# Proton Spin-lattice Relaxation in Amorphous States of Organic Molecular Solids

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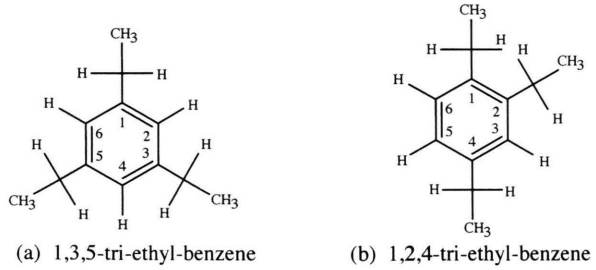
We have measured the temperature dependence of the proton spin-lattice relaxation rate $R$ at 8.50 and 22.5 MHz in solid 1,3,5-tri-ethyl-benzene and solid 1,2,4-tri-ethyl-benzene. Analysis of the data strongly suggests that we are studying amorphous states in these slowly solidified organic solids (that are liquids at room temperature). The ethyl groups are static on the Larmor frequency time-scale. There are no simple-model interpretations of the data, but a reasonable model for the dominantly-occurring amorphous state data observed with 1,3,5-tri-ethyl-benzene suggests that two of the three methyl groups are reorienting and the third is static on the proton Larmor frequency time scale. The same approach for the two amorphous states observed in 1,2,4-tri-ethyl-benzene suggests that all three methyl groups are reorienting in one state and that three of the six methyl groups in each pair of molecules are turned off in a second state. We discuss that, whereas specific dynamical statements are model dependent, the proton spin relaxation technique does make some general qualitative statements about the mesostructure of the solid.

*Key words:* Spin Relaxation, Amorphous Solids, Organic Solids.

## 1. Introduction

Comparing spin-lattice relaxation rate $R$ measurements in organic molecular solids composed of similar molecules can help in understanding the relationship between molecular geometry and molecular packing in the solid state. In this study we investigate the temperature dependence of the proton spin-lattice relaxation rate $R$ in two isomers of tri-ethyl-benzene (Fig. 1) at two Larmor frequencies.



(a) 1,3,5-tri-ethyl-benzene (b) 1,2,4-tri-ethyl-benzene

Fig. 1. Schematic pictures of (a) 1,3,5-tri-ethyl-benzene (1,3,5-TEB) and (b) 1,2,4-tri-ethyl-benzene (1,2,4-TEB).

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The spin-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 $\gamma$ [1]. An excited spin system can only relax via stimulated emission, and the relaxation rate is a measure of the number of (virtual) energy packets $\hbar \omega = \gamma \hbar B$ provided, per unit time, by the electromagnetic environment. These (virtual) photons are, in turn, produced by moving spins that reside on molecular moieties (in this case methyl groups) whose motion has components at a 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 $R$ can be linked to the motion. The temperature and magnetic field dependence of the relaxation rate provide information about which intramolecular groups are reorienting, the statistics associated with the motion (in the sense that one is monitoring many different rotors), the local geometry, and the state of the solid.

In the case of solids like the two isomers of tri-ethyl-benzene, reorienting methyl groups are providing the local oscillating magnetic fields. There are no other motions on the Larmor frequency time scale. There is no tunneling at the temperatures used here. The motion is described by thermally-activated hopping.

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## 2. Theory Review

The spin-lattice relaxation rate in ethyl-substituted systems is discussed in detail in [2]. $R$ is given by $R = C[j(\omega, \tau) + 4j(2\omega, \tau)]$ or a sum of such terms. If methyl group reorientation is the only motion and it is a simple random process characterized by a mean hop rate $\tau^{-1} = \tau_p^{-1}$ (where p refers to Poisson) then the correlation function is [3] $g(t) = \exp(-|t|/\tau_p)$ and the spectral density, the Fourier transform (times $(2\pi)^{1/2}$) of $g(t)$, is [4] $j(\omega) = 2\tau_p/(1+\omega^2\tau_p^2)$. The parameter $C$ (discussed further below) in the expression for $R$ is a measure of the magnitude of that part of the local magnetic field that is being modulated by the motion. The mean hop rate is given by $\tau_p^{-1} = \tau_{po}^{-1} \exp(-E_p/kT)$ for an activation energy (rotational barrier) $E_p$ (where the p again refers to Poisson) and infinite-temperature hop rate (or attempt frequency) $\tau_{po}^{-1}$. This dynamical model predicts that the slopes $\Delta(\ln R)/\Delta(T^{-1})$ at high and low temperatures are of equal magnitudes $E_p/k$. This is not observed for 1,3,5-tri-ethyl-benzene (Fig. 2), and the data for 1,2,4-tri-ethyl-benzene (Fig. 3) are inconclusive. This simple model also predicts that $R(\omega_1)/R(\omega_2) = (\omega_2/\omega_1)^2$ at low temperatures [4] and this is not observed for either system. This can be said despite the large scatter in the experimental data in Figure 3. This unique activation energy, random-motion model has three adjustable parameters: $C$, $E_p$, and $\tau_{po}$.

A simple four-parameter model that fits the data is the Davidson-Cole spectral density [4–6]. The model assumes that there is a distribution of mean hop rates with a low-frequency cutoff $\tau_{dc}^{-1}$ and a width characterized by $1-\varepsilon$ with $\varepsilon = 1$ giving a Dirac $\delta$-function distribution at $\tau_{dc}$ (in which case the unique $\tau = \tau_{dc} = \tau_p$). The characteristic cutoff frequency is given by $\tau_{dc}^{-1} = \tau_{dco}^{-1} \exp(-E_{dc}/kT)$. The spectral density is $j(\omega) = (2/\omega)\{\sin[\varepsilon \arctan(\omega\tau_{dc})]\}/\{(1+\omega^2\tau_{dc}^2)^{\varepsilon/2}\}$, and there are four parameters: $C$, $E_{dc}$, $\varepsilon$, and $\tau_{dco}$ [4, 5].

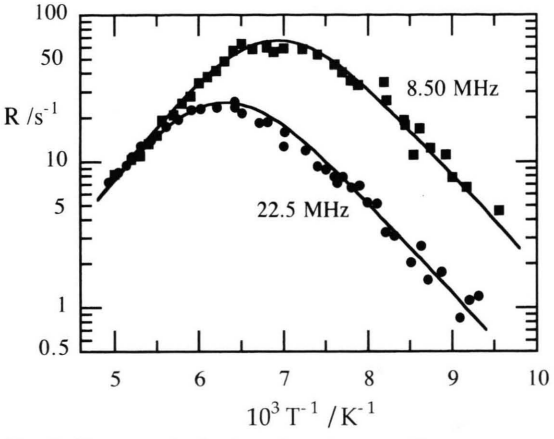


Fig. 2. Proton spin-lattice relaxation rate $R$ versus temperature $T$ in state one of solid 1,3,5-tri-ethyl-benzene at 22.5 and 8.50 MHz as indicated. The 22.5 MHz data are shown again in Figure 4. The two lines are a single four-parameter fit as discussed in the text.

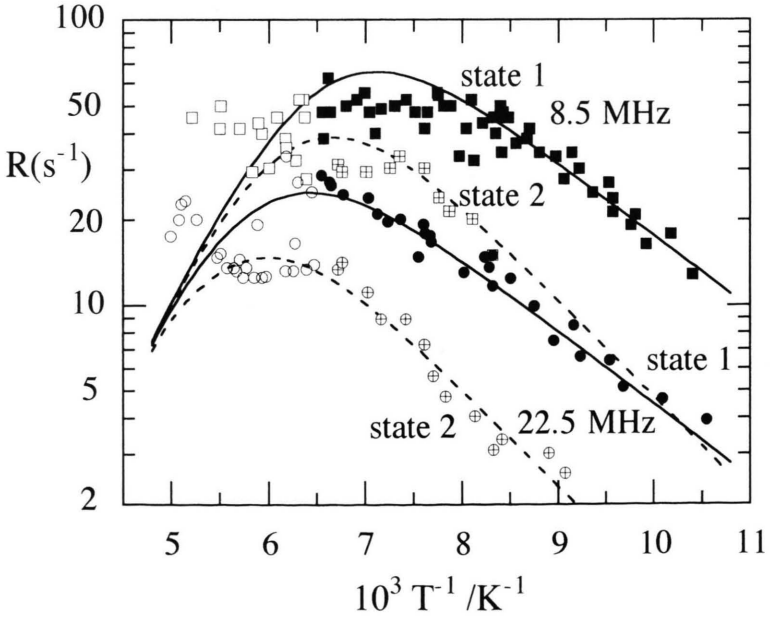


Fig. 3. Proton spin-lattice relaxation rate $R$ versus temperature $T$ in solid 1,2,4-tri-ethyl-benzene at 8.50 and 22.5 MHz as indicated. The closed squares and the closed circles refer to state one, and the open squares with plus signs superimposed and the open circles with plus signs superimposed refer to state two. Both states are characterized by a solid state line width of about 150 kHz. $R$ values corresponding to solid states with significant line narrowing at higher temperatures are shown at 8.50 MHz (open squares) and 22.5 MHz (open circles). The two solid lines are an example of a possible single fit to the low-temperature state one data, and the two dashed lines are an example of a possible single fit to the low-temperature state two data as discussed in the text.

It should be emphasized that there is no fundamental *a priori* reason for using the Davidson-Cole distribution of hop rates. It is simply the most algebraically tractable four-parameter model that fits relaxation rate data like those presented here. The model is very old and has its origin in dielectric relaxation in the 1950's [6]. It has been used extensively to model dynamics in a large range of systems, including polycrystalline [5, 7, 8] and glassy solids [9, 10].

We note that much work has been done comparing the Davidson-Cole spectral density (which is in the frequency domain) with the Kohlrausch-Williams-Watts or stretched-exponential correlation function $g(t)=\exp\{-(t/\tau_{kww})^{\beta}\}$ (which is in the time domain) [11, 12]. The problem is that, except for certain specific values of the width parameters (like $\beta=1/3$, $1/2$, and $2/3$ [12]), one of these functions must be numerically Fourier transformed before comparisons can be made. For a specific frequency, this can be done quite successfully and the two models are sufficiently close that one could not distinguish between them for most experimental data. However, they differ in significant ways [11] and we have shown that their frequency dependence is different in ways that allows them to be distinguished [13]. Namely, like the simple random process model (and like most experimental data, including that presented in Fig. 2 for solid 1,3,5-tri-ethyl-benzene), the Davidson-Cole model predicts that the spectral density is independent of the Larmor frequency in the short correlation time (high-temperature) limit. This is not the case for the (Fourier transform of the) Kohlrausch-Williams-Watts model [13]. This has not generally been appreciated in the literature. The Kohlrausch-Williams-Watts model is better compared [14] with the Havriliak-Negami model [4] which has two distribution parameters (whereas the Davidson-Cole model has only one, $\varepsilon$).

It is helpful to compare fitted values of $C$ in $R=C[j(\omega,\tau)+4j(2\omega,\tau)]$ with those computed assuming various models for the motion [2]. The parameter $C$ contains [2] both the factor $n/N$, where $n$ is the number of hydrogen nuclei involved with the motion and $N$ is the total number of hydrogen nuclei in the molecule, and the factors $r^{-6}$, where $r$ is the distance from each hydrogen nucleus involved in the motion to every other hydrogen nucleus in the sample. On the basis of these dependencies, various models for the motion can be tested so long as both the short correlation time ($\omega\tau<1$) and the long correlation time ($\omega\tau>1$) regimes are investigated and more than one Larmor frequency is used. This is the case for 1-3-5-tri-ethyl-benzene but not for 1-2-4-tri-ethyl-benzene. Finally, even though all motions may be thermally activated, if individual (i.e., non-superimposed) motions are very slow ($\omega\tau\geq 10^{4}$) or very fast ($\omega\tau\leq 10^{-4}$) at all temperatures and frequencies, the hydrogen nuclei involved will be indistinguishable from static nuclei.

We consider three models. They all assume that some dipolar interactions are being modulated by the motion and others are not. All dipolar interactions, whether modulated or not, are important, however, in that rapid spin diffusion (via energy conserving spin flips) allows all the (proton) spins in the molecule to relax equally. This occurs because the temperature-independent spin-spin relaxation rate (about $10^{5}\ s^{-1}$) is many orders of magnitude greater than the spin-lattice relaxation rate $R$ (Figs. 2 and 3) and all hydrogen atoms in the molecule are chemically equivalent (in the sense that the nmr line is about $10^{5}$ Hz compared with chemical shifts of tens of Hz). Also, since we only observe one maximum in $R$ and since it is not broadened appreciably, we can say that any model that assumes two motions are occurring must also assume that they are strongly correlated and that both motions are characterized by the same mean hop rate.

In the first model, only the three methyl groups are reorienting and $C=C_{m}=1.91\cdot 10^{9}\ s^{-2}$ for both isomers of tri-ethyl-benzene. This model usually works very well for ethyl-benzenes in the solid state [2]. In this case, the ethyl groups are static, meaning that the reorientation of the ethyl group, characterized by some $\tau_{e}$, is very slow on the Larmor frequency timescale (i.e., $\omega\tau_{e}\gg 1$) at all temperatures. In this model it is assumed that only intra-methyl spin-spin dipolar interactions are modulated by the motion. Palmer [15] has added to the calculation the modulation of the intra-ethyl, methyl – non-methyl spin-spin interactions. Assuming again that only the methyl group reorientation is modulating these interactions, taking into account these additional terms would raise $C$ from $C=C_{m}$ by about 8–12% with the precise amount depending on the equilibrium orientation of the methyl group. We will take a value of 10% and quote a theoretical value of $C=D_{m}=(2.10\pm 0.04)\cdot 10^{9}\ s^{-2}$, where the uncertainty in this theoretical value reflects the 8–12% range.

In the second model, the ethyl groups are reorienting rapidly on the Larmor frequency timescale ($\omega\tau_{e}\ll 1$) at all temperatures and again, only intra-methyl spin-spin dipolar interactions are assumed to be effectively

modulated by the motions. In this case, $C = C'_m = 5.65 \cdot 10^8\ s^{-2}$. The relaxation rate is less in this case because the methyl rotation is superimposed on a rapid rotation that has the effect of averaging out some portion of those spin-spin dipolar interactions whose modulation is responsible for the relaxation. This situation has never been observed in ethyl (and isopropyl) substituted aromatic systems in the solid state. The asymmetry of these groups will result in crystal packing that tends to prohibit these motions. (Whole alkyl group rotation *is* observed in *t*-butyl systems [16]. These groups have three-fold symmetry.) The additional effect of the modulation of intraethyl, methyl – non-methyl spin-spin interactions by methyl and ethyl reorientation on the value of $C'_m$ has not been determined. All that can be said is that it will increase by less, probably much less, than the 10% that increases $C = C_m$ to $C = D_m$. Including these effects, we set the theoretically-determined parameter $C = D'_m = (5.9 \pm 0.3) \cdot 10^8\ s^{-2}$.

The third case we consider is when both the ethyl groups and their constituent methyl groups are reorienting on the Larmor frequency timescale. In this case, $R = C[j(\omega, \tau) + 4j(2\omega, \tau)]$ is an approximation (since there is a term in $\tau/2$ resulting from the superimposed motions as well as one in $\tau$ resulting from the individual motions) with $C = C_{me} = 3.64 \cdot 10^9\ s^{-2}$. Again, the additional effects of considering the modulation of the intraethyl, methyl – non-methyl spin-spin interactions have not been determined but they will increase $C_{me}$ by less than 10%. We set the theoretical value that includes these effect to $C = D_{me} = (3.8 \pm 0.2) \cdot 10^9\ s^{-2}$.

A useful benchmark with which any $\tau_o$ (like $\tau_{po}$ in the Poisson model or $\tau_{dco}$ in the Davidson-Cole model) can be compared is obtained using the large barrier harmonic approximation [17] $\tau_o = (2\pi/3)\ (I/2E)^{1/2}$, where $E$ (like $E_p$ or $E_{dc}$) is the activation energy (determined independently from fitting the data) and $I$ is the moment of inertia. The model is crude and is only a benchmark. However, the dependence on the moment of inertia means that $\tau_o$ for, say, methyl group reorientation and, say, whole molecule reorientation, differ considerably.

## 3. Experiment

The samples of 1,2,4-tri-ethyl-benzene (1,2,4-TEB) and 1,3,5-TEB (Fig. 1) were purchased from Aldrich Chemical (USA). They are both liquids at room temperature. The quoted purities and melting points are 98% and 195 K for 1,2,4-TEB and 98% and 207 K for 1,3,5-TEB. Two evacuated and sealed samples of each were made using many cycles of a freeze-pump-thaw process. On the basis of the relaxation rate measurements, the two samples of 1,2,4-TEB were indistinguishable. The same is true for the two samples of 1,3,5-TEB.

The spin-lattice relaxation rate $R$ measurements were made using a $\pi$-$t$-$\pi/2$-wait pulse sequence with the wait time greater than $8\,R^{-1}$. The $R$ versus $T$ data at 8.50 and 22.5 MHz are presented in Figs. 2 (1,3,5-TEB) and 3 (1,2,4-TEB). The 22.5 MHz data for 1,3,5-TEB are shown again in Fig. 4, where different sets of measurements are indicated with different symbols. (A "set" is defined below.) The relaxation was exponential to within experimental accuracy, and the uncertainties in each $R$ measurement are between 5 and 10%, the latter only marginally larger than the size of the symbols in the figures. Sample ten-percent error flags are shown in Fig. 4 (several closed circles) for one set of measurements.

The evacuated, sealed samples were prepared with specific thermal histories for each set of measurements. Following solidification, the sample remained solid throughout each set. For 1,3,5-TEB, a powdery-looking state was reproducibly produced by slowly freezing the room-temperature liquid sample over a period of several tens of minutes. We refer to this state as state one, and all the data in Figs. 2 and 4 were taken when the sample was in this state. A glassy-

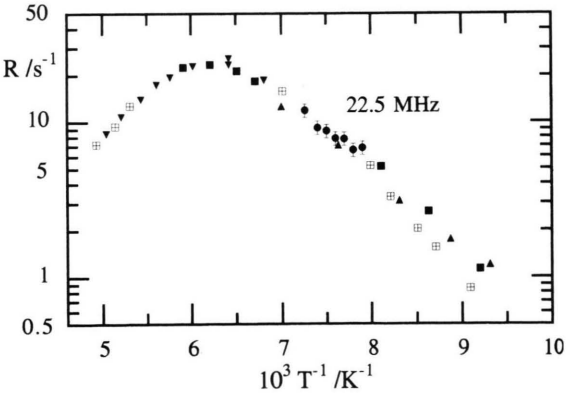


Fig. 4. Proton spin-lattice relaxation rate $R$ versus temperature $T$ in solid 1,3,5-tri-ethyl-benzene at 22.5 MHz. The different symbols refer to different sets of measurements as discussed in the text. All these data are shown in Figure 2. Ten percent error flags are shown for the experiments in one set (closed circles).

looking state could be obtained by a more rapid freezing, and the relaxation rates below about 130 K ($10^3\ T^{-1} > 7.7\ K^{-1}$) were significantly greater than those found in state one. These $R$ versus $T$ data are not shown.

The carefully investigated powdery-looking state one for 1,3,5-TEB is not a unique solid state since the set-to-set scatter in $R$ versus $T$ (up to about 30% at low temperatures) is significantly greater than the 5–10% uncertainty for each $R$ value. This is particularly true at lower temperatures. In Fig. 4, we show different sets of measurements (presumably different thermal preparations, unintended as that may be) in different symbols for 1,3,5-TEB at 22.5 MHz. (All the data in Fig. 4 are also shown in Figure 2.) A "smooth curve" (consistent with the 5–10% uncertainties associated with each measurement) can be drawn through each set of measurements. Ten percent error flags are shown for one set. At higher temperatures, thermal history has little effect and the scatter in the data is generally within the expected 5–10% uncertainties for individual measurements.

For 1,2,4-TEB, the situation was very much more complicated. Sometimes a powdery-looking solid was produced and sometimes a glassy-looking solid was produced, regardless of how slowly the sample was cooled. We divide the $R$ versus $T$ data into two temperature regions. For temperatures below about 150 K ($10^3\ T^{-1} > 6.5\ K^{-1}$), the free induction decay was characterized by a decay time of about 5–8 μs corresponding to a typical nmr line width (perhaps even somewhat broader than usual) for these kinds of organic solids. These data are represented by closed squares and open squares with superimposed plus signs at 8.50 MHz, and by closed circles and open circles with superimposed plus signs at 22.5 MHz in Figure 3. For temperatures above about 150 K, the nmr line began to narrow (usually, but not always) and the free induction decay was characterized by times ranging from 5–1000 μs in an inconsistent (from set-to-set) manner. We suggest that the different thermal histories lead to different local structures, and that these different structures allow for different degrees of additional motions as the temperature increases. These extra motions could be whole-molecule rotation or translation. The molecule is very symmetric (but quite large) and whole-molecule rotation seems more likely than does translation. Measurements taken under these conditions of some degree of line narrowing are indicated by open circles at 22.5 MHz and by open squares at 8.50 MHz. It is important to note that when a single set of $R$ versus $T$ measurements is investigated, one can draw a smooth line through the data with a point-to-point scatter indicative of the 5–10% uncertainty in each measurement, as shown in Fig. 4 for 1,3,5-TEB. Also, even for the narrowest line width (about one kHz), spin diffusion is still rapid. That is, we are still very far from the "isotropic liquid-line" limit.

For 1,2,4-TEB, we further subdivide the region below about 150 K into two states. State one is defined by $R$ values indicated by closed squares at 8.50 MHz and by closed circles at 22.5 MHz, and state two is defined by $R$ values indicated by open squares with superimposed plus signs at 8.50 MHz and by open circles with superimposed plus signs at 22.5 MHz. Even though each of these two solid states is clearly a collection of (a continuum of different) amorphous states, there seems to be a clear cut distinction between the two (groups), particularly at low temperatures at 22.5 MHz where more data is available. As in the case of 1,3,5-TEB, whereas adjacent $R$ values within each of these two states differ greatly (for example by more than a factor of three at 22.5 MHz at the lowest temperatures, $8 < 10^3\ T^{-1} < 9\ K^{-1}$), adjacent data points measured consecutively in the same set generally differed by amounts typical of 5–10% uncertainty in the determination of each $R$ value. It would be reassuring to be able to conclude that one of these states always corresponded to a glassy-looking state and the other to a powdery-looking state *but this was not the case.* Whereas visual appearance gives information concerning whole-sample, macroscopic structure, the relaxation rate is sensitive to local interactions and therefore to the "state" at the level of at most a few molecules.

## 4. Analysis and Discussion

The 1,3,5-TEB data are well-fitted using a Davidson-Cole spectral density. Figure 2 shows two solid lines which are a *single* fit to both frequencies with $E_{dc} = 13 \pm 2$ kJ mole$^{-1}$, $\varepsilon = 0.90 \pm 0.05$, $C = (1.35 \pm 0.07) \cdot 10^9\ s^{-2}$ and $\tau_{dco} = (2.5 \pm 1.3) \cdot 10^{-13}$ s. The significant uncertainties in some parameters result from the scatter in the data and the algebraic manner in which they are related to $R$ [5]. Forcing $\varepsilon = 1$ leads to a bad fit, so a single mean correlation time cannot be ascribed to the motion. The value of $\varepsilon = 0.9$, however, means that

most methyl groups experience barriers very close to $E_{dc}$ [2]. As such it is not unreasonable to associate $E_{dc}$ with "the methyl barrier." (At the same time, however, we note the extreme sensitivity of the technique to a very small distribution of barriers.) This value $E_{dc} = 13$ kJ mole$^{-1}$ is typical of methyl groups in ethyl [2] and isopropyl [18, 19] groups; it is dominated by the intraalkyl (electrostatic) interactions.

The value of $C$ resulting from the single fitted curve to the 1,3,5-TEB data is interesting and unusual. Cast in terms of the theoretical values of the three $D_i$ discussed in the Theory Review, $C/D_m = 0.64 \pm 0.05$, $C/D_m' = 2.3 \pm 0.3$ and $C/D_{me} = 0.36 \pm 0.04$. The uncertainties fold in both the 5% uncertainty in the experimentally-determined $C$ and the uncertainties in the theoretical values of the $D_i$. All three of these ratios are too far from unity to conclude that any of the models is reasonable. All three models have taken into account the motional modulation of both the dominant intramethyl proton spin-spin interactions and the intraethyl, methyl proton – non-methyl proton interactions. The modulation of spin-spin interactions between methyl protons and other protons in the same molecule are completely negligible [15]. The modulation of spin-spin interactions between methyl protons and protons on adjacent molecules may increase the $D_i$ slightly but not by very much because these Van der Waals solids simply don't allow the molecules to come that close together [20]. So, fitted values of $C/D_i$, say, up to 10% greater than unity may result from the modulation of these additional intermolecular spin-spin interactions. The fitted value of $C/D_m' = 2.3 \pm 0.3$ completely rules out the model whereby the ethyl groups are reorienting rapidly on the Larmor frequency timescale. This is as expected. On the other hand, ratios of $C/D_i$ significantly less than unity are impossible since the calculated value of the $D_i$ are minimum values within the confines of the dynamical model. They rely only on the well-understood geometry of an ethyl group. We conclude from this interesting dilemma that the most likely scenario is that only two of the three methyl groups are reorienting (with none of the ethyl groups reorienting). This would decrease the predicted value of $D_m$ by 2/3 and make the fitted $C/D_m = 0.96 \pm 0.08$. Alternatively, we could assume that two ethyl groups and their constituent methyl groups are frozen and that one ethyl group is reorienting rapidly with its constituent methyl group reorienting on the Larmor timescale. This would decrease $D_{me}$ by a factor of three and make $C/D_{me} = 1.1 \pm 0.1$. This seems a physically unlikely scenario (that two ethyl groups are so crowded by other molecules and the third ethyl group is so free) given the asymmetry of ethyl groups and the way these kinds of molecules like to pack together, but we cannot rule it out. The solid state crystal structure of these room-temperature liquids is not known. One can, however, imagine a local, few-molecule structure [20] involving $2n$ ($n = 1$, 2, or maybe 3) molecules, where one of the three ethyl groups in every molecule is close enough to a neighboring molecule to give the methyl group a very high barrier, effectively turning it off on the Larmor frequency timescale. Herring bone structures are common in organic molecular solids and such a structure could lead to this situation. This situation is arising in, what on a macroscopic level is an amorphous structure. There are other possible combinations of structure and motion that will account for the observed value of $C$ but they are all highly contrived.

We emphasize that the above discussion assumes that the Davidson-Cole spectral density chosen to fit the data is appropriate. Whereas one must always allow for the possibility that other equally successful (and to date unknown) spectral densities might lead to different mathematical representations of the dynamical models, it seems reasonable that these different (and unknown) spectral densities should lead to the same conclusions concerning the values of the parameter $C$. We only say this because all spectral densities must satisfy the same normalization [4] and, in the present case, the parameters are *over* determined by fitting the data. All four Davidson-Cole parameters can be determined by the temperature dependence of the relaxation rate at a single Larmor frequency so long as both the short correlation time ($\omega \tau \ll 1$) and the long correlation time ($\omega \tau \gg 1$) limits are observed. Equivalently, if the relaxation rate is observed only in the long-time correlation time limit but at two Larmor frequencies, again, all four parameters can be determined [21]. As such, one can consider the solid line for the data at one Larmor frequency in Fig. 2 as fitted to the data whereas the other is uniquely determined with *no adjustable parameters.*

The value of $\tau_{dco} = (2.5 \pm 1.3) \cdot 10^{-13}$ s for 1,3,5-TEB gives $\tau_{dco}/\tau_o = 1.7 \pm 0.8$, where the theoretical value of $\tau_o$ is discussed in the Theory Review. This supports those aspects of the model suggesting that only methyl groups are reorienting. The parameter $\tau_o \propto (I/E)^{1/2}$. If we used the moment of inertia for whole-molecule

motion to determine $\tau_o$, for example, the fitted value of $\tau_{dco}/\tau_o$ would be very much smaller.

It is impossible to arrive at a unique fit of the 1,2,4-TEB data (Fig. 3) on the basis of the data alone. The only parameter that can be uniquely fitted for the Davidson-Cole distribution is $\varepsilon$ for the state one values at lower temperatures (solid squares and solid circles). For the Davidson-Cole spectral density, $R(\omega_1)/R(\omega_2)=(\omega_2/\omega_1)^{1+\varepsilon}$ at low temperatures [4]. The low-temperature data in Fig. 3 (solid circles and solid squares for $10^3\ T^{-1} > 8.5\ K^{-1}$ give $\varepsilon = 0.4 \pm 0.1$. This is considerably less than unity and suggests a large distribution of mean hop rates [4]. This conclusion is consistent with the independently observed set-to-set variation in the observed temperature dependence of the spin-lattice relaxation rate.

We acknowledge that it may be premature to fit the 1,2,4-TEB relaxation data. However, the temptation is overwhelming and we offer, for completeness, a few example fits from among many possibilities. Those we consider are consistent with the 1,3,5-TEB fits and with previous work in ethyl [2] and isopropyl [18, 19, 21] systems. We emphasize that these fits are only possible examples. We show two fits to the low-temperature data: the full curve characterizes state one and the dashed curve characterizes state two (both at both frequencies). We have *fixed* $E$ at $E \equiv 12$ kJ mole$^{-1}$, a value typical for methyl groups in ethyl and isopropyl groups. (The fitted value for 1,3,5-TEB was $13 \pm 2$ kJ mole$^{-1}$).

For the example fit to state one (solid line in Fig. 3), the other two parameters (fixing $E \equiv 12$ kJ mole$^{-1}$ and $\varepsilon \equiv 0.4$) are $C = (2.0 \pm 0.4) \cdot 10^9\ s^{-2}$ and $\tau_{dco} = (9 \pm 5) \cdot 10^{-13}$ s. These values give $C/D_m = 0.9 \pm 0.2$, $C/D_m^{/} = 3.3 \pm 0.9$, $C/D_{me} = 0.5 \pm 0.1$ and $\tau_{dco}/\tau_o = 6 \pm 1$. The fitted value of $C/D_m = 0.9 \pm 0.2$ is consistent with the three methyl groups reorienting on the Larmor frequency timescale as found in other systems [2]. The other two ratios are either too much greater than unity or too much smaller than unity. Other models are effectively ruled out (within the confines that $E$ has been fixed independently of the data) *even considering the very large uncertainties in the fitted parameters resulting from the very considerable scatter in the experimental data.*

With $E_{dc}$ fixed at 12 kJ mole$^{-1}$, $\varepsilon = 0.5$ (with a large uncertainty) gives a reasonable fit to the more limited state-two data (open circles with plus signs superimposed and open squares with plus signs superimposed) as indicated by the dashed lines. With $E_{dc}$ and $\varepsilon$ fixed at these values, the other two parameters are $C = (1.0 \pm 0.2) \cdot 10^9\ s^{-2}$ and $\tau_{dco} = (1.4 \pm 0.7) \cdot 10^{-12}$ s, which gives $C/D_m = 0.5 \pm 0.1$, $C/D_m^{/} = 1.7 \pm 0.4$, $C/D_{me} = 0.26 \pm 0.07$ and $\tau_{dco}/\tau_o = 9 \pm 5$. If we assume again that only the methyl groups are reorienting, the value of $C/D_m$ suggests that half of the methyl groups are "turned off." One can imagine 2 (or 4 or 6, etc.) molecules per "group" with the 1- and 2-ethyl groups on one molecule "locked" with the 4-ethyl group on a neighbouring molecule. Several other models will work as well. Given the state of the data, any further fitting procedure would be (further?) overanalysing the data.

It is significant, however, that in 1,2,4-TEB, *state one displays twice the relaxation rate than does state two.* Assuming that the ethyl groups are not reorienting in either state, a situation found in all other ethyl and isopropyl systems where the analysis can be more complete, this says that *however many methyl groups are reorienting in state one, about half of them are turned off in state two.*

## 5. Summary and Discussion

The temperature dependence of the proton spin-lattice relaxation rate $R$ (Fig. 2) in solid 1,3,5-tri-ethylbenzene (Fig. 1 a) is consistent with a model whereby two of the three methyl groups are reorienting and the ethyl groups are static on the Larmor frequency timescale. The third methyl group is also static. The activation energy of 13 kJ mole$^{-1}$ is typical of methyl reorientation in ethyl (and isopropyl) groups. A low temperature X-ray study is needed to confirm this interpretation. Although there is a distribution of activation energies, it is very narrow.

The $R$ versus $T$ measurements (Fig. 3) in solid 1,2,4-tri-ethyl-benzene (Fig. 1 b) show that below about 150 K the system goes into one of two states even though the sample was slowly cooled the "same" way for each set of measurements. We suggest that these are two distinct amorphous states. That each is amorphous follows from the considerable spread in $R$ versus $T$ data within each state and from a model-independent fitting parameter that is uniquely determined by the frequency dependence of $R$ at low temperatures. The latter suggests a large distribution of activation energies that characterize the motion. The data cannot be uniquely fitted because the nmr line narrows considerably (sometimes) above about 150 K,

indicating additional motion. These motions also affect the relaxation rate which is apparent from the fact that the temperature dependence does not follow the usually-found pattern. The usual high-temperature limit of the $R$ versus $T$ curve characteristic of methyl group rotation only, is not, therefore, observed. However, if we assume an activation energy of 12 kJ mole$^{-1}$ (characteristic of ethyl and isopropyl methyl groups) then a reasonable model suggests that in one state (solid lines and solid symbols in Fig. 3) all three methyl groups are reorienting and in the other state (dashed lines and open symbols with plus signs superimposed) half the methyl groups are frozen on the Larmor frequency timescale.

Independently of the specific models for the motion, the data show that the proton spin relaxation technique is very sensitive to the (local) state of the solid. Whatever it is that is reorienting in state one in 1,2,4-tri-ethyl-benzene, half of "them" are turned off in state two. The spread in adjacent data points shows that the set-to-set structure is different, even within each (what we are calling a) state. So, the technique is very sensitive to the *mesoscopic* structure that concerns how several molecules are packing together in these amorphous states. The drawback to the technique is that the directly-measured experimental variable (i.e., the decay, in time, of an excited nuclear magnetization) is an average over many molecules. As such, the dynamics at the single-molecule level can only be extracted via statistical models. Low temperature X-ray studies of these systems would prove very interesting and very helpful.

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