_3 shift (15.01 ppm). Further, onset of $CH_2(5)$ motion at 348 K splits the CH_3 singlet (14.97 ppm) into a doublet. Finally at the mesophase, there is a sudden change in the shifts (~1.5 ppm) of all the alkyl carbon atoms as also that of C=O and aromatic carbon atoms. However, from meso to isotropic phase (353–360 K) the shifts are virtually unchanged. This indicates that intermolecular bonds/interactions are broken/removed in the mesophase itself. This is in line with the IR spectra of Sorai and Suga.[5] However, the groups in the isotropic phase are more shielded than that in the isotropic solution of BH7 in $CDCl_3$[18] due to solvent interaction. Thus, shielding in general increases on passing from solid to mesophase/isotropic phase.

As expected, the aromatic carbons are the least affected. Though most shielded at 150 K, after the phase transition at 227 K, the shielding gradually decreases. This may be explained as follows: At the lowest temperature of 150 K, the up and down C=O groups are more deshielded than when they lie in the aromatic core plane. Thus, the normally electronegative C=O group tends to donate electrons to the aromatic core, increasing the shielding of aromatic carbons. But in structure II (287 K) where the carbonyl carbons are in the plane of the core, the shielding decreases (Table II).

DISCUSSION

NMR studies definitely score a point above IR studies, as it throws light on how further disordering effects occur in steps throughout the mesophase, leading to an extended trans configuration in the isotropic phase. This also explains the comparatively large entropy change on passing from meso to isotropic phase due to important structural relaxations, as well as the non-linear change in volume from 353–357 K observed by Smith and Hecke.[21] It may however be pointed out that X-ray studies reveal that the paraffinic chains are not fully extended[1,3,8] in the mesophase in many cases. Thus X-ray data for BH7 indicates a diameter[1] of 22.2 Å, whereas for fully extended chains, the diameter should have been 24.0 Å. VanderHart[22] while studying n-alkanes has noted that librational motion of the chains produces an apparent bond distance shortening and bond angle widening.

In this connection, it would be relevant to compare our HRNMR results on BH7 with the recently reported ^{2}H and ^{13}C wide line NMR of specifically labelled benzene-hexa-*n*-hexanoate (BH6)[23] in various solid phases. Here also, the spectra exhibit dynamic line shapes which change discontinuously at the phase transitions. As in our case, the results have been interpreted in terms of sequential 'melting' of the side chains in going from the low temperature phase IV to I. Proton decoupled ^{13}C NMR of enriched C=O in phases IV–II indicated a rigid C=O (an axially symmetric powder line), whereas in Phase I a biaxial spectrum was attributed to a fast dynamic process. Further, chain dynamics were studied from BH6 deuterated at the different CH_3 and CH_2 sites and ^{2}H NMR splittings were studied from 250 K (Phase IV) to phase I. Phase IV corresponded to the rigid phase observed in BH7 at around 150 K. On going to phase III, a more structured spectra was observed and was interpreted in terms of jumps of CH_2 groups between two sites. Phase II could not be fitted by a simple two site jump model (interacting chain system in our case) and Phase I exhibited complicated dynamics. Though ^{2}H NMR does give information on dynamics, one has to bear in mind that the electric field gradient in BH6 is composed of a static and a dynamic part. Thus when CH_3 motion sets in, not only is the electric field gradient affected at the CH_3 site but it affects other CH_2 sites also, though they may be still rigid. Similar is the case, when other CH_2 group rotation/jumps occur. Thus Lifshitz *et al.*[23] observed that at the different phases, all the CH_2 groups show changes and were thus unable to detect the stepwise melting of the chains, as observed by us. Basically then, the results do support the stepwise conformational melting mechanism proposed by Sorai *et al.* Only in our model (Figure 2) the lowest temperature phase has a gauche structure, whereas Sorai *et al.*[4] assumed an extended trans configuration.

CONCLUSION

Thus NMR studies not only corroborate the rich polymorphism in the crystalline phase but strongly points to the presence of hydrogen-bonded asymmetric gauche structures I and II. Apart from static structure, it reveals interesting aspects of dynamic effects. Thus it pinpoints onset of group motion from outer CH_3 to the innermost CH_2 (Table I) and correlates the structural transitions involving breaking and forming of (C—)H . . . O 'hydrogen bonds' with observed phase transitions. Further, NMR studies indicate that for a number of CH_2 group melting, no heat change is evident (no DTA peak), but thermal energies are sufficient to melt CH_2 in a chain. However, when a 'hydrogen bond' involving a CH_2 group is broken, DTA peaks involving large entropy changes are evident leading to phase transitions. Finally, the changing segmental motion within the paraffinic chains in the mesophase seen for the first time is very revealing, pointing to the need for the intermediate mesophase.

Thus NMR upholds the picture of conformational melting, progressing from the periphery of the molecule into it's inside but in a complicated manner. Though $CH_3(1)$ melting is followed by C(2) and later C(3) and C(4), the melting of C(5) before the mesophase possibly gives rise to steric repulsions between columns resulting in core tilting (triplet splitting of aromatic carbon) and causing restriction to free CH_3 rotation (appearance of a doublet). Further, at the mesophase along with increased fluidity the gauche paraffin chain (II) rearranges step by step to a trans configuration (non-linear volume change from 354–357 K) leading to the isotropic phase.

Acknowledgements

Our thanks are due to Prof. M. Sorai for kindly providing the BH7 sample and to Dr. M. Ziliox of Bruker Analytische Messtechnik, Karlsruhe for help in recording the NMR spectra. This work is supported by the Council of Scientific and Industrial Research, Govt. of India.

References

1. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, **9**, 471 (1977).
2. C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984).
3. P. A. Heiney, E. Fontes, W. H. de Jeu, A. Riera, P. Carroll and A. B. Smith, III., *J. Phys. France*, **50**, 461 (1989).
4. M. Sorai, K. Tsuji, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, **59**, 33 (1980).
5. M. Sorai and H. Suga, *Mol. Cryst. Liq. Cryst.*, **73**, 47 (1981).
6. M. Sorai, H. Yoshioka and H. Suga, *Mol. Cryst. Liq. Cryst.*, **84**, 39 (1982).
7. D. Goldfarb, E. Lifshitz, H. Zimmerman and Z. Luz, *J. Chem. Phys.*, **82**, 5515 (1985).
8. M. Vilfan, G. Lahajnar, V. Rutar, R. Blinc, B. Topic, A. Zann and J. C. Dubois, *J. Chem. Phys.*, **75**, 5250 (1981).
9. V. Rutar, R. Blinc, M. Vilfan, A. Zann and J. C. Dubois, *J. Phys.*, Paris, **43**, 761 (1982).
10. C. L. Khetrapal, S. Raghothama, N. Suryaprakash and A. C. Kunwar, *Liquid Crystals*, **3**, 413 (1988).
11. G. R. Hays, R. Huis, B. Coleman, D. Clague, J. W. Verhoeven and F. Rob, *J. Am. Chem. Soc.*, **103**, 5140 (1981).
12. C. A. McDowell, A. Naito, J. R. Scheffer and Yiu-Fai Wong, *Tetrahedron Letters*, **22**, 4779 (1981).
13. D. K. Dalling, K. W. Zilm, D. M. Grant, W. A. Heeschen, W. J. Horton and R. J. Pugmire, *J. Am. Chem. Soc.*, **103**, 4817 (1981).
14. G. R. Hays, *J. Chem. Soc. Perkin Trans. II*, 1049 (1983).
15. M. Cotrait, P. Marsau, C. Destrade and J. Malthete, *J. Phys.*, **40**, L-519 (1979).
16. R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, **104**, 5063 (1982).
17. T. Banerjee and S. Chaudhuri, *Can. J. Chem.*, **64**, 876 (1986).

18. S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusudana, S. Kumar, R. Shashidhar and G. Venkatesh, *J. Phys.*, **40**, C3-120 (1979).
19. G. E. Balimann, C. J. Groombridge, R. K. Harris, K. J. Packer, B. J. Say and S. F. Tanner, *Phil. Trans. R. Soc. London*, Ser. A., **299**, 643 (1981).
20. J. E. Anderson, P. A. Kirsch and J. S. Lomas, *J. Chem. Soc., Chem. Commun.*, 1065 (1988).
21. T. H. Smith and G. R. Van Heche, *Mol. Cryst. Liq. Cryst.*, **68**, 23 (1981).
22. D. L. VanderHart, *J. Magn. Reson.*, **44**, 117 (1981).
23. E. Lifshitz, D. Goldfarb, S. Vega, Z. Luz and H. Zimmermann, *J. Am. Chem. Soc.*, **109**, 7280 (1987).