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Proton spin–lattice relaxation, methyl group rotation and states of an organic solid

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Abstract. We have measured the temperature-dependence of the proton spin–lattice relaxation rate in the solid state of 1,3-di-isopropyl-benzene at nuclear magnetic resonance Larmor frequencies of 8.50, 22.5 and 53.0 MHz. We are able to determine, as predicted, that only the four methyl groups are reorienting on the nuclear magnetic resonance Larmor frequency time scale. We can also conclude that the spectral density is well characterized by a Davidson–Cole distribution of activation energies (with a cut-off of $E_{dc} = 12 \pm 1 \text{ kJ mol}^{-1}$ and a width parameter of $\epsilon_{dc} = 0.7 \pm 0.1$) even though we are unable to observe the high-temperature frequency-independent regime. This distribution of barriers arises from the non-crystalline macro-state of the solid. There is considerable scattering in the observed relaxation rate in the solid state due to slightly different thermal preparations of the room-temperature liquid sample. We speculate on the state of the solid at the ‘several-molecule’ level. Finally, there are additional motions, probably translation or whole-molecule rotation, present for about 50 °C below the melting point, as indicated by the narrowing of the nuclear magnetic resonance line. However, these motions do not have a significant effect on the spin–lattice relaxation rate. Previous work from our laboratory is reviewed and the present study put into context.

1. Introduction

Proton spin–lattice relaxation measurements [1,2] in organic molecular solids yield information about intra-molecular motions and about the states of the solid. This paper presents the proton spin–lattice relaxation rate R_1 as a function of temperature T and Larmor frequency $\omega/(2\pi)$ in the solid state of 1,3-di-isopropyl-benzene. The molecule is shown in figure 1, in which the numbering scheme for the benzene ring is also presented. The R_1 versus T data for three values of ω are shown in figure 2. This work is part of a continuing study that exploits systems with nuclear spin relaxation rates due largely, but not completely, to the modulation of a single, simple intra-molecular proton spin dipolar interaction by a simple, single intra-molecular motion. However, the differences, sometimes very small, sometimes very significant, between ideal (see section 3) and real behaviour present a way to use the nuclear spin system as a qualitative dynamic probe into how molecules pack together at the nearest-neighbour level, the ‘several-molecule’ level and the macroscopic level. Other techniques must be brought to bear before quantitative analyses of structure can be determined.

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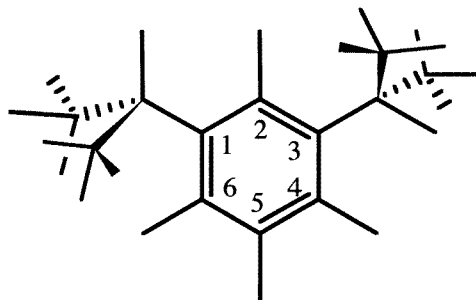


Figure 1. A schematic diagram of 1,3-di-isopropylbenzene $C_6H_4X_2$ with $X = \text{isopropyl} = \text{CH}(\text{CH}_3)_2$. Carbon atoms are at the coming together of four bonds. Hydrogen atoms are at the ends of bonds. The C_6 benzene backbone is planar. Full lines represent bonds in (or nearly in) planes parallel to the page, full wedges represent bonds coming out of the page and broken wedges represent bonds going into the page.

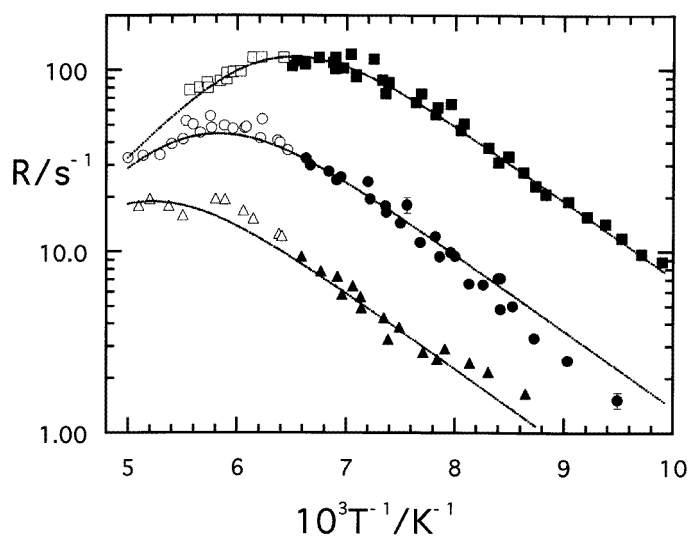


Figure 2. The temperature T -dependence of the proton spin-lattice relaxation rate R_1 in 1,3-di-isopropylbenzene at nuclear magnetic resonance frequencies of 8.50 (■, □), 22.5 (●, ○) and 53.0 (▲, △) MHz. The full symbols correspond to the low-temperature region in which the spin-spin relaxation rate R_2 takes on its temperature-independent value of $1.7 \times 10^5 \text{ s}^{-1}$. The open symbols correspond to the high-temperature region in which the sample is becoming more liquid-like as indicated by a narrowing line width. The three full lines are a *single* fit to the four-parameter Davidson-Cole spectral density as discussed in the text.

2. Review of previous work

We review our previous studies relevant to the current report, put the current project into a greater context and explain why 1,3-di-isopropylbenzene was chosen for an in-depth study. Isopropyl groups ($\text{CH}(\text{CH}_3)_2$ (a central carbon bonded tetrahedrally to one hydrogen atom, two methyl groups (CH_3) and the rest of the molecule (see figure 1 and any elementary chemistry textbook like [3])) and ethyl groups (two instead of one hydrogen atoms, one

instead of two methyl groups) are ideal molecular moieties for the study of how intramolecular motion can be used as a probe of intermolecular interactions and the states of solids. The overall strength of the proton spin relaxation, determined by the various proton spin dipole–dipole interactions, is dominated by the pairwise interactions between the protons (hydrogen nuclei) in the methyl groups. The form of the magnetic field (the Larmor frequency) and the temperature-dependence of the relaxation rate results from the modulation of the dipolar interactions by the motion [1, 2]. We choose systems in which methyl rotation is the only motion on the nuclear magnetic resonance Larmor frequency time scale (say about 10^{-11} to about 10^{-6} s), at least over an appreciable temperature range. For intra-ethyl and intra-isopropyl methyl rotation, the barriers are largely determined by electrostatic interactions within the ethyl and isopropyl groups. This barrier, referred to as an ‘electronic’ barrier, is about 12 kJ mol^{-1} , about 4 kJ mol^{-1} for each of the three C–H bonds that are eclipsed during rotation [3]. However, the observed strength of the relaxation rate can be increased and the electrostatic barrier changed (increased *or* decreased) if parts of neighbouring molecules come close enough. Van der Waals solids do not usually permit encounters sufficiently close [4], however, to have intermolecular interactions dominate the relaxation.

The many-body problem becomes important if the structure is not crystalline (or polycrystalline). In this case, the perturbations to the ideal behaviour must be modelled by distributions of added interactions [2] as discussed further in section 3. This is the key to using proton spin relaxation measurements as dynamic probes of some aspects of solid state structure, including thermal history effects.

Our R_1 versus T studies in ethyl- [5] and isopropyl- [6–9] substituted benzenes form the backdrop for the current study. Lone methyl groups [10, 11] can also be used as a probe in systems in which ethyl and isopropyl group environments are mimicked (for the methyl groups) but this involves Van der Waals (steric) interactions with other parts of the host molecule. Also, tertiarybutyl group (three methyl groups bonded to a carbon) dynamics can also be exploited [12–18] but these systems have the additional feature (often useful, often not) that, at least in some systems, the entire tertiarybutyl group will rotate on the nuclear magnetic resonance Larmor frequency time-scale because of its highly symmetric structure.

Most of the ethyl-benzenes and the isopropyl-benzenes are liquids at room temperature and this allows a variety of solid state structures depending on how the material is frozen. In principle, at least, one can obtain polycrystalline or amorphous (glassy) structures, although extremely pure samples and extremely slow freezing is required to achieve the polycrystalline state in most of these kinds of organic solids [19, 20]. The system used for the current study is 1,3-di-isopropyl-benzene as shown in figure 1. Previous studies with isopropyl-substituted benzenes have all been helpful but have all had drawbacks which the current study has at least partially rectified. Previous studies include isopropyl-benzene (just one isopropyl group) [6], 1,4-di-isopropyl-benzene (see figure 1 for where the groups, in this case, isopropyl groups, go on the benzene ring) [8, 9], 1,3,5-tri-isopropyl-benzene [8] and 1,2,4,5-tetra-isopropyl-benzene [7]. Several other systems have been investigated but have not offered new insights. Isopropyl-benzene [6] is the simplest isopropyl system but its low melting point, its myriad of amorphous solid states and its long-time thermal history effects made system-independent conclusions difficult to obtain, even though the R_1 versus T data were successfully interpreted in terms of methyl group rotation. The molecule 1,4-di-isopropyl-benzene has been studied using both relaxation [8] and spectroscopic [9] NMR. Pockets of ‘liquid-like’ regions whose spins do not communicate with those in the ‘solid-like’ regions exist at temperatures far below the freezing point. At the same time, however, the temperature- and frequency-dependences of the relaxation rate could

be uniquely interpreted in terms of methyl group rotation. These two systems established that the isopropyl- substituted benzenes could be used as systems that were simultaneously 'ideal' yet full of surprises with respect to their dependence on the state of the solid. Although presented with the 1,4-di-isopropyl-benzene data, the 1,3,5-tri-isopropyl-benzene data [8] was clearly influenced by an additional motion on the nuclear magnetic resonance Larmor frequency time scale at higher temperature, which made it difficult to draw useful general conclusions concerning the state of the solid. In looking at several more related systems we found that 1,2,4,5-tetra-isopropyl-benzene [7] was a solid at room temperature and showed none of the thermal history or preparation effects characteristic of many of the other systems. Here we were able to show that all eight methyl groups in this crowded system behaved like 'normal' ethyl/isopropyl methyl groups and interesting small effects associated with crystal packing could be studied.

Even though the motion in tertiarybutyl systems is more complicated (in that the whole tertiarybutyl group can re-orient with methyl group re-orientation superimposed), the tertiary butyl systems are all solids at room temperature and have mimicked many of the isopropyl results. For example, 1,4-di-tertiarybutyl-benzene [14, 16, 18] has the same overall R_1 versus T pattern as 1,4-di-isopropyl-benzene [8] and 1,4-di-ethyl-benzene [5] (all *para*-substituted benzenes) in that all three systems are the closest to ideal behaviour. That is, a straightforward application of Poisson statistics with a unique activation energy for methyl group rotation *almost* works. The data, in fact, are characterized by very narrow distributions of activation energies for methyl rotation; the small but finite breadth of the distribution arises solely from the small but not negligible distributions of intermolecular electrostatic interactions. *Thus, the para-substituted alkyl-benzenes (alkyl = methyl, ethyl, isopropyl or tertiarybutyl), regardless of their very different chemical and physical characteristics, are teaching us about general aspects of packing in this class of organic solids in a way that is independent of the individual molecules.*

Unlike in the case of the *para*-substituted alkyl-benzenes, the temperature-dependence of the proton spin-lattice relaxation rate in the three compounds with a lone alkyl group (tertiarybutyl-benzene [13], ethyl-benzene [5] and isopropyl-benzene [6]) is very unusual. These systems are more fragile solids and give rise not so much to wide distributions of activation energies as they do to a very considerable dependence on thermal preparation (ethyl-benzene and isopropyl-benzene) or several distinct molecular sites (tertiarybutyl-benzene).

The 1,3-systems are different for the tertiarybutyl [15, 17, 18] and ethyl [5] cases and part of the current study is to understand this better by studying the analogous isopropyl system. Solid 1,3-di-tertiarybutyl-benzene [15] (and its close relative 3,5-di-tertiarybutyl-hydroxy-benzene [17, 21]) has, or can have if prepared appropriately, a very broad distribution of activation energies; so broad in fact that one questions the interpretation of the relaxation rate data in terms of a distribution of barriers. The solid 1,3-di-ethyl-benzene on the other hand [5], behaves just like the single-ethyl ethyl-benzene.

Finally, we note for completeness, that R_1 versus T in 1,3,5-tri-isopropyl-benzene [8], discussed above, was difficult to interpret whereas R_1 versus T in 1,3,5-tri-tertiarybutyl-benzene [12, 21] is a fascinating system that can be prepared in very distinct states that thermally evolve over time scales of years [12, 22]. Indeed, room temperature for 1,3,5-tri-tertiarybutyl-benzene seems to be a very low temperature insofar as glass dynamics is concerned [19, 20].

3. Theoretical review

The spin- $\frac{1}{2}$ proton system communicates with its environment via spin flips that exchange energy $\Delta E = \gamma \hbar B$ for magnetic field B and proton magnetogyric ratio γ [1]. An excited spin system can only relax via stimulated emission and the relaxation rate is a measure of the density of energy packets $\hbar\omega = \gamma \hbar B$ in the electromagnetic environment. These photons are, in turn, produced by spins that reside on molecular moieties whose motion has components at frequency $\omega/(2\pi)$. Thus this modulation of the proton spin dipole–dipole interaction causes nuclear spin relaxation and a measurement of the relaxation rate can, in turn, be linked to the motion. The strength of the relaxation rate provides information about which intra-molecular groups are re-orienting and the temperature- and magnetic-field-dependences provide information about the motion itself.

The spin–lattice relaxation rate is given by $R_1 = A[j(\omega) + 4j(2\omega)]$ [1, 2]. The spin–spin dipolar interaction is a pairwise interaction and the two terms originate from single and double spin flips.

If methyl re-orientation is a simple random process characterized by a mean hopping rate τ_p^{-1} (where p refers to Poisson) then the correlation function is $g_p(t) = \exp(-|t|/\tau_p)$ [23] and the spectral density, the Fourier transform (times $(2\pi)^{1/2}$) of $g_p(t)$ is $j_p(\omega) = 2\tau_p/(1 + \omega^2\tau_p^2)$. The parameter A in the expression for R_1 is a measure of the strength of the local magnetic field [1, 24]. If j is indeed given by j_p then A can be obtained directly from the value of R_1 at its maximum. (Some investigators model the motion solely on the value of R_1 at its maximum even though j is clearly not given by j_p . This is inappropriate.)

The mean time hopping rate is $\tau_p^{-1} = \tau_{po}^{-1} \exp[-E_p/(kT)]$ for activation energy E_p and infinite-temperature hopping rate (or attempt frequency) τ_{po}^{-1} . The single poisson process model predicts that $R_1(\omega_1)/R_1(\omega_2) = (\omega_2/\omega_1)^2$ at low temperatures at which $\ln R_1 \propto T^{-1}$ with slope $-E_p$ [2]. This is not observed in figure 2, which shows R_1 versus T^{-1} for 1,3-di-isopropyl-benzene (and is discussed further in the next section). This simple model has three adjustable parameters (A , E_p and τ_{po}) and predicts slopes of equal magnitude at high and low temperatures in a $\ln(R_1)$ versus T^{-1} plot. For R_1 versus T experiments in most substances this ideal behaviour is more the exception than the rule.

A simple four-parameter model that fits the data is the Davidson–Cole (DC) spectral density [2, 11]. This model assumes that there is a distribution of mean hopping rates with a low-frequency cut-off τ_{dc}^{-1} and a width characterized by $1 - \epsilon_{dc}$ with $\epsilon_{dc} = 1$ giving a Dirac δ -function distribution at τ_{dc} (in which case $\tau_{dc} = \tau_p$). The characteristic cut-off frequency is given by $\tau_{dc}^{-1} = \tau_{dco}^{-1} \exp[-E_{dc}/(kT)]$. The spectral density is $j_{dc}(\omega) = (2/\omega)\{\sin[\epsilon_{dc} \arctan(\omega\tau_{dc})]\}/\{(1 + \omega^2\tau_{dc}^2)^{\epsilon_{dc}/2}\}$ and there are four parameters: A , E_{dc} , ϵ_{dc} and τ_{dco} [2, 11]. The value of R_1 at its maximum depends on ϵ_{dc} as well as on A [2].

It is helpful to compare values of A derived from fitting data with theoretical values of A assuming specific motions and specific proton spin–proton spin interactions. For example, if only methyl groups are re-orienting and if only intra-methyl spin–spin interactions are considered, then [11, 24] $A = A_m = (n/N)(3.80 \times 10^9 \text{ s}^{-2})$ where n ($= 12$ for 1,3-di-isopropyl-benzene) is the number of hydrogen atoms in methyl groups and N ($= 18$ for 1,3-di-isopropyl-benzene) is the total number of hydrogen atoms in the molecule. The contribution to A from each spin–spin interaction involves r^{-6} for spin–spin separation r . The relatively small value of $r = 0.18$ nm for the proton–proton separation in a methyl group [3] means that intra-methyl contributions to the value of A can dominate, sometimes overwhelmingly.

In addition, a useful benchmark against which any τ_o (like τ_{po} or τ_{dco}) can be measured is obtained from [25] $\tau_o = (2\pi/3)(2I/E)^{1/2}$, where E is the activation energy (determined from fitting the data) and I is the moment of inertia of the re-orienting group. The dependence on the moment of inertia means that τ_o for, say, methyl group re-orientation and, say, whole-molecule re-orientation, differ by orders of magnitude.

4. Experimental details

The 1,3-di-isopropyl-benzene was purchased from Aldrich Chemical. It is a liquid at room temperature with a purity of 97% and a quoted freezing point of 210 K. Several evacuated sealed samples were made using many cycles of a freeze–pump–thaw process to eliminate dissolved gases (of which there was a great deal). Four samples were used and the R_1 versus T data from the different samples were indistinguishable.

The proton spin–lattice relaxation rate R_1 was measured at 8.50, 22.5 and 53.0 MHz using a π – t – $\pi/2$ –wait sequence with the waiting time greater than $8R_1^{-1}$. The data is presented in figure 2. The signal-to-noise ratio was good and the uncertainties in the R_1 values are in the range 5–10%. Two representative 10% error flags at 22.5 MHz are shown at $10^3T^{-1} = 7.6 \text{ K}^{-1}$ and 9.5 K^{-1} . The error flags are just barely larger than the size of the symbols. Note that the scattering in adjacent data points is significantly greater than the uncertainties in each measured R_1 value.

Based solely on visual inspection, two solid states could be observed after freezing the de-gassed, evacuated and sealed samples: a glassy-looking state and a powdery-looking state. It was difficult to determine a procedure that resulted in a sample preparation that simultaneously produced a sample that appeared the same to the naked eye and gave reasonably reproducible R_1 versus T results. Even taking 1 h in going from room temperature to 77 K did not produce consistently looking samples or those that gave consistent R_1 versus T data. It was easy to produce both glassy-looking and powdery-looking samples but R_1 could differ by an order of magnitude from one preparation to the next even though the sample looked the same.

A ‘reasonably reproducible’ (see below) procedure was obtained by quickly quenching the room temperature liquid sample in liquid nitrogen (77 K) for several seconds until it was frozen in a glassy state. Then the sample was removed and warmed by hand for about 5 s. This was not enough time for the sample to liquefy. This ‘77 K then hand-warmed’ cycle was repeated until the sample turned into a fine powdery-looking state. At this point it was returned to liquid nitrogen until the NMR cell was ready at the temperature of the first measurement. As might have been expected from the preparation procedure, it eventually became clear that this powdery-looking state was not a usual polycrystalline state in which an overwhelming fraction of the molecules are to be found in the bulk crystalline state. Indeed, much of the scattering in adjacent data points (up to about 30% in some regions) in figure 2 is probably due to the sample being in slightly different states on different days. It is important to note, however, that on a single day’s run of 5–10 R_1 values, the scattering in adjacent data points was never more than 10%, which is about the largest uncertainty in individual R_1 values.

The spin–spin relaxation rate R_2 [1] was also monitored. The free induction decay is not purely exponential so R_2 is not uniquely defined. However, some consistent measure of the time duration of the free-induction decay allows comparisons at different temperatures to be made. In figure 2, the R_1 versus T data plotted with solid symbols correspond to a temperature-independent $R_2 = 1.7 \times 10^5 \text{ s}^{-1}$, characteristic of a dipole-broadened solid state NMR line. Above about 150 K ($10^3T^{-1} = 6.7 \text{ K}^{-1}$), however, the NMR line began

to narrow rapidly. By 175 K ($10^3 T^{-1} = 5.7 \text{ K}^{-1}$), R_2 had decreased by a factor of 100 and by 210 K the sample melted. The R_1 versus T data seem relatively insensitive to this slow change of macro-state. When R_2 was observed to be measurably smaller than its low-temperature limiting value, R_1 measurements are indicated in figure 2 by open symbols. At the highest temperatures at which R_1 was measured (200 K), the sample still had its powdery-looking appearance even though R_2 was typical of a liquid.

5. Data analysis and discussion

The data were fitted [11] to a Davidson–Cole spectral density using only those low-temperature R_1 measurements for which $R_2 = 1.7 \times 10^5 \text{ s}^{-1}$ was independent of temperature (full symbols in figure 2). *Note that the three full lines represent a single fit.* The parameters are $A = (2.58 \pm 0.26) \times 10^9 \text{ s}^{-2}$, $\tau_{dco} = (1.7 \pm 0.3) \times 10^{-12} \text{ s}$, $E_{dc} = 11.6 \pm 1.2 \text{ kJ mol}^{-1}$ and $\epsilon_{dc} = 0.7 \pm 0.1$. The uncertainties in these parameters are quite large as a consequence of the large differences in R_1 resulting from day-to-day differences in the state of the sample. In a sense, they are not so much uncertainties as they are day-to-day variations. If ϵ_{dc} were set to unity to force a unique poisson process, the fit would be very poor.

The fitted value of the cut-off E_{dc} is characteristic of methyl group re-orientation. The fitted value of A gives the ratio $A/A_m = 1.03 (\pm 10\%)$ (A_m is discussed in section 3) and this suggests very strongly [5] that only the methyl groups are re-orienting (on the nuclear magnetic resonance Larmor frequency time scale). If isopropyl or whole-molecule re-orientation were occurring on the Larmor frequency time scale, A/A_m would be much larger. The fitted value of $\tau_{dco}/\tau_o = 11 (\pm 20\%)$ supports this interpretation.

The value for ϵ_{dc} is difficult to interpret. Of the four fitted parameters, its interpretation is more dependent on understanding why the Davidson–Cole spectral density is so successful in fitting data like these. A distribution of mean hopping rates is consistent with having a polycrystalline or amorphous powder with many molecular environments. This could be because there are several molecules per unit cell or because the crystallites are very small with a significant fraction of molecules at crystallite boundaries or because there is no medium- or long-range structure at all. Despite several decades of discussion, the success of the Davidson–Cole distribution of correlation times is not understood.

An interesting aspect of this study is that the high-temperature R_1 versus T data (open symbols in figure 2) are well fitted by the fit to the low-temperature data (full symbols). By the highest temperatures (200 K), the NMR line width was characteristic of a liquid. The extra motion (that in addition to methyl group re-orientation) could be whole-molecule rotation or translational diffusion. Whatever it is, the time scale characterizing the process is too long to affect the proton Zeeman relaxation rate R_1 significantly. On the one hand, this means that we cannot really say anything specific about this extra motion. On the other hand, this also means that the comparison of theoretical models with the data is not complicated by these extra motions. This insensitivity results from the combination of the dominance (but not total) of the intra-methyl spin–spin interaction in determining the overall strength of R_1 (namely the value of A) and the dominance (but again not total) of the intra-methyl electronic interactions (namely the value of E) in determining the dynamics of the methyl group.

6. Summary

This work is part of a programme that exploits intra-molecular rotors in small organic molecules to understand and characterize both the dynamics of the rotors themselves and the environment that determines their dynamical properties. We have measured the spin-lattice relaxation rate R_1 in 1,3-di-isopropyl-benzene as a function of temperature at three Larmor frequencies. These three sets of data have been fitted with a single four-parameter model. The fitted parameters support a model whereby only the methyl groups are re-orienting on the nuclear magnetic resonance Larmor frequency time scale (say about 10^{-11} to about 10^{-6} s) over the entire temperature region. (This was expected and is consistent with previous work.) This is the case despite the fact that the spin-spin relaxation rate (the inverse of the NMR line width) clearly shows an additional motion (whole-molecule rotation or translation) at higher temperatures.

The activation energy for methyl group re-orientation, 12 ± 1 kJ mol $^{-1}$, is typical of methyl groups with this alkyl group environment. The barrier is dominated by the intra-alkyl electronic contribution. Similar values for the barrier are found for some methyl groups in aromatic compounds in which the methyl group has local interactions similar to those found for methyl groups in ethyl and isopropyl groups. One example is some methyl-substituted phenanthrenes [10, 11]. In addition, similar barriers are found in some methyl groups in tertiarybutyl groups [18]; namely, in cases in which the methyl groups sit outside the plane of an aromatic ring and re-orient much faster than the whole tertiarybutyl group. Finally, this barrier is also found in ethyl-substituted benzenes [5] and other isopropyl-substituted benzenes [6–8]. We note that ‘isolated’ methyl groups, like that in methyl-benzene, have barriers that are much lower and usually completely determined by intermolecular interactions.

One strength of the solid state spin-lattice relaxation technique lies in the ability to determine which intra-molecular groups are re-orienting and what the rotational barriers are. The ability to determine these matters is reasonably independent of the state of the solid from day to day, the origin of the independence being the dominance of the intra-alkyl (alkyl = ethyl, isopropyl and sometimes tertiarybutyl) contribution to the barrier (giving rise to the observed rotational barrier E) and the dominance of the intra-methyl spin-spin interaction in determining the strength of the local field (giving rise to the parameter A). The structure of the solid makes a small but non-negligible contribution to these parameters. Thus the technique can probe structure as a secondary goal. The parameter ϵ , for example, is a measure of the distribution of mean hopping rates. If all molecules were identical (or if there were only a few molecules per unit cell), ϵ should be unity, which reflects a single Poisson process. On the other hand, the technique cannot give the details of the solid state structure. Other techniques, such as variable-temperature x-ray diffraction, must be brought to bear.

In spite of the dominance of intra-molecular interactions, the day-to-day relaxation experiments show that the structure is changing. Whereas the methyl barrier (E) is determined largely by nearest-neighbour (in this case, intra-isopropyl) interactions, the spin-spin interactions (that determine A) have some long-range contributions. Indeed, this is often mentioned as a drawback to the technique since it limits the ability to determine precise quantitative information with high precision. The parameter A is proportional to a sum of terms each of which involve r^{-6} for each spin-spin separation r (such that at least one spin in the pair is involved in the motion). For methyl group re-orientation, the intra-methyl $r = 0.18$ nm distances dominates this sum [24]. However, there is clearly enough of a contribution from terms involving interactions between methyl protons and protons on

neighbouring molecules to change A by as much as 30% as reflected in the day-to-day scattering in the measurements. Thus, the spin–lattice relaxation technique can at least help in elucidating some local phenomena involved in the complicated structure of organic molecular solids. The interesting question that remains is that of whether the sample from day-to-day involves different arrangements of crystallites and amorphous regions, depending on the details of the thermal preparation, or whether it involves completely different but only amorphous structures.

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