Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Multinuclear NMR studies of lead(II) soaps II. ^{13}C and ^{1}H studies of solid and liquid-crystalline phases

G. Feio[a]; H. D. Burrows[b]; C. F. G. C. Geraldes[b]; T. J. T. Pinheiro[b]
[a] Centro de Física da Matéria Condensada (CFMC), Lisboa Codex, Portugal [b] Departamento de Química, Universidade de Coimbra, Coimbra, Portugal

To cite this Article Feio, G. , Burrows, H. D. , Geraldes, C. F. G. C. and Pinheiro, T. J. T.(1991) 'Multinuclear NMR studies of lead(II) soaps II. ^{13}C and ^{1}H studies of solid and liquid-crystalline phases', Liquid Crystals, 9: 3, 417 — 432
To link to this Article: DOI: 10.1080/02678299108045575
URL: http://dx.doi.org/10.1080/02678299108045575

LIQUID CRYSTALS, 1991, VOL. 9, NO. 3, 417–432

Multinuclear NMR studies of lead(II) soaps

II. ^{13}C and ^{1}H studies of solid and liquid-crystalline phases†

by G. FEIO
Centro de Física da Matéria Condensada (CFMC), Av. Gama Pinto, 2,
1699 Lisboa Codex, Portugal

H. D. BURROWS*, C. F. G. C. GERALDES and T. J. T. PINHEIRO
Departamento de Química, Universidade de Coimbra,
3049 Coimbra, Portugal

(*Received 19 July 1990; accepted 29 September 1990*)

The solid and liquid-crystalline phases of two long chain lead(II) carboxylates have been studied by ^{13}C and ^{1}H NMR spectroscopy. High resolution ^{13}C NMR spectra of the solid phase of lead(II) decanoate and octadecanoate, reveal splittings of the peaks attributed to the carboxylate and adjacent methylene groups. This may result from two different environments for the carboxylate chains coordinated to the same Pb(II) ion. On going from the solid to liquid-crystalline or liquid phases, this splitting is lost, and small changes in chemical shift of the bands due to the methyl and methylene groups are observed. These are attributed to the onset of conformational disordering, and analysis of the data gives a gauche population in good agreement with that from Raman spectra and theoretical calculations. Longitudinal ^{13}C relaxation times are reported. From these, and from spectral data, the $-CH_3$ group is seen to have different dynamics from the rest of the chain, and to retain high mobility even in the solid phase. Further information on the structural changes comes from proton NMR spectroscopy. The transverse ^{1}H relaxation of lead(II) decanoate shows two components, which are suggested to arise from a crystalline, and a relatively amorphous region of the compound. Study of the evolution of these as a function of temperature shows that the amorphous fraction is relatively low up to 335 K, but then increase rapidly, until at 365 K, close to the transition to the L_α phase, it is 99 per cent. In parallel to these observations, changes in band shape were also observed and suggest a progressive fusion of the chains up to the temperature of this transition. The global ^{1}H spin–lattice relaxation was also studied as a function of temperature, and two components were observed between room temperature and approximately the first phase transition. These are associated with populations of hydrogen nuclei with different mobilities.

1. Introduction

Apart from their industrial importance [2], the long chain carboxylates (soaps) of heavy metal ions like lead(II) possess interesting phase behaviour. The study of this can be informative on the behaviour of more complex lipid systems. The straight chain lead(II) carboxylates having up to twelve carbon atoms show two mesophases between

---

* Author for correspondence.

† Reference [1] is considered as Part I of this series.

the solid and isotropic liquid, whilst the longer chain homologues show only one [3–7]. The high temperature mesophase observed with the shorter chain members has been assigned a lamellar L_α (smectic A) structure, whilst the low temperature mesophase in these systems, which is the only intermediate phase observed with the long chain lead(II) soaps is suggested to have a highly ordered three dimensional lamellar structure based on ionic layers [7]. Although an alternative assignment is that this is a solid phase [5], the fact that it can be sheared, and that the transition from the L_α or liquid phase to this one shows little supercooling suggest that it is not a truly crystalline phase [7]. Different polymorphic forms of the solid phase can, however, be observed in some cases on recrystallization and on cooling from a melt [7].

Whilst X-ray powder diffraction studies suggest that the solid phase consists of all-trans carboxylate chains arranged orthogonal to planes containing Pb^{2+} ions [5–8], it has not yet proved possible to produce single crystals suitable for detailed structural analysis. High resolution, solid state NMR spectroscopy provides a powerful alternative strategy for determining atomic environments in these systems, and high resolution, high power decoupling, cross polarization, magic angle spinning (HPD, CP, MAS) ^{207}Pb NMR spectra have been reported for two lead(II) carobxylates at room temperature [1]. These showed similar behaviour, with a single metal ion coordination site, and the spectra showing modest shielding anisotropy.

High resolution, solid state ^{13}C NMR spectroscopy is also a valuable way of probing structures of paraffin type systems [9], and the present study applies this technique to two representative lead(II) soaps. In addition, the study of both ^{13}C and ^{1}H NMR spectral and relaxation data as a function of temperature provides a useful means of following, at a molecular level, the processes involved in the phase transitions in these systems. ^{1}H NMR spectral behaviour has been reported for mesophase formation in a number of anhydrous alkali metal [10–18], thallium(I) [19], and copper(II) [20] carboxylates, and the application of ^{13}C NMR studies to the problem of polymer dynamics is well documented [9]. The value of metal ion NMR studies in these systems has been demonstrated by results on sodium [21, 22], thallium(I) [19], and lead(II) [1] soaps, and our ^{207}Pb NMR studies on lead(II) carboxylates have shown that the ordered smectic phase, designated KM in [7], gives a broad signal, comparable to that of the solid phase, whilst the lamellar L_α and liquid phases show fairly sharp, apparently isotropic signals [1]. These results, associated with AC impedance measurements [23], suggest that the onset of significant motion of the cation only occurs on formation of the L_α phase in the shorter chain soaps and the liquid in the longer chain homologues. Further, the ^{207}Pb chemical shifts are very sensitive probes of coordination environment [24, 25], and although the observed signals are temperature dependent [1], there appear to be no major changes in metal ion coordination environment associated with the phase transitions. There are minor changes in ^{207}Pb chemical shifts at the phase transitions [1], but these are most probably associated with changes in paramagnetic shielding. Here we study the effect of temperature on the ^{13}C and ^{1}H resonances to obtain information on changes occurring in the hydrocarbon region.

2. Experimental

The preparation, purification and characterization of the lead(II) carboxylates have been described elsewhere [6, 7]. Although elemental analysis on one of the samples of lead(II) octadecanoate used in this study was not very satisfactory, no significant differences were observed between the spectral behaviour of this and purer samples.

Various NMR techniques were used to study the ^1H and ^{13}C signals of these compounds. The majority of experiments were carried out on a Bruker CXP 100 spectrometer in the Laboratory of Physical Spectroscopy of the University of Grenoble. High resolution ^{23}CNMR spectral of solids were measured in a superconducting coil at 25 MHz using normal HPD, CP, MAS techniques. The study of transverse (T_2) and longitudinal (T_1) proton relaxation was made at 60 MHz in an electromagnet using a high power, variable temperature probe. Field stability was maintained using an external deuterium lock. The ^{13}C high resolution NMR spectra in solids were obtained at 60°C using 3 kHz rotation at the magic angle, a contact time of 1 ms, and high power, proton decoupling. Carbon T_1 measurements for each peak were made using the method of Torchia [26]. Chemical shifts were determined using adamantane ($\delta = 843{\cdot}72$ ppm relative to TMS) as a secondary reference. Global T_1 measurements of ^1H as a function of temperature were carried out on lead(II) decanoate using the inversion–recovery technique. The evolution of the longitudinal magnetization of the protons was followed globally by the amplitude of a solid echo at 10 μs after the inversion–recovery sequence to compensate for the dead-time of the receiver (10 μs) [27]. The relaxation was observed on-field (i.e. with zero off-set) to eliminate all modulation in the signal. The signal was studied without quadrature and digitized with a dwell time of 4 μs to allow a rigorous analysis of the initial part of the proton relaxation. Any heterogeneities in the field will only affect the form of the signal over long times (*c.* 200 μs), although heterogeneities in magnetic susceptibility due to the sample and its geometry may eventually modulate the relaxation at shorter times. After allowing for all experimental artefacts, the ^1H relaxation time dependence of lead(II) decanoate at room temperature clearly showed the existence of two components, one which decayed rapidly (*c.* 20 μs) and corresponds to a highly crystalline region, and a second which decays much more slowly, and which had still not disappeared at the end of the data acquisition time (16 ms). This slow component revealed the existence of an amorphous region in the sample, where the hydrogen nuclei have a certain mobility. Analysis of this slow component and study of its thermal evolution were carried out in the frequency domain. For this, the proton signal was digitized with a dwell time of 20 μs, which allowed us to obtain a spectral window of 25 kHz for the Fourier transform of only the slowly relaxing component of the protons.

The proton longitudinal relaxation time of lead(II) decanoate was calculated using the MINUIT minimization program of the CERN library, which uses alternatively, with optimization the Simplex, Monte Carlo and Fletcher methods. The numerical data fitting was carried out at the CFMC, Lisbon. For all temperatures below 370 K, it was only possible to fit the experimental points with two exponentials, each with a discrete T_1 value. Above 370 K the relaxation of all the protons in lead(II) decanoate could be fitted to a single T_1 value.

Some variable temperature ^1H and ^{13}C NMR experiments were also carried out in Coimbra using a Varian XL200 spectrometer operating at 200·06 MHz (^1H) or 50·31 MHz (^{13}C). ^{13}C chemical shifts were determined using an external standard of 1,4-dioxane ($\delta = 67{\cdot}4$ ppm relative to TMS [28]). Longitudinal relaxation times of ^{13}C and ^1H were determined on this apparatus using the inversion–recovery method on previously melted and degassed samples. This pulse sequence, schematically represented as $180°\text{–}\tau\text{–}90°\text{–}T_a\text{–}D$, was used with the parameters $10\,\text{ms} < \tau < 40\,\text{s}$, $T_a = 0{\cdot}4$ s for ^{13}C, and $65\,\text{ms} < \tau < 10\,\text{s}$, $T_a = 2$ s for ^1H, and $T_a + D > 5T_{1,\text{max}}$. The measurements were carried out using broadband proton decoupling and NOE, and as such might be considered qualitative. However, there is good agreement between this data and that obtained at Grenoble for similar temperature ranges.

3. Results

3.1. *High resolution ^{13}C NMR spectra*

High resolution HPD, CP, MAS ^{13}C NMR spectra were obtained of lead(II) decanoate and octadecanoate at 60°C. The spectrum observed for the decanoate is shown in figure 1, and the chemical shifts for the different carbon atoms in the two compounds are presented in the table. Assignment of the bands was made by comparison with literature data on related compounds [29–32]. The ^{13}C NMR spectra were also run of the liquid and mesophases for lead(II) decanoate (see figure 2). In the solid phases of both the decanoate and octadecanoate, the bands associated with the carbon atoms closest to the metal ion ($-CO_2$, $-CH_2(2)-$ and $-CH_2(3)-$) appeared as doublets, with the splitting on C(2) greater than that on C(3) in both the decanoate and octadecanoate. The central carbon atoms gave a band with similar chemical shifts in the two compounds, although the resolution of these was, not surprisingly, rather better in the decanoate. The ^{13}C spectrum of the liquid phase was rather simpler than

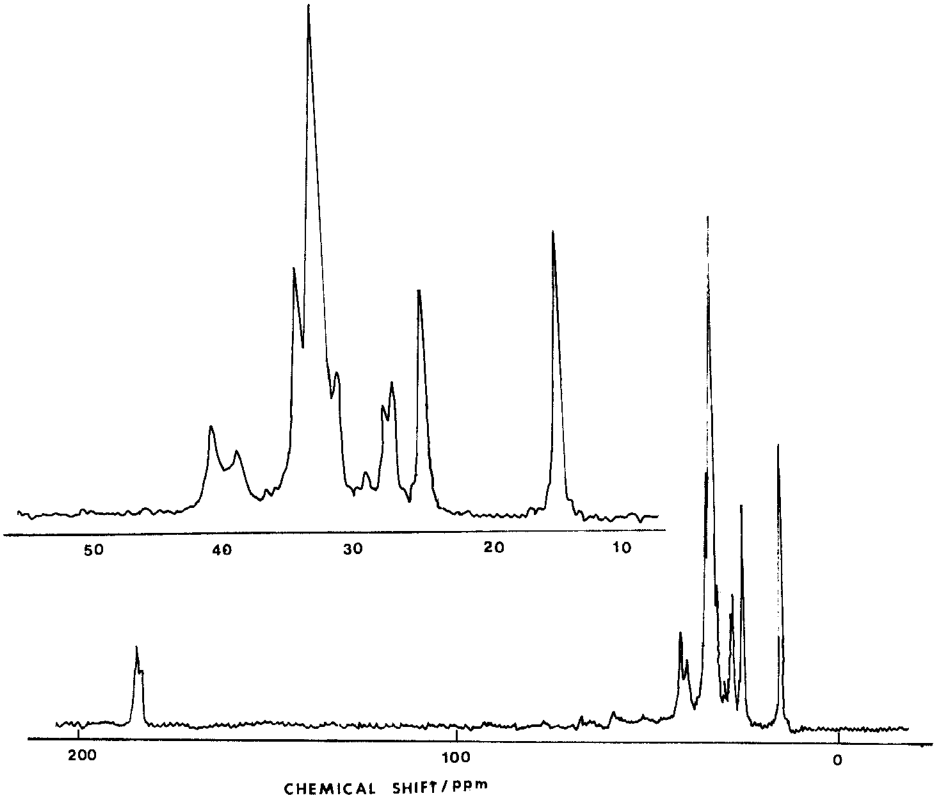

Figure 1. High resolution HPD, CP, MAS ^{13}C NMR spectrum of lead(II) decanoate at 60°C. Inset shows an expansion of the aliphatic chain region.

^{13}C Chemical shifts (*a*) and longitudinal relaxation times for lead(II) decanoate and octadecanoate.

	Lead(II) decanoate										Lead(II) octadecanoate	
	Solid (60°C)(*b*)		Solid (75°C)(*c*)		Mesophase I(*d*)		Mesophase II(*e*)		Liquid (125°C)(*c*)		Solid (60°C)(*b*)	
	δ/ppm	T_1/s	δ/ppm	T_1/s	δ/ppm	T_1/s	δ/ppm	T_1/s	δ/ppm	T_1/s	δ/ppm	T_1/s
$-CO_2$	183·8	—	183·1	—	183·1	—	182·7	—	183·5	—	184·1	—
$-CH_2(2)-$	40·8	349·7	—	—	—	—	40·5	0·5	40·1	0·5	40·8	—
	38·9	70·4									38·7	95·1
$-CH_2(3)-$	27·7	75·4	—	—	25·7	—	25·7	0·9	25·3	0·8	27·6	418·3
	27·1	166·4									27·0	1330·7
$-CH_2^{int}-(f)$	32·7	110·9	30·2	—	29·8	—	30·2	1·1	29·4	1·1	32·8	150·5
	31·3	73·1										
$-CH_2(\beta)-(g)$	34·2	74·8	—	—	31·9	—	31·9	2·3	31·5	2·2	—	—
$-CH_2(\alpha)-(h)$	24·9	54·8	22·8	—	22·0	—	22·0	4·1	22·0	5·1	24·7	25·3
$-CH_3$	14·8	2·1	14·0	1·4	13·6	3·5	14·0	7·7	13·2	10	13·95	1·2

(*a*) Relative to TMS; (*b*) obtained using HPD, CP, MAS; (*c*) obtained using conventional FT NMR techniques; (*d*) ordered smectic; (*e*) L_α (smectic A); (*f*) C(4) to C(7) for decanoate and C(4) to C(16) for octadecanoate; (*g*) C(8); (*h*) C(9) for decanoate and C(17) for octadecanoate.

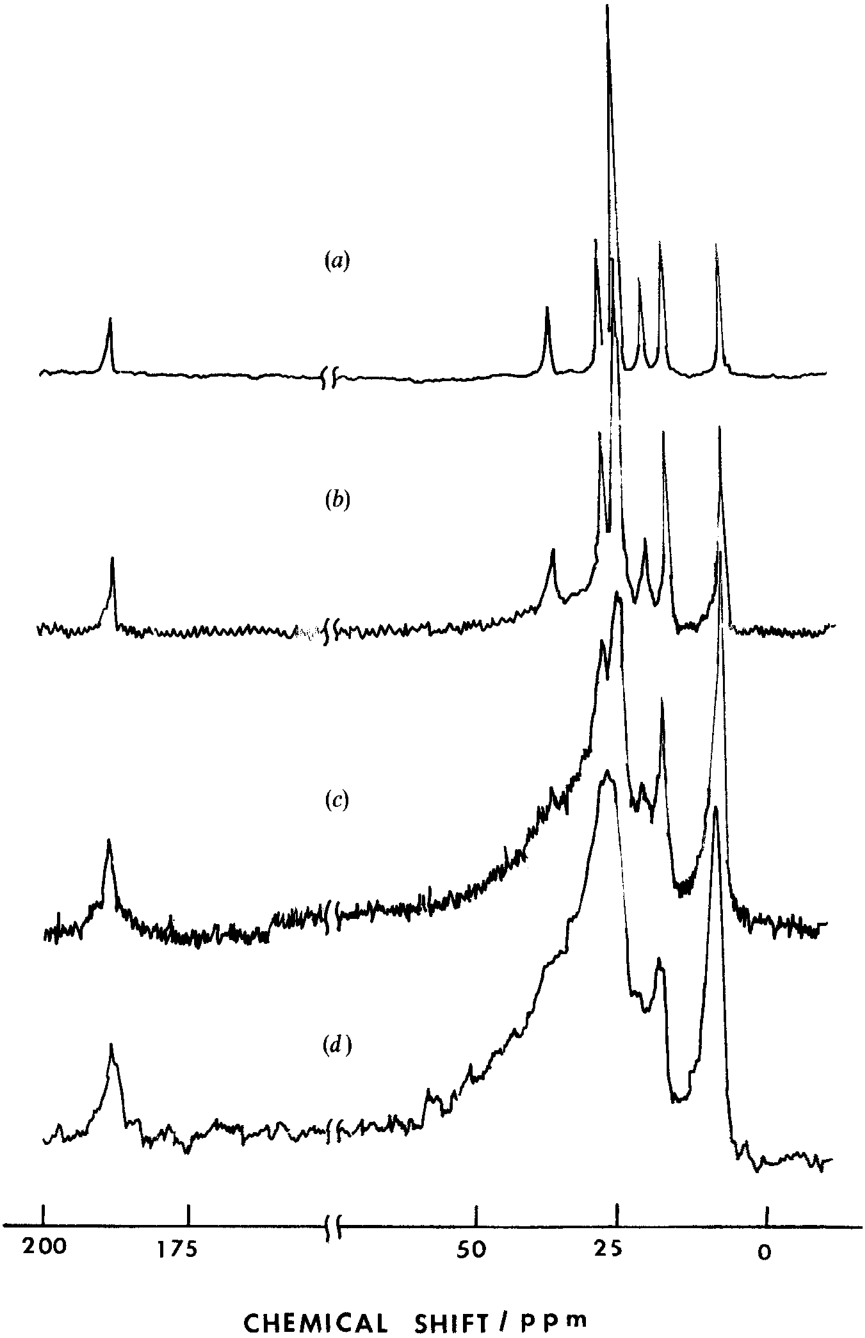

Figure 2. ^{13}C NMR spectrum of lead(I) decanoate at: (*a*) 125°C (liquid); (*b*) 100°C (L_α phase); (*c*) 85°C (ordered smectic phase); (*d*) 75°C (solid phase) obtained using conventional FT NMR techniques.

that of the solid, and did not show any splitting. The chemical shifts of the carboxylate and $-CH_2(2)-$ were fairly similar in the solid and liquid phases. Also, studies of the ^{13}C spectra as a function of temperature on cooling from the liquid to the solid phase (see figure 2) confirmed the lack of significant temperature dependence of the position of the carboxylate peak. However, the other peaks showed a shift of 2–3 ppm on going from solid to liquid. In the variable temperature spectra without HPD, CP, MAS (see figure 2), it is worth noting that although the central peaks collapsed on cooling to the solid, the terminal methyl and adjacent methylene carbon atoms continued to be resolved, suggesting that the tails of the carboxylate chains still have considerable mobility.

Longitudinal relaxation of the different peaks in the high resolution specta of solid lead(II) decanoate and octadecanoate was studied by the method of Torchia [26], and the T_1 values thus obtained are also presented in the table. For comparison, values obtained at Coimbra for the various phases of lead(II) decanoate are included, although in this case for the solid and ordered smectic phases it was only possible to observe relaxation of the terminal methyl group. The methyl group relaxes rapidly in the solid phase of both the carboxylates, which indicates different dynamics and higher mobility compared with those of the methylene groups. This agrees with the above spectral observations. The remaining methylenic carbon atoms, except that adjacent to the $-CH_3$ group, show relaxation times arounf 10^2 s. The rather higher T_1 values observed for the methylenic carbons in the octadecanoate suggest a slower motion of the longer carboxylate chain.

3.2. *Transverse ^1H relaxation of lead(II) decanoate*

At room temperature, the proton signal of lead(II) decanoate, obtained by a solid echo, undergoes a transverse magnetic relaxation process which consists of two well-defined components. The fast component has a characteristic relaxation time of *c.* 10 μs, and is assigned to a crystalline region of the carboxylate. The slowly decaying component, which leads to an adsorption of bandwidth *c.* 10^2 Hz, implies the existence of an amorphous region in lead(II) decanoate where rotational diffusion of the C–C segments is sufficiently important that motional line narrowing occurs. The evolution of this component with temperature was studied by measuring the signal amplitude of the PbC_{10} proton relaxation at 20 μs, taking the highest point of the solid echo as the time origin. Under these conditions, the signal due to the crystalline fraction has virtually completely decayed. To allow for temperature effects on the amplitude, its value at the origin was normalized to 100. On increasing the temperature progressively, four distinct regions of growth of this amorphous fraction were observed (see figure 3). For convenience, transition temperatures as observed by DSC are also included in this diagram. Between room temperature and 335 K, the fraction of the mobile protons increased very slowly, and was never more than 25 per cent (zone A). However, after a melting–solidification cycle this percentage increased to about 30 per cent, probably due to polymorphism in the solid phase as suggested by other techniques [7]. Above 335 K, a second region was observed (zone B), where the amorphous fraction increased sharply, until at around 357 K it reached 70 per cent. In this region effects resulting from the thermal history of the sample disappeared. After a short steadying of the rate of growth, the amorphous component continued to increase markedly, until it reached 99 per cent at 365 K (zone C). Above this temperature the movements of the different protons associated with the chains are sufficiently rapid, and have enough degrees of freedom, that in zone D the NMR method cannot distinguish between them.

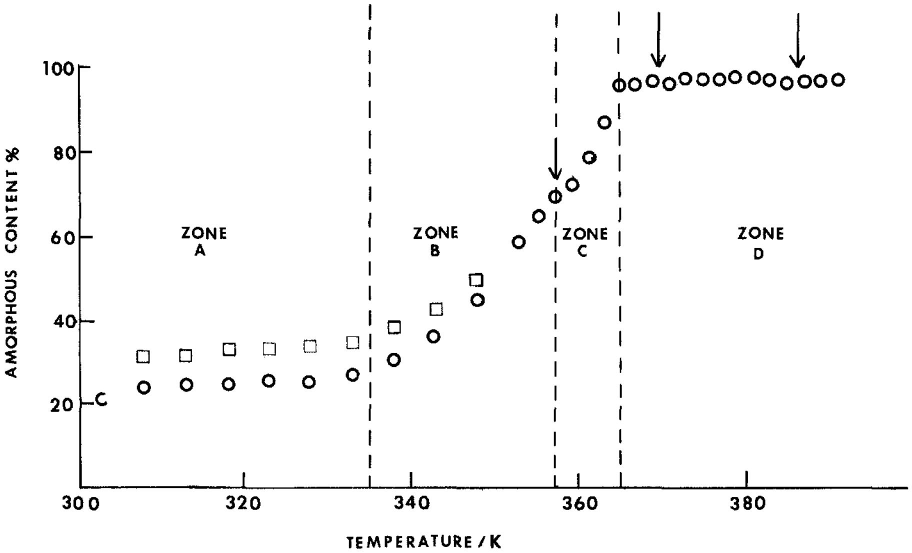

Figure 3. Amorphous content of lead(II) decanoate as a function of temperature obtained from the initial amplitudes of the two components of transverse ^1H NMR relaxation of lead(II) decanoate for fresh (circles) and premelted (squares) samples. The phase transitions observed by DSC are indicated by arrows.

In parallel to the observation of the thermal behaviour of the amorphous region by its amplitude in the ^1H transverse relaxation curve, the corresponding changes in the band shape for this fraction were also analysed as a function of temperature. At room temperature, the resonances of the mobile protons of PbC_{10} give an unresolved band having three components at increasing fields, associated, respectively, with the groups $-CH_2(2)-$, $-CH_2(3\text{–}9)-$ and $-CH_3$ (see figure 4(*a*)). The peak width at half height is around 100 Hz, which indicates a marked motional narrowing. The unequivocal presence of a shoulder corresponding to the $-CH_2(2)-$ resonance appears to imply that the amorphous fraction is composed, at least in part, by whole molecules of lead(II) decanoate which cannot be incorporated into the crystal lattice. The presence of such amorphous regions has previously been suggested by ^1H NMR studies on some sodium and caesium soaps [18]. The other part of the PbC_{10} signal could be due to terminal $(CH_3(CH_2)_x-$ regions of the molecules in the crystalline component, where there is already significant movement, as confirmed by longitudinal relaxation (T_1) measurements. In zone A of the evolution of the amorphous fraction between 304 and 335 K, there are no significant alterations in the spectrum. In zone B between 335 and 357 K, where the amorphous fraction increases, the spectra show that the central band keeps its shape and width, although it increases in area, while the side bands, particularly the lower field one ($-CH_2(2)-$), keep roughly the same area (see figure 4 (*b*)). These observations suggest that the increase in amorphous phase in this temperature range results from progressive activation of conformational interconversions in the aliphatic chains, without, however, reaching the polar region. The carboxylate, adjacent methylene group and an undetermined part of the chain remain relatively immobile, and lead the system to retain the lamellar order, which is stabilized by the ionic forces involved in the Pb^{2+}–carboxylate interactions. Zone B, therefore, seems to involve progressive fusion of the aliphatic chains from the methyl group in the direction of the polar region, but without introduction of any significant disorder in the internal

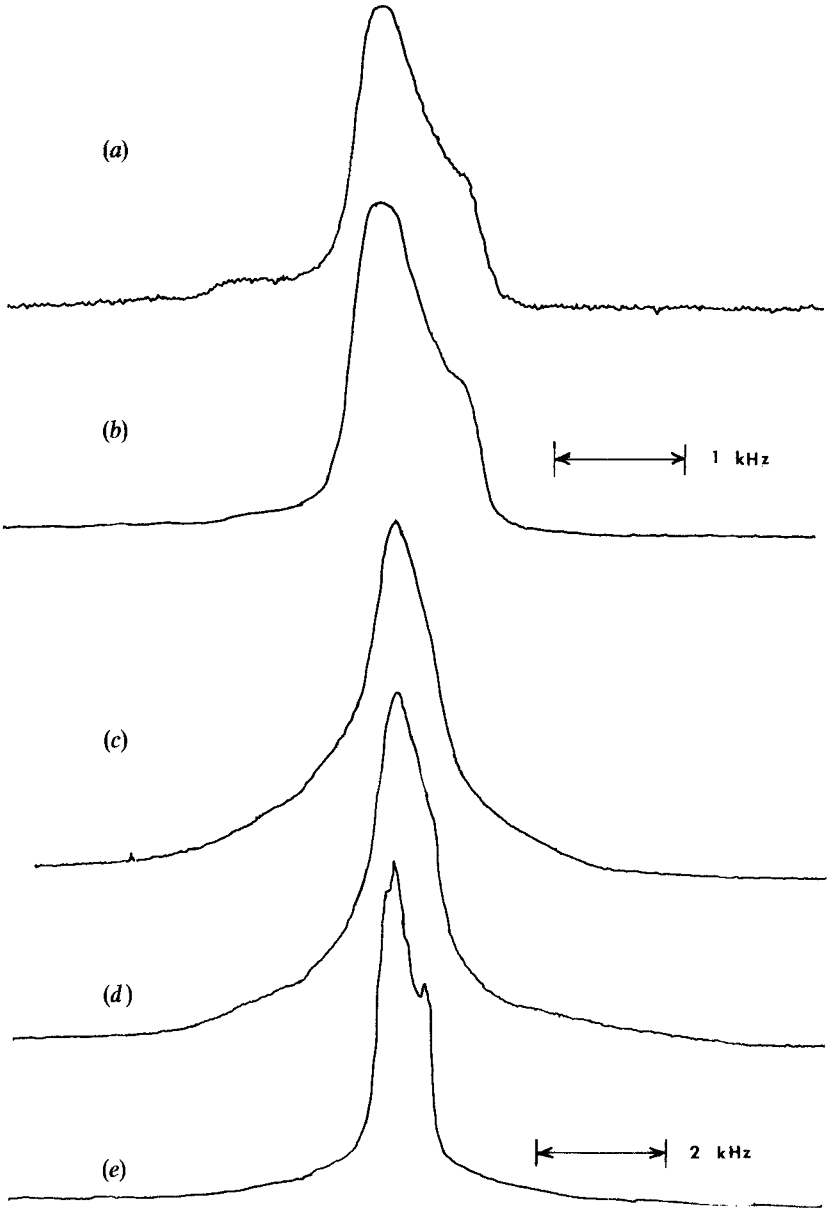

Figure 4. ^{1}H NMR spectra of lead(II) decanoate at: (*a*) 303 K; (*b*) 353 K; (*c*) 363 K; (*d*) 368 K; (*e*) 393 K. Note the change in abscissa between (*b*) and (*c*).

structure of the bilayer. This agrees with the results of dilatometry studies [7], which show coefficients of expansion typical for a crystalline phase in this region. The end of this gradual fusion process occurs at 357 K with the formation of the ordered smectic phase [6, 7]. The increase in entropy in the end region of the chains destabilizes the three dimensional order, and may provoke a sliding of the bilayers, but at the same time the order within each carboxylate–metal–carboxylate inverse bilayer is preserved. X-ray diffraction [5, 7] shows that this phase still gives many crystal-like reflections, which can be attributed to three dimensional ordering at the level of the ionic head groups. However, both Raman spectra and calorimetric data suggest that a small amount of disordering of the hydrocarbon chains is present [6, 7]. Above 357 K the solid band, which had been buried in the base line at lower temperatures, begins to sharpen and to give rise to a peak in the spectrum (see figure 4 (*c*)). There is, however, little change in the linewidth of the band already present. This behaviour corresponds to the onset of rotation of the C–C segments closest to the polar region, although their mobility is considerably lower than that of the end regions of the chain, which does not change noticeably in this range. The shape of this spectrum becomes constant around 365 K, where zone C ends and D starts, as the constrained rotations of the inner segments of the hydrocarbon chains are unable to overcome the overall smectic ordering.

The transition between the ordered smectic and smectic A (L_α) mesophases at 369 K [6] shows up by the apperance of a very large band in the spectrum (see figure 4 (*d*)), which disappears at higher temperatures. The thermal activation of the rigid segments around the Pb^{2+} cation, in spite of its constrained motion, leads to the destruction of the overall ordering round the polar region. This process is also observed in the ^{207}Pb NMR spectra [1], where the relatively unrestricted motion of the metal ion shows up as an apparently isotropic signal. The motions of the C–C bonds in the polar region seem to acquire immediately the same degrees of freedom as the other interior parts of the bilayer chains (see figure 4 (*e*)).

Melting at 387 K is not observed in these studies. The $L_\alpha \rightarrow$liquid transition destroys the bidimensional smectic order, but the local dynamics of the carboxylate molecules as seen by NMR are not significantly changed. This behaviour is reminiscent of the absence of any change in the proton $T_{1\rho}$ value for 1,2-dipalmitoylphosphatidylcholine monohydrate on going from the lamellar to cubic phase [33]. In moletn PbC_{10} we continue to observe a large contrast between the rapid fluctuations of the terminal methyl region and the slow movements of the segments in the neighbourhood of the polar region. This is probably due to the formation of aggregate structures in the liquid phase consisting of a small number of molecules with a polar, relatively immobile centre from which highly flexible hydrocarbon chains radiate out. Such aggregates have previously been suggested for this phase on the basis of both viscometric [34] and thermal [3] data.

3.3. *Global ^1H relaxation of lead(II) decanoate*

Between room temperature and roughly the temperature of the first transition from the solid to the ordered smectic phase there are unequivocally two components in the ^1H spin–lattice relaxation. These are associated with two populations of hydrogen nuclei, one of which has low mobility ($T_1 \approx 1$ s) and the other possesses relatively fast dynamics ($T_1 \approx 0{\cdot}1$ s). The behaviour is similar to what is observed with tristearin [35], where it is suggested that these result from different polymorphs. The evolution of this global relaxation time (see figure 5) and of the relative amplitudes of the two components in the low temperature region (see figure 6) were studied for PbC_{10} as a function of temperature. From 308 to 315 K, the fraction of the mobile protons increases until it becomes constant at about 30 per cent of the total (see figure 6); it then stays virtually constant until about 335 K. This behaviour could correspond to the progressive activation of the sample. The dynamic structure as seen by these measurements remains relatively constant, although both populations continue to be thermally activated, as seen by the evolution of the T_1s in figure 5. Above 335 K, the fraction of the more mobile hydrogen nuclei continues to grow due to the increasing

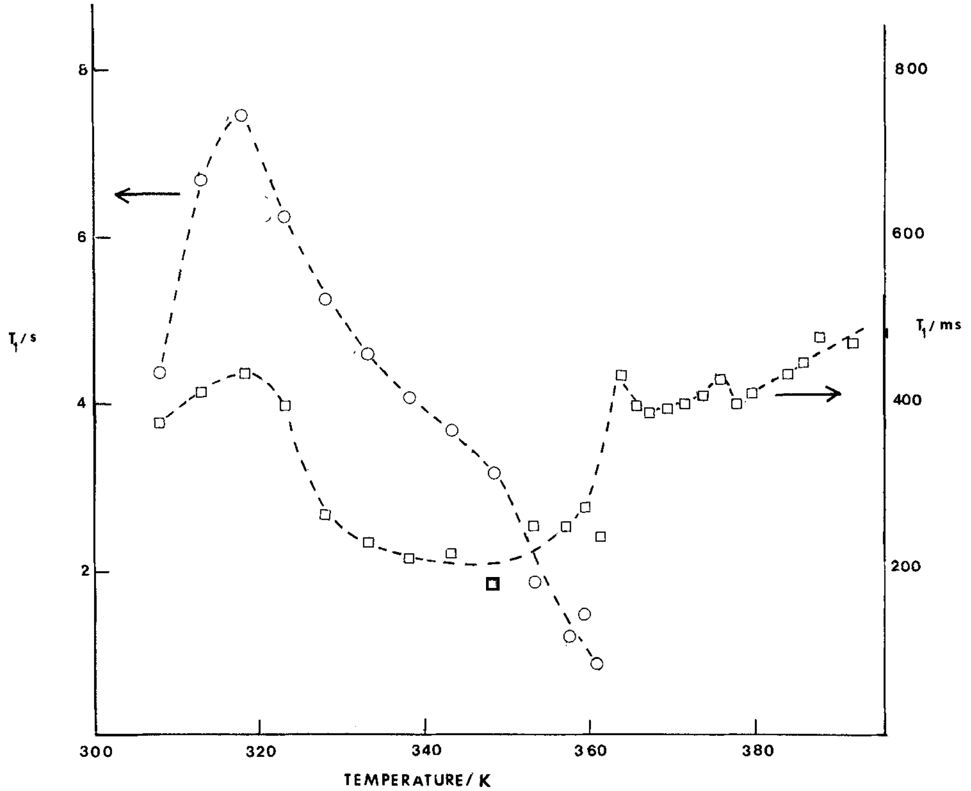

Figure 5. Global ^{1}H spin–lattice relaxation times for lead(II) decaonate as a function of temperature. The circles correspond to the slow component and the squares to the fast component in the fit to a bi-exponential decay.

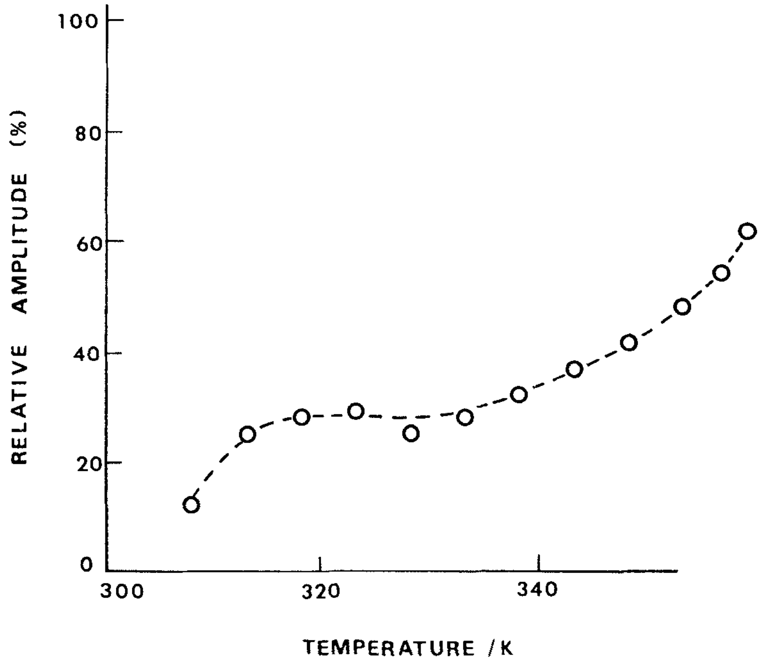

Figure 6. Relative amplitude of the fast component in the global ^{1}H spin–lattice relaxation of lead(II) decanoate as a function of temperature.

mobility of the methyl end of the chain, while the T_1 value of this component passes through a minimum. The behaviour continues to 362 K, roughly the temperature of the first transition, where the proton relaxation can now only be fitted by a single exponential. Thermal agitation of high frequency is introduced along the chains until the ordered structure of the solid phase disintegrates to produce the low temperature mesophase. A pronounced discontinuity is observed in the evolution of T_1 at the temperature of this transition, which indicates an abrupt change in the molecular dynamics of all or part of this system on forming this ordered smectic phase. This argues against the phase being strictly crystalline as suggested by Ellis [5], and lends support to the idea given in the previous section, and elsewhere [6, 7] that its character is intermediate between a true crystal and a disordered smectic phase.

A further discontinuity in the global ^{1}H relaxation is observed around 376 K, rather higher than the temperature observed by DSC for the ordered smectic→L_α transition, but within the accuracy of these measurements no other transitions are observed at the high-frequency (60 MHz) dynamic level. Studies using a somewhat different technique [36] do, however, suggest that there is a small change in the proton T_1 on going from the L_α to the liquid phase.

4. Discussion

Whilst previous X-ray powder diffraction [5–7], ^{207}Pb NMR [1], Raman [6, 7] and infrared [7, 37] spectral studies have provided important insights into the structures of the even chain length lead(II) carboxylates, and have shown that the solid phase consists of a lamellar layer structure, consisting of planes containing equivalent metal ions with the carboxylate chains arranged in an all-trans conformation at right angles to these planes, certain details are still missing regarding the packing of the chains and the coordination round the Pb^{2+}. High resolution, solid state ^{13}C NMR spectroscopy provides a powerful tool for obtaining some of this information.

The high resolution, ^{13}C NMR spectra of solid lead(II) decanoate and octadecanoate show a rather surprising splitting of the bands attributed to the three carbon atoms closest to the metal. Splittings of a similar magnitude have been observed in solid polyethylenes [38], attributed to the presence of crystalline and non-crystalline components. The fact that the ^{1}H transverse relaxation measurements in this study also support the presence of crystalline and relatively amorphous regions in lead(II) decanoate suggests that this explanation may also be tenable here. However, it is surprising in this case that only the carboxylate and adjacent two methylene peaks are split. An alternative explanation is that the splitting results from the non-equivalence of the carboxylates linked to the same Pb^{2+}. The presence of a single metal site in lead(II) decanoate has been shown by ^{207}Pb NMR spectroscopy [1], whilst the fact that the coordination of this is not completely symmetric is suggested by both the moderate chemical shift anisotropy seen in this case, and the observation of a large Stokes shift in the luminescence of this compound [39, 40]. Only a limited amount of structural data has been reported on lead(II) carboxylates. However, the detailed structures of lead(II) formate, and of some solvated carboxylates have been determined by single crystal, X-ray diffraction [41]. In all of these compounds, the lead(II) has an overall coordination number of eight, with varying stereochemical arrangements. With the anhydrous lead(II) formate, there is a three dimensional polymeric structure involving bridging formate groups. These are divided into two types, with one having equal carbon–oxygen distances and the other not. In the latter case, there is also one short and one long oxygen–lead contact. In the long chain carboxylates, the structure is dictated both by lead(II)–carboxylate interactions, and by the hydrocarbon chain packing, which will preclude the polymeric arrangement observed with the formate. However, it seems reasonable that the Pb^{2+} will retain its preference for eightfold coordination. X-ray powder diffraction studies show that the lead(II) atoms are in a plane, with the hydrocarbon chains above and below this [5–8]. The similarities between the high resolution, solid state ^{13}CNMR spectra of the decanoate and octadecanoate suggest that the assignment of a monolayer molecular organization of the lamellar structure for longer chain lead(II) carboxylates and a bilayer structure for the shorter chain ones (42) is not correct, and that the crystalline phases of these compounds have a common structure. ^{207}Pb NMR spectra [1] support this interpretation. Electron diffraction measurements on a lead(II) octadecanoate multilayer [43] suggest that there may be two different arrangements for the carboxylate anions. It has been suggested, based on the results of the carboxylate stretch bands in the infrared spectra of various divalent metal carboxylates, that the coordination in the lead(II) carboxylates is intermediate berween monodentate and chelating bidentate [37]. These results are probably better interpreted as there being two different metal–carboxylate coordinations. Although the possible existence of two non-equivalent carboxylate groupings does provide an attractive explanation for the observed splittings in the high resolution ^{13}C NMR spectra, it leaves unresolved the nature of the differences between the chains. One possibility is that conformational differences are involved [44], and that as in the related copper(II) carboxylates [45], or the B form of stearic acid [46], there may be a distortion from the normal all-trans arrangement of one of the hydrocarbon chains by rotation about the first two C–C bonds at the carboxylate end. However, other factors, such as variations in local magnetic susceptibility [47], may equally be involved.

A dependence of the chemical shift on the crystal habit has been noted in the high resolution ^{13}C NMR spectra of alkanes [48]. Whilst the unit cell of these compounds has not been established, infrared spectral studies on lead(II) decanoate [7], and electron diffraction studies on lead(II) octadecanoate [43] suggest that they are probably orthorhombic or monoclinic. The chemical shifts seen here for solid lead(II) decanoate for the methyl, and α and β methylene groups agree well, within experimental error, with those expected [48] for such structures, and rule against there being a triclinic unit cell. The chemical shift for the methyl group of solid lead(II) octadecanoate appears to be rather closer to the liquid value than that of any crystal structure. However, this may be an artefact, as the chemical shifts of the other carbon atoms are close to those observed for the corresponding positions in the decanoate. The T_1 values observed for the CH_3 and α-CH_2 groups fall in the range expected for alkanes [49], although interpretation of the values for the internal methylene groups is complicated by the strong dependence of these on crystallite thickness [50]. The differences between the decanoate and octadecanaoate may well reflect variations in the chain dynamics.

On going from the solid to the liquid phase, whilst, within experimental error, there is no change in the positions of the carboxylate and the high field component of the adjacent methylene signals, there is a shift of c. 2 ppm in the positions of the other methylene resonances in lead(II) decanoate. Similar changes have previously been observed in various alkanes [51] and lipid systems [52], and are attributed to conformational disordering in the chain [44]. Although some ambiguity may exist in the assignment of some of the peaks, the fact that all of the methylene peaks beyond –

$CH_2(2)$– show this shift indicates that chain disordering in the liquid occurs along the chain and is not localized. Further, in principle it is possible to estimate the fraction of gauche conformers per chain (f_g) from the chemical shift differences [38, 51]. It is necessary to recognize that differences in experimental techniques and chemical shift references for the solid and liquid phase limit the accuracy of these calculations. However, if conformational differences are the only cause of the differences between the chemical shifts of the solid (δ_s) and liquid (δ_l), these values can be related to f_g by [38]

$$f_g = \frac{\delta_s - \delta_l}{(\delta_{\text{trans}} - \delta_{\text{gauche}})},$$

where $(\delta_{\text{trans}} - \delta_{\text{gauche}})$ is the difference in chemical shift associated with this conformational change. The difficulty is knowing the value of this term [38], which may well be dependent upon the position of the CH_2 group in the chain. However, if we use a typical value of 6·52 ppm for $(\delta_{\text{trans}} - \delta_{\text{gauche}})$ [38], and assume that –$CH_2(2)$– is not involved in conformational disordering, we can estimate that there are $2 \cdot 3 \pm 0 \cdot 4$ gauche conformations per chain in the liquid phase. Although there are a number of assumptions here that are certainly not fully justified, it can be noted that this value compares favourably with the results of Raman spectroscopy [6], which suggest an average of *c.* 1·9 gauche bonds per chain. If we also include results from molecular dynamics [53] and single chain model [54] calculations, we can reasonably conclude that on average there are about $2 \cdot 0 \pm 0 \cdot 5$ gauche conformations per chain in molten lead(II) decanoate.

In the ^1H NMR of the solid state of lead(II) decanoate, there are indications of a relatively fluid amorphous region from the band shape, and from the transverse and longitudinal proton relaxation. This, at first, appears to conflict with the observation of sharp crystal-like reflections in the X-ray diffraction of this compound [5–8, 42]. However, it is important to remember that at room temperature the fraction of this mobile component is relatively small (*c.* 20 per cent) and also that, because of the strong scattering by the Pb^{2+} ions, the observed X-ray pattern depends mainly on the positions and ordering of these species. That is, whilst there is a well-defined three dimensional ordering of the lead(II) carboxylate species as seen in the X-ray diffraction studies, this does not preclude the mobility of some fraction of the hydrocarbon chains. The existence of some degree of chain fluidity in solid aliphatic systems is not uncommon, and we note, in particular, the observations by vibrational [55, 56] and ^1H NMR [56] spectroscopies of mobility of fatty acid chains at temperatures considerably below their melting points. Although it is necessary to be aware that impurities can be an important factor in such behaviour [57], there is no evidence for significant levels of impurities in any of these systems. Instead, we believe that the behaviour is well described by the model proposed by Zerbi *et al.* [55] for the fatty acids, where although the chains are in their fully extended all-trans conformations, a certain fraction have considerable longitudinal mobility as a result of thermal expansion of the lattice. It is striking that the amorphous fraction observed in the present study is virtually identical to the percentage of mobile methyl groups (22 per cent) observed by these workers.

On heating, as described earlier, the proton NMR measurements show a progressive increase in the mobile fraction in the solid phase, although no significant disorder is introduced into the overall structure until the first phase transition to form an ordered smectic structure at around 357 K. This transition is also accompanied by the onset of considerably rotational movement within the chain. Although, as noted previously [7], this transition is not just a crystalline to rotator phase transition, it is possible that there is a double transition involving first the onset of rotational motion of the type described by McClure [58], followed closely by formation of this new phase, which T_1 measurements confirm has considerable fluidity. Whilst formation of the lamellar L_α phase can be seen in these measurements at temperatures close to those observed by DSC, no further insight is obtained upon the structure, except to confirm that the hydrocarbon chains here already have very similar fluidity to the liquid phase.

One of us (G.F.) thanks Professor J. P. Cohen Addad for his generous hospitality, and for allowing him to use the facilities at Grenoble, where the majority of the experimental work was carried. Valuable discussions and advice from Drs A. Guillermo and R. Dupeyre are also acknowledged. We thank I.N.I.C., J.N.I.C.T. and the French Embassy for financial support.

References

[1] Burrows, H. D., Geraldes, C. F. G. C., Pinheiro, T. J. T., Harris, R. K., and Sebald, A., 1988, *Liq. Crystals*, **3**, 853.

[2] Buono, F. J., and Feldman, M. L., 1979, *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 8, 3rd edition, edited by H. F. Mark, D. F. Othmer, C. G. Overberger and G. T. Seaborg (Wiley), p. 34.

[3] Adeosun, S. O., and Sime, S. J., 1976, *Thermochim. Acta*, **17**, 351.

[4] Adeosun, S. O., and Sime, S. J., 1978, *Thermochim. Acta*, **27**, 319.

[5] Ellis, H. A., 1986, *Molec. Crystals liq. Crystals*, **139**, 281.

[6] Amorim da Costa, A. M., Burrows, H. D., Geraldes, C. F. G. C., Teixeira-Dias, J. J. T., Bazuin, C. G., Guillon, D., Skoulios, A., Blackmore, E., Tiddy, G. J. T., and Turner, D. L., 1986, *Liq. Crystals*, **1**, 215.

[7] Bazuin, C. G., Guillon, D., Skoulios, A., Amorim da Costa, A. M., Burrows, H. D., Geraldes, C. F. G. C., Teixeira-Dias, J. J. T., Blackmore, E., and Tiddy, G. J. T., 1988, *Liq. Crystals*, **3**, 1655.

[8] Pinheiro, T. J. T., 1989, M.Sc. Thesis, University of Coimbra.

[9] Saitô, H., and Ando, I., 1989, *A. Rep. NMR Spectrosc.*, **21**, 209.

[10] Grant, R. F., Hedgecock, N., and Dunell, B. A., 1956, *Can. J. Chem.*, **34**, 1515.

[11] Grant, R. F., and Dunell, B. A., 1960, *Can. J. Chem.*, **38**, 1951, 2395.

[12] Grant, R. F., and Dunell, B. A., 1961, *Can. J. Chem.*, **39**, 359.

[13] Janzen, W. R., and Dunell, B. A., 1963, *Trans. Faraday Soc.*, **59**, 1260.

[14] Barr, M. R., and Dunell, B. A., 1964, *Can. J. Chem.*, **42**, 1098.

[15] Lawson, K. D., and Flautt, T. J., 1965, *J. phys. Chem.*, **69**, 4256.

[16] Janzen, W. R., and Dunell, B. A., 1969, *Can. J. Chem.*, **47**, 2722.

[17] van Putte, K., 1970, *J. magn. Reson.*, **2**, 23.

[18] Ripmeester, J. A., and Dunell, B. A., 1971, *Can. J. Chem.*, **49**, 731.

[19] Klose, G., Volke, F., Hentschel, M., and Mops, A., 1983, *Molec. Crystals liq. Crystals*, **90**, 245.

[20] Grant, R. F., 1964, *Can. J. Chem.*, **42**, 951.

[21] Bonekamp, J., Eguchi, T., and Jonas, J., 1980, *Chem. Phys. Lett.*, **75**, 360.

[22] Bonekamp, J., Artaki, I., Phillips, M. L., Piesko, S., and Jonas, J., 1983, *J. phys. Chem.*, **87**, 4991.

[23] Adeosun, S. O., and Sime, S. J., 1979, *J. chem. Soc. Faraday Trans. I*, **75**, 953.

[24] Harris, R. K., Kennedy, J. D., and McFarlane, W. F., 1978, *N.M.R. and the Periodic Table*, edited by R. K. Harris and B. E. Mann (Academic), p. 309.

[25] Granger, P., 1983, *N.M.R. of the Less Common Nuclei*, Vol. 2, edited by P. Laszlo (Academic), p. 406.

[26] Torchia, D. A., 1978, *J. magn. Reson.*, **30**, 613.

[27] Powles, J. G., and Mansfield, P., 1962, *Physics Lett.*, **2**, 58.

[28] Levy, G. C., Lichter, R. L., and Nelson, G. L., 1980, *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd edition (Wiley–Interscience).

[29] Metcalfe, T. C., Birdsall, N. J. M., Feeney, T., Lee, A. G., Levine, Y. K., and Partington, P., 1971, *Nature, Lond.*, **233**, 199.

[30] Doddrell, D., and Allerhand, A., 1971, *J. Am. Chem. Soc.*, **93,** 1558.

[31] Levine, Y. K., Birdsall, N. J. N., Lee, A. G., and Metcalfe, J. C., 1972, *Biochemistry*, **11,** 1416.

[32] Drakenberg, T., and Lindmann, B., 1973, *J. Colloid Interface Sci.*, **44,** 184.

[33] Salsbury, N. J., and Chapman, D., 1970, *Trans. Faraday Soc.*, **66,** 1554.

[34] Ekpe, U. J., and Sime, S. J., 1976, *J. chem. Soc. Faraday Trans. I*, **72,** 1144.

[35] Azoury, R., Aronhime, J. S., Sarig, S., Abrashkin, S., Mayer, I., and Garti, N., 1988, *J. Am. Oil Chem. Soc.*, **65,** 964.

[36] Feio, G., Burrows, H. D., Geraldes, C. F. G. C., and Pinheiro, T. J. T., *Liq. Crystals* (submitted).

[37] Mesubi, M. A., 1982, *J. molec. Struct.*, **81,** 61.

[38] Earl, W. L., and Vanderhart, D. L., 1979, *Macromolecules*, **22,** 762.

[39] Burrows, H. D., 1988, *Materials Lett.*, **6,** 191.

[40] Blasse, G., 1989, *Chem. Mat.*, **1,** 294.

[41] Harrison, P. G., and Steel, A. T., 1982, *J. organometall. Chem.*, **239,** 105.

[42] Ellis, H. A., and DeVries, A., 1988, *Molec. Crystals liq. Crystals*, **163,** 133.

[43] Stephens, J. F., and Tuck-Lee, C., 1969, *J. appl. Crystallogr.*, **2,** 1.

[44] Saitô, H., 1986, *Magn. Reson. Chem.*, **4,** 835.

[45] See, for example: Lomer, T. R., and Perera, K., 1974, *Acta crystallogr.* B, **30,** 2912.

[46] Goto, M., and Asada, E., 1978, *Bull. chem. Soc. Japan*, **51,** 2456.

[47] Vanderhart, D. L., Earl, W. L., and Garroway, A. N., 1981, *J. magn. Reson.*, **44,** 361.

[48] Vanderhart, D. L., 1981, *J. magn. Reson.*, **44,** 117.

[49] Okazaki, M., and Toriyama, K., 1989, *J. phys. Chem.*, **93,** 2883.

[50] Axelson, D. E., Mandelkern, L., Popli, R., and Mathieu, R., 1983, *J. Polym. Sci. Polym. Phys. Edn.*, **21,** 2319.

[51] Okazaki, M., and McDowell, C. A., 1984, *J. molec. Struct.*, **118,** 149.

[52] Forbes, J., Bowen, J., Shan, X., Moran, L., Oldfield, E., and Moscarello, M. A., 1988, *J. chem. Soc. Faraday Trans. I*, **84,** 3821.

[53] van der Ploeg, P., and Berendsen, H. J. C., 1983, *Molec. Phys.*, **49,** 233.

[54] Gruen, D. W. R., 1985, *J. phys. Chem.*, **84,** 146.

[55] Zerbi, G., Conti, G., Minoni, G., Pison, S., and Bizoto, A., 1987, *J. phys. Chem.*, **91,** 2386.

[56] Barr, M. R., Dunell, B. A., and Grant, R. F., 1963, *Can. J. Chem.*, **41,** 1188.

[57] Broadhurst, M. G., 1962, *J. Res. natn. Bur. Stand.* A, **66,** 241.

[58] McClure, D. W., 1968, *J. chem. Phys.*, **49,** 1830.