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Nuclear Magnetic Resonance Spectroscopy and Relaxation in Molecular Solids containing Isopropyl Groups

Part 2.—The Large Two-phase Temperature Region in 1,4-Di-isopropylbenzene

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We report a proton n.m.r. study of the large, long-lived two-phase temperature region in 1,4-di-isopropylbenzene (DIB). The proton spectra are characterized by a narrow line superimposed on a 42 kHz broad line. The narrow line shows the chemical shift structure of DIB. When the sample is in the solid state the narrow lines are sharp (<30 Hz) near the melting point of 256 K and they broaden to *ca.* 1.5 kHz at *ca.* 170 K where they disappear. A variety of selective and non-selective Zeeman relaxation experiments as well as a Goldman-Shen exchange experiment were performed. It is concluded that the two sets of spins do not communicate on any timescale shorter than the spin-lattice relaxation times. The most likely interpretation of these results is that macroscopic pockets of molecules undergoing liquid-like motions are maintained in the solid, even 90 K below the melting point.

In Part 1 of this study it was observed that the n.m.r. free induction decay (f.i.d.) of solid 1,4-di-isopropylbenzene (DIB) contained both a wide line (small spin-spin relaxation time T_2) and a narrow line (long T_2) component.¹ This occurred over a 60 K temperature range below the melting point of 256 K. The long T_2 f.i.d. contained beats characteristic of the methyl proton-ring proton chemical shift implying liquid-like motion for *ca.* 15% of the molecules. This behaviour over such a large temperature range is somewhat unusual for such a small molecule. Liquid-like motion occurs in larger molecules in the solid state, particularly in those having long alkyl chains,² but even then the two-phase region is not as large as the 90 K which is reported here. We have performed further spectroscopic and relaxation studies with DIB to help determine the structure of this two-phase region. We conclude that there are macroscopic regions of molecules in a liquid-like state.

Experimental

DIB was purchased from Aldrich. The quoted purity was 97% and the reagent was not further purified. A 400 MHz high-resolution spectrum showed no hydrogen-bearing impurities. Two types of samples were used. Samples of one type were thoroughly degassed with many freeze-pump-thaw cycles and sealed in low-pressure helium atmospheres in 5 mm o.d. tubes. These samples were 3 cm long. Another type of sample was not degassed, but was made by putting the liquid into a 5 mm tube and inserting a Teflon plug to make a 3 mm long sample. All experiments reported in the following discussion were performed on both samples and there was no difference in the results. N.m.r. spectra and Zeeman relaxation rates were measured at 200 and 400 MHz on Brüker CXP-200 and WH-400 spectrometers. Temperature was varied by blowing nitrogen gas

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over the sample using Brüker's variable-temperature apparatus and temperature controller. Absolute temperature was known to ± 3 K and differences in temperature over a few h or less were known to ± 0.5 K. The specific experiments are discussed in the next section.

Results and Analysis

A high-resolution room-temperature proton spectrum at 400 MHz of dilute DIB in CDCl_3 showed the 1.629 ± 0.003 p.p.m. alkyl proton-methyl proton chemical shift and the 4.278 ± 0.003 p.p.m. alkyl proton-ring proton chemical shift. It also showed the 7 Hz splitting of the methyl peak due to the alkyl proton and the 7 Hz separation between the seven lines in the alkyl proton line due to the methyl groups. The ring protons gave rise to a single line.

Solid-state spectra were taken as a function of temperature for increasing and decreasing temperature. This was done several times at both 200 and 400 MHz. On increasing the temperature there is a single 42 kHz wide solid line below *ca.* 160 K as shown in fig. 1. Above this temperature a narrow line appears, as shown in the same figure. The intensity (area) of the narrow line increases from 0% at 160 K to *ca.* 10–30% of the total intensity by 180 K, where it has narrowed sufficiently for the 5.9 p.p.m. (1.2 kHz at 200 MHz) methyl proton-ring proton chemical shift to be observed. The alkyl proton line is in the wing of the methyl line, but is not resolved at 200 MHz. This structure is shown on an expanded scale next to the 180 K spectrum in fig. 1. The relative intensities of this 10–30% narrow line, 90–70% wide line superposition change little between 180 and 220 K. The range in the stated compositions reflects the differences between experiments and the $\pm 15\%$ uncertainty associated with measuring integrated areas. The relative composition in any given run changes very little in this 40 K range although the narrow line continues to narrow as temperature is increased. Above 220 K the intensity of the narrow line increases until the wide line disappears by *ca.* 260 K. The 260 K spectrum in fig. 1 comes from the 100% liquid-state spectra with the methyl proton-alkyl proton and alkyl proton-methyl proton chemical shifts of 1.6 and 4.3 p.p.m., respectively. This 90 K two-phase region changes slightly from run to run, but the general features are reproduced. The 200 MHz spectra in fig. 1 were taken with the wide-band, high-power CXP spectrometer employing 1 μs r.f. pulses which allowed for a distortion-free solid-state spectrum. The 260 K isotropic liquid spectra in fig. 1 have linewidths of *ca.* 30 Hz which are characteristic of the set up: the main source of field inhomogeneity is the solid-state probe, but, in addition, the magnet was not shimmed at each temperature. On decreasing temperature, the wide line first appeared at *ca.* 230 K and its intensity increased in a few degrees to 70–90% of the total signal, where it remained to *ca.* 190 K. Between 190 and 170 K the narrow line disappeared. These experiments were repeated at 400 MHz, but the WH-400 is a high resolution instrument. The particular instrument used had a maximum spectral width of 50 kHz and a probe which was able to withstand less r.f. power than that employed with the CXP. Thus the wide line could not be seen at 400 MHz, at least not without considerable distortion. However, the narrow line could be monitored and an example of the temperature dependence of the narrow line on decreasing temperature is shown in fig. 2. The fraction of liquid-like spins could be determined by comparing the observed intensity with the intensity when the sample was 100% isotropic, taking into account the temperature dependence of the Curie law. The larger chemical shifts at 400 MHz allow the alkyl proton peak to be identified even though it is in the wings of the methyl line as the peaks broaden below 180 K. As a standard, to ensure the spectrometers and the variable temperature systems were functioning as expected, spectra of 1,4-di-*t*-butylbenzene (DTB) were run as a function of temperature, with temperature increasing and decreasing. DTB has no two-phase region. A typical broad-line spectrum, such as the bottom

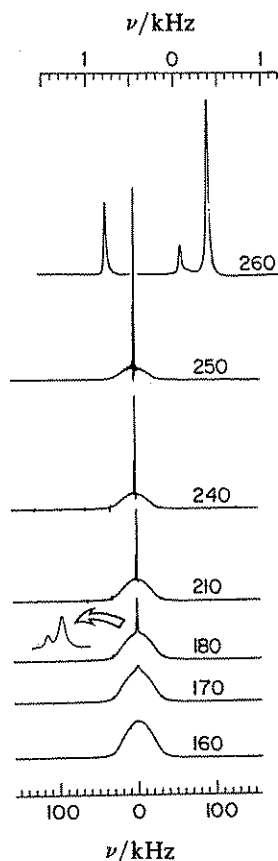


Fig. 1.

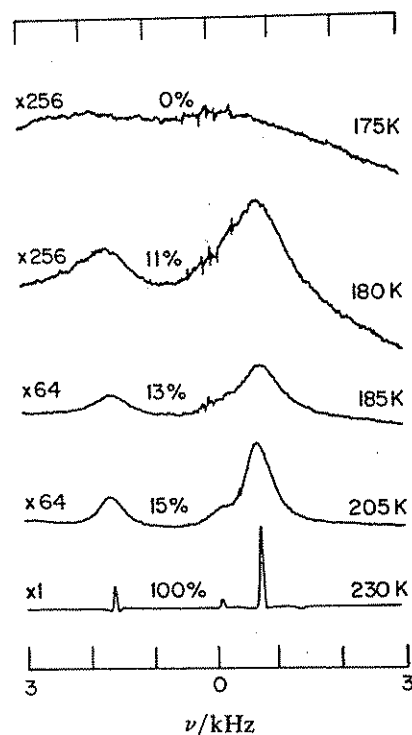


Fig. 2.

Fig. 1. Proton 200 MHz n.m.r. spectra of DIB at various temperatures (K) as indicated. Temperature was increased from 150 K. For the 160–250 K spectra a spectral width of 417 kHz was used and the central 300 kHz is shown. The top scale applies to the top spectrum only. A spectral width of 13 kHz was used and the central 2.7 kHz is shown. The inset at 180 K shows the narrow line on an expanded frequency scale. The methyl proton–ring proton chemical shift is 1.18 kHz (5.91 p.p.m.). No artificial line-broadening was used. The periodically spaced glitches arise from having truncated the narrow-line free induction decay. There is no broad line under the narrow lines at 260 K. The 35 Hz width of the narrow lines at 260 K, as well as their odd shapes, arises from the static field inhomogeneity and is typical of the solid-state high-power probe when the static field is not shimmed at each temperature.

Fig. 2. Proton 400 MHz n.m.r. spectra of DIB at various temperatures (K) as indicated. Temperature was decreased from 290 K. A spectral width of 13 kHz was used, the central 6 kHz of which is shown. The wide line shows up as a distorted baseline; the fraction of signal intensity in the narrow line is indicated in %. The vertical scale is increased, as shown, as temperature is decreased.

trace in fig. 1, was always observed in the solid state. A liquid–solid two-phase region resulting from a temperature gradient along the sample was <1 K. For DIB it was noted in Part 1 that there was no chemical shift structure in the narrow line (long T_2 component of the f.i.d.) at 8.5 MHz and the chemical shift structure observed at 53 MHz disappeared at *ca.* 200 K on decreasing the temperature. This is in complete agreement with the observed temperature dependence of the width of the narrow line at 200 and 400 MHz and it suggests that the behaviour reported here for DIB is quite general and does not depend on how the sample is prepared or on its thermal history. Such details as whether 10 or 30% of the sample is liquid-like may depend on these factors. A 240 K two-phase spectrum (see fig. 1) for the undegassed, unsealed sample was monitored on the CXP

for 18 h and there was no change. This suggests that if this two-phase region is a non-equilibrium structure then it is long lived.

Several relaxation studies were performed and although all are in agreement with the results and conjectures of Part 1 we are able to make more definitive statements here. In Part 1 the temperature dependence of the Zeeman relaxation rate for the wide line at 8.5 and 53 MHz was successfully fitted using a simple Lorentzian spectral density characteristic of thermally activated random hopping motion of the methyls with a unique activation energy. It was concluded that isopropyl reorientation was not occurring on the Larmor time scale. Maxima in the Zeeman relaxation rate R ($\omega\tau \approx 1$ where τ is the correlation time characterizing methyl reorientation and $\omega/2\pi$ is the Larmor frequency) of 120 s^{-1} at 155 K and 19 s^{-1} at 185 K were observed at 8.5 and 53 MHz, respectively. These low-frequency R maxima imply maxima in R of 5.1 s^{-1} at 210 K and 2.6 s^{-1} at 230 K at 200 and 400 MHz, respectively, for the wide line. Even though the relaxation of the wide line is non-exponential, as discussed below, these maxima in R serve as guides as to which motional regime is appropriate at each temperature and frequency.

At 280 K, where the sample is all liquid, a 400 MHz Zeeman relaxation study using both the degassed and undegassed samples showed that the ring and alkyl protons had the same R ($0.59 \pm 0.06 \text{ s}^{-1}$), whereas that for the methyls was $0.91 \pm 0.09 \text{ s}^{-1}$. These values are in agreement with the 53 MHz values reported in Part 1 where only an average rate for all the protons in the narrow line was measured. At 280 K, $\omega\tau \ll 1$ at and below 400 MHz, so R is frequency independent.

A Zeeman relaxation study in the two-phase region at 210 K and at 200 MHz is shown in fig. 3. The pulse sequence for all the non-selective Zeeman relaxation experiments reported here was $\pi - t - \pi/2 - t_r - \pi/2 - t_r$ where the repetition period is $t_r > 8R^{-1}$. The f.i.d. is added to computer memory after the first $\pi/2$ pulse and subtracted from computer memory after the second $\pi/2$ pulse. This leads to difference spectra which decay from twice the equilibrium signal to zero as t is varied. This is shown in fig. 3 where six of the 19 relaxation difference-spectra used in this experiment are shown. R values were determined from the time dependence of the areas of the wide and narrow lines separately. The Zeeman relaxation of the wide line (fig. 3) was clearly non-exponential, confirming this suggestion made in Part 1. As a qualitative guide to the degree of non-exponentiality, the difference magnetization plot against t for the solid line can be characterized by $R \approx 5 \text{ s}^{-1}$ at small t values ($0 < t < 50 \text{ ms}$) and by $R \approx 4 \text{ s}^{-1}$ at large t values ($500 < t < 700 \text{ ms}$). These values of R were determined both from the total area under the wide line and by performing a 'relaxation profile' across the line, which just means calculating R at many frequencies across the spectrum using the height of the spectrum at various positions away from the central narrow line. Both procedures gave the same result, within experimental error. This non-exponential relaxation arises from the correlated motion of the three proton-proton vectors in a methyl group and is well understood as discussed in Part 1, where references to this phenomenon may be found. The value of $R \approx 5 \text{ s}^{-1}$ is in agreement with the predicted maximum in R based on the 8.5 and 53 MHz data and discussed above. The narrow line (fig. 3) relaxes with $R = 2.7 \pm 0.3 \text{ s}^{-1}$ with a non-exponential tail at long t values ($0.7 < t < 1.2 \text{ s}$). Having chosen a large spectral width to accurately characterize the wide line, including a large region of baseline, there was insufficient digital resolution to separately characterize the individual components of the narrow line. A second relaxation experiment was performed where the accumulation of the f.i.d. was delayed $80 \mu\text{s}$, thus completely eliminating the wide line, since the latter is characterized by $T_2 \approx 8 \mu\text{s}$. This is shown in fig. 4, where five of the 17 relaxation difference spectra used in this experiment are shown. The linewidths at this temperature are comparable with the 1.6 p.p.m. (320 Hz at 200 MHz) methyl proton-alkyl proton chemical shift. The ring protons relaxed with $R = 1.9 \pm 0.2 \text{ s}^{-1}$ and the relaxation was exponential. The isopropyl $(\text{CH}_3)_2 + \text{H}$ composite

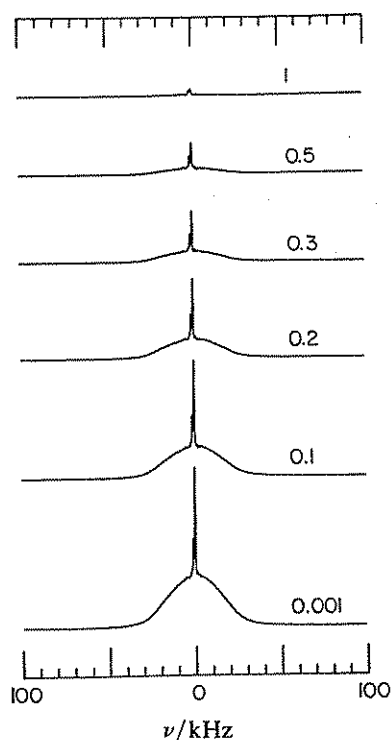


Fig. 3.

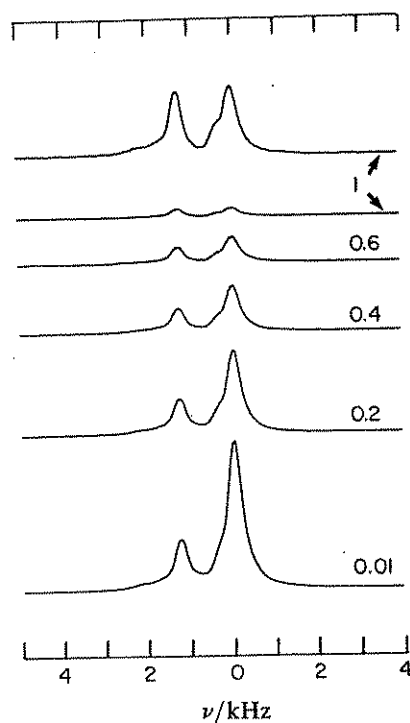


Fig. 4.

Fig. 3. Proton relaxation difference spectra at 200 MHz for DIB at 240 K. The delay times t are indicated in s. The spectral width was 455 kHz, of which the central 200 kHz is shown.

Fig. 4. Proton relaxation difference spectra at 200 MHz for DIB at 240 K. A spectral width of 50 kHz was used of which the central 9 kHz is shown. The acquisition of the free induction decay was delayed for 80 μ s to ensure the wide line signal ($T_2 \approx 8 \mu$ s) had decayed to zero. The delay times t are indicated in s and the $t = 1$ s difference spectrum is shown on both $\times 1$ and $\times 8$ (top spectrum) vertical scales.

line relaxed with $R = 2.9 \pm 0.3 \text{ s}^{-1}$ and, although there was no observed departure from exponentiality within the experimental uncertainty, it is evident from comparison of the 10 ms and 1 s difference spectra in fig. 4 that the alkyl proton is relaxing slower than its neighbouring methyl protons. These rates of 2.9 and 1.9 s^{-1} account for the non-exponential behaviour discussed above where the two narrow lines were treated together.

The relaxation experiments discussed above suggest that the two components in the spectrum arise from two different macroscopic regions or sets of regions in the sample. Two sets of relaxation experiments were performed to determine the degree of coupling between these two regions. In the first, a π - t - $\pi/2$ - t_r sequence with a selective π pulse was used. The repetition period is $t_r > 8R^{-1}$. For this π pulse, a train of short r.f. pulses was used to excite a narrow band of spins at the centre of the spectrum.³ For n pulses of duration t_p and separation t_s the length of the π pulse is approximately nt_p (depending on how t_p is defined relative to rise and fall times). The intensity of the r.f. irradiation varies approximately as $(\sin x)/x$ with $x = n\pi(t_p + t_s)\Delta\nu$ where $\Delta\nu$ is the frequency offset from the centre of the spectrum. Fig. 5 shows a selective inversion recovery experiment at 240 K on the CXP-200 spectrometer with $t_s = 1 \mu$ s, $t_p = 0.25 \mu$ s and $n = 100$. If the zero crossings of the $(\sin x)/x$ envelope are taken as a measure of the selectivity, then this is $2/[n(t_p + t_s)]$ which, for the case of fig. 5, is 16 kHz. The narrow line has no chemical shift structure because a line-broadening of 1 kHz was used to improve signal-to-noise. Since the broadline has a full width at half height of 43 kHz, an

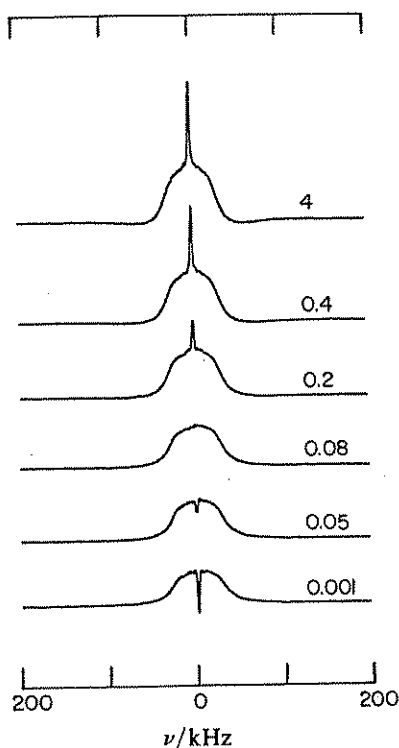


Fig. 5.

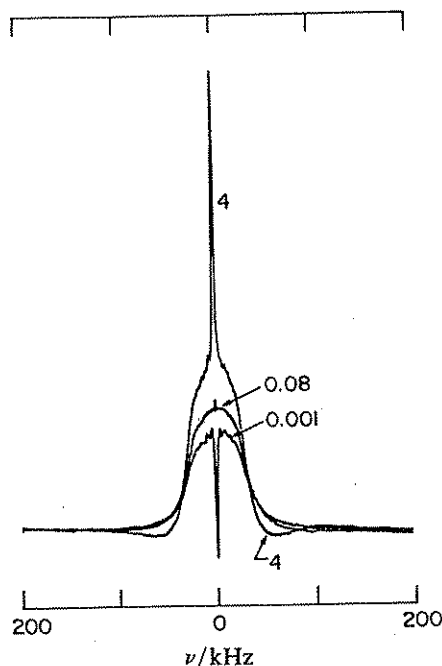


Fig. 6.

Fig. 5. Proton selective inversion recovery spectra of DIB at 200 MHz and at 180 K. The spectral width was 454 kHz of which the central 400 kHz is shown. The full widths at half height of the wide and narrow lines are 43 and 2 kHz, respectively, and a selectivity of 16 kHz was employed. The 2 kHz linewidth for the narrow line results from the 1 kHz chemical shift, the 1 kHz natural linewidth and 1 kHz artificial line-broadening to improve signal-to-noise. The delay times t are indicated in s and the $t = 4$ s spectrum is essentially the equilibrium spectrum.

Fig. 6. Proton selective inversion recovery spectrum of DIB at 200 MHz and at 180 K. The three spectra are taken from fig. 5 and show the degree to which the wide 43 kHz line was affected by the 16 kHz selective inversion pulse. The delay times are indicated in s.

appreciable part is effected by the selective π pulse. This is better seen in fig. 6 where three of the spectra in fig. 5 are superimposed. Experiments using selectivities of ca. 5 kHz and 500 Hz were also performed and, although the wide line is less affected by these narrower excitations for technical reasons peculiar to the spectrometer used, it is more difficult to invert the central narrow line. These details are not particularly important. The central result here is that the narrow line can be inverted (i.e., a hole can be burned in the wide line at its centre) and it relaxes with $R \approx 3.9 \text{ s}^{-1}$ at 240 K and not with the wide line spin-spin relaxation rate ($\approx 10^5 \text{ s}^{-1}$), which would be the case if the two types of molecules were very near each other. This 3.9 s^{-1} is as expected for the narrow line and is the same as that obtained at this temperature if a normal non-selective experiment is performed in the whole system.

The final relaxation experiment was a Goldman-Shen three-pulse experiment⁴ used to determine if limits could be placed on the exchange rates between the two types of spins. The basic sequence is $(\pi/2)_x - t_1 - (\pi/2)_{-x} - t_2 - (\pi/2)_x - t_r$, where $t_r > 8R^{-1}$. The subscripts on the pulses refer to the phase of the r.f. The time t_1 is long compared with the $T_2 \approx 8 \mu\text{s}$ of the wide line, but well within the $T_2 \approx 1 \text{ ms}$ f.i.d. of the narrow line. The time t_2 is varied. There is no signal after the second pulse. There is no short T_2 f.i.d. after the second pulse because it has already decayed to zero after the first pulse and since $t_1 \ll R^{-1}$, the $M_z = 0$ created by the first pulse prevails. There is no narrow-

line signal because the first pulse takes M_z into M_y and the second, phase-reversed pulse, puts it back again. At the time of the third pulse, the spin system characterized by the wide line is saturated and the spin system characterized by the narrow line is close to equilibrium. The third pulse brings back the narrow line, but not the solid line unless there was exchange in the time t_2 . If there is spin diffusion between relaxed narrow-line spins and saturated wide-line spins then there will be some relaxed wide-line spins at t_2 and a short T_2 f.i.d. will be generated by the third pulse. If such a wide-line signal is observed, its amplitude as a function of t_2 can be used to measure the exchange rate so long as it is much greater than the Zeeman relaxation rate R . In the present case, no such wide line f.i.d. was observed, in agreement with the other spectroscopy and relaxation experiments presented here. These Goldman-Shen three-pulse experiments can be difficult to do properly and require proper phase cycling to eliminate, or at least reduce as much as possible, wide-line signals following the third pulse, whose origins lie in the detection of multiple quantum coherences.⁵ In the present case, if the appropriate phase cycling was not done, a sizeable wide-line signal was observed after the third pulse. The key that this signal was arising from multiple quantum coherences was that the signal height was relatively insensitive to t_1 and t_2 . We also performed this experiment in the 100% liquid state at 300 K and the 100% solid state at 150 K to check that the spectrometers were functioning as they should and that the above interpretations were correct.

Summary and Conclusions

There is a large temperature region in DIB where a wide solid-like n.m.r. line and a narrow liquid-like line are superimposed. The very different relaxation behaviour for the two signals, plus the absence of spin diffusion between them, suggests there are two sets of macroscopic regions in the sample. The Larmor frequency and temperature dependence of the Zeeman relaxation rate of the wide line and the observed non-exponential relaxation is consistent with this interpretation of the wide line coming from those molecules in the normal polycrystalline state. The narrow line must originate from liquid-like pockets in the otherwise solid sample. Local heating of the outside surface of the sample by the r.f. pulses, thereby melting a thin film of the sample, can be ruled out absolutely. The observed chemical shift of the liquid-like signal clearly indicates that it is coming from DIB and the linewidths suggest very rapid motion, at least at higher temperatures. There is a 30–40 K range within the 60–90 K two-phase region where the relative fraction of liquid-like to solid-like molecules does not change, but the liquid-like spectrum broadens considerably to the point where the linewidth is characteristic of a glassy state. The reason for the existence of these mobile pockets in the solid is not clear. It has been suggested that in the case of long-chain fatty acids they appear either at the sites of impurities or at other types of crystal imperfections.² By varying the concentration of impurity sites, Cyr *et al.*² concluded that the latter was more likely. In that there was no difference in the results obtained with 97 and 99% pure samples in Part 1 of this study, we concur that it is unlikely that these liquid-like pockets form around chemical impurities. The possibility of a crystal structure which leaves some molecules in the unit cell reorientationally disordered, as found in solid methane at low temperatures, can be ruled by the outcome of the selective relaxation experiments and the Goldman-Shen exchange experiments reported here.

N.m.r. can find and study many features of these interesting phases, but ultimately other spectroscopies, such as neutron scattering and X-ray scattering, are needed to probe the structure at a microscopic level.

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