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Methyl and *t*-butyl reorientation in an organic molecular solid

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Abstract

We have determined the molecular and crystal structure of 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene and measured the ^1H spin-lattice relaxation rate from 87 to 270 K at NMR frequencies of $\omega/2\pi = 8.50, 22.5, \text{ and } 53.0 \text{ MHz}$. All molecules in the crystal see the same intra and intermolecular environment and the repeating unit is half a molecule. We have extended models developed for ^1H spin-lattice relaxation resulting from the reorientation of a *t*-butyl group and its constituent methyl groups to include these rotors and the 9-methyl groups. The relaxation rate data is well-fitted assuming that the *t*-butyl groups and all three of their constituent methyl groups, as well as the 9-methyl groups all reorient with an NMR activation energy of $15.8 \pm 1.6 \text{ kJ mole}^{-1}$ corresponding

to a barrier of $17.4 \pm 3.2 \text{ kJ mole}^{-1}$. Only intramethyl and intra-*t*-butyl intermethyl spin-spin interactions need be considered. A unique random-motion Debye (or BPP) spectral density will not fit the data for any reasonable choice of parameters. A distribution of activation energies is required.

1. Introduction

The motion of nuclear spins modulates their nuclear spin-spin (dipole-dipole) interactions and this results in the relaxation of an excited nuclear spin system. As such, the observed nuclear magnetic resonance (NMR) spin-lattice relaxation rate can be related to models of the motion. We have developed dynamical models for the case where the motion is the reorientation of *t*-butyl groups and their constituent methyl groups on planar aromatic molecules [1]. These intramolecular reorientations are the only motions on the NMR time scale in these types of molecular solids. (The NMR timescale in the experiments reported here is approximately 10^{-12} to 10^{-5} s; 6-8 orders of magnitude.) The molecular structure in this class of compounds, as determined by X-ray diffraction experiments, show the *t*-butyl groups oriented such that one methyl group is in the aromatic plane, or nearly so, and two methyl groups are out of the plane [1]. The in-plane methyl group reorients at the same rate as the *t*-butyl group, whereas the two out-of-plane methyl groups usually reorient more rapidly, though in some cases, like that reported here, a very simple model can be used whereby all four rotors reorient at the

same rate [2]. An important aspect of the mathematical models used to interpret the observed spin-lattice relaxation rates is that the number of rotors reorienting on the NMR time scale are properly accounted for. (Many publications in this field ignore modeling the absolute magnitude of the relaxation rate.) That is, one can easily see if, for example, one of the methyl groups is not reorienting on the NMR time scale. As such, we seek to test the robustness of the model to include some rotor or rotors in addition to the four rotors in a *t*-butyl group. The simplest extension is to have an additional methyl group and, to that end, we present an investigation of 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene in this paper. We have determined the molecular and crystal structure using X-ray diffraction (Figs. 1 and 2) and we find that the simplest possible version of our extended model correctly accounts for the two additional methyl groups (i.e., not in *t*-butyl groups). In addition, as perhaps might have been expected from the high degree of molecular symmetry (Fig. 1), the two 9-methyl groups in this molecule have, to within the uncertainties resulting from both the experimentally and theoretically modeled parameters, the same barrier as the out-of-plane methyl groups in the *t*-butyl groups.

2. Spin-Lattice Relaxation Theory Review

The X-ray diffraction data show that there is a mirror plane perpendicular to the plane of the page in figure 1b ($Z' = \frac{1}{2}$) and we assume that the two *t*-butyl groups are

"equivalent," as are the two 9-methyl groups. Equivalent, here, means that they have the same intra- and inter-molecular environment and that their motion will be described by the same dynamical equations. The ^1H spin-lattice relaxation rate is taken to be

$$R = R_t + R_m, \quad (1)$$

with the relaxation rate resulting from the reorientation of the *t*-butyl groups and their constituent methyl groups given by [1]

$$R_t = \frac{n_t}{N} [K_b h(\omega, t_b) + K_{bb} h(\omega, t_{bb}) + K_c h(\omega, t_c) + K_{bc} h(\omega, t_{bc})], \quad (2)$$

and the relaxation rate resulting from the reorientation of the 9-methyl groups given by [3]

$$R_m = \frac{n_m}{N} K^{intra} h(\omega, t_m). \quad (3)$$

All the parameters are discussed below. Eqn. 2 accounts for the relaxation resulting from the modulation of the intra-*t*-butyl *intramethyl* spin-spin interactions by methyl group

reorientation and the relaxation resulting from the modulation of the intra-*t*-butyl, *intermethyl* spin-spin interactions by *t*-butyl reorientation. The latter is accounted for by condensing the three proton spins of each of the three methyl groups to the center of their respective triangles. This allows us to keep the model very simple; the *K* values in Eqn. 2 involve fixed distances that can be expressed in convenient closed algebraic forms [1]. The relaxation resulting from the modulation of *intermethyl* spin-spin interactions by methyl group reorientation is not accounted for. The justification for this model is that it fits the data very well and provides a simple conceptual interpretation of the relationship between the reorientations and the nuclear spin relaxation. We note also that the theoretical *K* values with which the fitted *K* values will be compared have, themselves, approximately $\pm 10\%$ uncertainties. These are indicated below. The difference between our simplified theoretical model and one that would properly account for the modulation of the *intermethyl* spin-spin interactions resulting from both methyl and *t*-butyl group reorientation is well below this 10% level.

From an equilibrium structural perspective, the two 9-methyl groups look very much like the two out-of-plane methyl groups in a *t*-butyl group. These two methyl groups differ dynamically from the out-of-plane methyl groups in a *t*-butyl group in that there is no superimposed reorientation. At the level of the model outlined above for the *t*-butyl group, we assume that the magnitude of the additional relaxation resulting from the

modulation of the spin-spin interactions between the protons on the two 9-methyl groups due to methyl group reorientation is considerably below the level of accuracy needed.

In Eqns. 2 and 3, $\omega = \gamma B$ is the NMR (Larmor) angular frequency for magnetic field B and proton magnetogyric ratio γ . Numerical values for these parameters are presented in the Experimental Section.

The additive form of the relaxation rate in Eqn. 1 assumes that 9-methyl group reorientation is independent of (i.e., uncoupled from) the coordinated four reorientations involving the *t*-butyl groups. The smallest distance between a 9-methyl proton and a *t*-butyl proton is approximately 0.5 nm, compared with the intramethyl proton-proton distance of approximately 0.18 nm which sets the scale. The spin-spin interaction strength is proportional to r^{-6} for proton-proton distance r and $(0.5/0.18)^{-6} = 0.002$ so the "direct" through-space interactions between *t*-butyl group protons and 9-methyl group protons are negligible. All reorientations distort the molecule slightly when the rotors go through transition states but we assume that this effect is small. Given the simplicity of our model and the uncertainties determined for the barrier heights, when theoretical and experimental uncertainties are both factored in, this is a reasonable assumption.

In Eqns. 1 and 2,

$$h(w, t) = j(w, t) + 4j(2w, t), \quad (4)$$

where the two terms account for single and double spin flips in the relaxation process [4].

The spectral density $j(\omega, t)$ is discussed below. There are $n_t = 18$ H nuclei in *t*-butyl groups (Eqn. 2), $n_m = 6$ H nuclei in (non-*t*-butyl group) methyl groups (Eqn. 3), and $N = 28$ H nuclei in the molecule (Eqns. 2 and 3).

The reorientation is modeled with Poisson statistics with a mean time τ between instantaneous $2\pi/3$ hops. (We use the words "reorientation" and "hops," meaning instantaneous hops in the quantum mechanical sense, and not the word "rotation" which invokes a more classical concept of continuous motion.) In Eqn. 2, t_b is the mean time between hops of both the *t*-butyl groups and their in-plane methyl groups. Steric hindrances prevent the in-plane methyl group from reorienting unless the *t*-butyl group also reorients. The mean time between hops for the out-of-plane methyl groups is t_c . In Eqn. 3, t_m is the mean time between hops for the 9-methyl groups. Eqn. 2 also accounts for the superimposed motions of the methyl groups and the *t*-butyl groups with $t_{bb}^{-1} = t_b^{-1} + t_c^{-1}$ and $t_{bc}^{-1} = 2 t_b^{-1}$. In turn, these mean times between hops are modeled by an Arrhenius relationship;

$$t_i = t_{\infty i} \exp\left(-\frac{E_i}{kT}\right) \quad (5)$$

for $i = b, c, m$. The NMR activation energy is E_i and the "infinite temperature mean time between hops" (a.k.a. the preexponential factor) is $t_{\infty i}$. The NMR activation energy is related to the barrier height in the Conclusions Section. A convenient benchmark for $t_{\infty i}$ is the simple harmonic model [5];

$$\tau_{\infty i} = \frac{2\rho}{3} \sqrt{\frac{2I}{E_i}}, \quad (6)$$

where I is the moment of inertia of the reorienting group (methyl or *t*-butyl). When $t_{\infty i}$ is taken as a fitting parameter once E_i has been determined, $t_{\infty i}/\tau_{\infty i}$ should be within an order of magnitude or so from unity, given the simplicity of the model.

We can calculate K^{intra} in Eqn. 3 assuming that only the six spin-spin dipole-dipole interactions involving the three protons in a methyl group are involved [3]. We call this computed value \tilde{K}^{intra} which is given by

$$\tilde{K}^{intra} = \frac{9}{40} \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{\hbar\gamma^2}{r^3} \right)^2 = (4.24 \pm 0.43) \times 10^9 \text{ s}^{-2}, \quad (7)$$

for proton magnetogyric ratio $\gamma = 2.675 \times 10^8 \text{ s}^{-1} \text{ T}^{-1}$, $\mu_0/4\pi \sim 10^{-7} \text{ N A}^{-2}$ (where μ_0 is the magnetic constant), and proton-proton separation $r = 0.1765 \text{ nm}$ in a methyl group. In previous works [1, 3], we used an H–H distance of $r = 0.1797 \text{ nm}$ which assumed an idealized tetrahedral geometry with idealized C–H bond lengths. However, recent electronic structure calculations [6] suggest that the lower value is more appropriate. Although this is only a 1.8% change in r , $\tilde{K}^{intra} \propto r^{-6}$ so this results in an 11% increase in the value of \tilde{K}^{intra} . We suggest that the uncertainty in the calculated value of \tilde{K}^{intra} , as a consequence of the uncertainty in r , is approximately $\pm 10\%$ as indicated in Eqn. 7. If dipole-dipole interactions between methyl H's and non-methyl H's are significant, the observed value of K^{intra} will be larger than \tilde{K}^{intra} . It is convenient to use $K^{intra}/\tilde{K}^{intra}$ as a fitting parameter which cannot be less than unity within the uncertainty of both its theoretical and experimental constituents.

Three of the four K values in Eqn. 2 are [1] $\tilde{K}_{bb} = (19/9) \tilde{K}^{intra} = 8.95 \times 10^9 \text{ s}^{-2}$, $\tilde{K}_c = (16/9) \tilde{K}^{intra} = 7.53 \times 10^9 \text{ s}^{-2}$, and $\tilde{K}_{bc} = (38/9) \tilde{K}^{intra} = 1.79 \times 10^{10} \text{ s}^{-2}$, each with approximately a $\pm 10\%$ uncertainty from the dependence on \tilde{K}^{intra} in Eqn. 7. In deriving Eqn. 2, dipole-dipole interactions between H spins on different methyl groups are taken into account but, as discussed above, a simplifying assumption is made and the result is that the calculation of \tilde{K}_b is more complicated, giving [1] $\tilde{K}_b = 1.88 \times 10^{10} \text{ s}^{-2}$. Again, the observed values of the K 's will be higher if dipole-dipole interactions between the nine ^1H

spins in a *t*-butyl group and other ^1H spins (either on the same molecule or on neighboring molecules) are significant. The ratios $K_b/\tilde{K}_b = K_{bb}/\tilde{K}_{bb} = K_c/\tilde{K}_c = K_{bc}/\tilde{K}_{bc} \sim K/\tilde{K}$ are fixed and treated as a single adjustable parameter.

There are, then, three mean times between hops in the perfect crystal; t_b , t_c , and t_m . If all molecules are truly equivalent (as suggested by the X-ray study, which uses a small single crystal), then the correlation functions for the three motions will be $g(t, t_i) = \exp(-t/t_i)$ for $i = b, c, m$ and the spectral densities in Eqn. 4 will be the random-motion Poisson (or Debye, or BPP) spectral density

$$j(\omega, t_i) = \frac{2 t_i}{(1 + \omega^2 t_i^2)}. \quad (8)$$

From the above discussion, there are several potentially adjustable parameters; E_b and $t_{\nabla b}/\tilde{t}_{\nabla b}$ for the *t*-butyl groups and their in-plane methyl groups, E_c and $t_{\nabla c}/\tilde{t}_{\nabla c}$ for the *t*-butyl groups' out-of-plane methyl groups, E_m and $t_{\nabla m}/\tilde{t}_{\nabla m}$ for the 9-methyl groups, K/\tilde{K} for the *t*-butyl groups and their constituent methyl groups, and $K^{\text{intra}}/\tilde{K}^{\text{intra}}$ for the 9-methyl groups. However, as shown below, the spectral density in Eqn. 8 cannot be used to fit the data for *any* choices of the adjustable parameters discussed above, regardless of how many. This is independent of the modeling of τ such as in Eqn. 5. The failure of the

unique-correlation time spectral density in Eqn. 8 lies solely in its frequency dependence at low temperatures. As such, we use the Davidson-Cole spectral density [7],

$$j(\omega, t_{DC}, \epsilon) = \int_0^\infty L(t, t_{DC}, \epsilon) \frac{2t}{1 + \omega^2 t^2} dt, \quad (9)$$

with

$$\begin{aligned} L(t, t_{DC}, \epsilon) &= \sin(\epsilon \rho) \frac{1}{\rho} \frac{t}{t_{DC} - t} & t < t_{DC} \\ &= 0 & t > t_{DC}, \end{aligned} \quad (10)$$

which gives

$$j(\omega, t_{DC}, \epsilon) = \frac{2}{\omega} \frac{\sin[\epsilon \arctan(\omega t_{DC})]}{(1 + \omega^2 t_{DC}^2)^{\epsilon/2}}. \quad (11)$$

The parameters t_{DC} and ϵ have subscript i 's (for $i = b, c, m$). The parameter t_{DC} in the Davidson-Cole Model can be treated like τ in the Poisson model and linked to a parameter E_{DC} . The parameter t_{DC} , or E_{DC} via

$$t_{DC} = t_{\infty DC} \exp(E_{DC}/kT), \quad (12)$$

is an upper limit to a distribution of values of t (or E). Again, the parameters E_{DC} and $t_{\infty DC}$ can have subscript i 's (with $i = b, c, m$) to distinguish the various motions. This model reduces to the Poisson Model when $\varepsilon = 1$ and ε is the only additional parameter. (The details of fitting data with the Davidson-Cole Model can be found elsewhere [3].) We note that as complicated as the Davidson-Cole distribution of Poisson spectral densities appears, with its single additional adjustable parameter, it is "simpler" than even the sum of two Poisson spectral densities which has, at least, two additional adjustable parameters. Because of the logarithmic (i.e., integrable) singularity at $t = t_{DC}$, a very small distribution of τ 's (or E 's) leads to a significant departure from $\varepsilon = 1$. The most likely origin of the distribution of NMR activation energies for methyl and *t*-butyl group reorientation is that rotors on or near surfaces of crystallites or near imperfections in crystallites have lower activation energies. This is, however, just a conjecture, and the reason for the success of the Davidson-Cole distribution of mean times between hops is not known.

3. Experiments

The X-ray diffraction experiments were performed in the Chemistry Department at Villanova University. A single colorless needle (0.07 X 0.09 X 0.17 mm) was mounted using Paratone® oil onto a glass fiber and cooled to the data collection temperature of 100 K. Data were collected on a Brüker-AXS APEXII CCD diffractometer with 0.7107 Å Mo-K α radiation. Unit cell parameters were obtained from 90 data frames, 0.5° Ω , from three different sections of the Ewald sphere yielding $a = 11.9756(7)$, $b = 28.3444(17)$, $c = 6.2130(4)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90^\circ$, $V = 2108.9(2)$ Å³. 24316 reflections ($R_{\text{int}} = 0.0424$) were collected (2610 unique) over $\theta = 1.44$ to 28.39°. The systematic absences in the diffraction data were consistent with the centrosymmetric orthorhombic space group, $Pnma$. The data-set was treated with SADABS absorption corrections based on redundant multi-scan data (Sheldrick, G, Bruker-AXS, 2001) $T_{\text{max}}/T_{\text{min}} = 1.37$. The molecule was located on a mirror plane resulting in $Z = 4$, and $Z' = 0.5$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located from the difference map and allowed to refine freely. The goodness of fit on R^2 was 1.039 with $R1(wR2)$ 0.0310(0.0824) for [I/σ > 2(I)] and with largest difference peak and hole of 1.408 and -0.416 e/Å³ resulting from heavy atom noise around the bromine atom. The molecular structure in the solid is shown in Fig. 1 and the crystal structure is shown in Fig.

The ^1H spin-lattice relaxation rates R were measured in the Solid State NMR Laboratory in the Physics Department at Bryn Mawr College. The sample, 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene, was purchased from Sigma-Aldrich and recrystallized from 30 mL tetrahydrofuran/10 mL 95 % ethanol to provide a fine white powder for use in the ^1H spin-lattice relaxation rate experiments. The relaxation rates R were measured from 87 K to 270 K at NMR frequencies of $\omega/2\pi = 8.50, 22.5,$ and 53.0 MHz (corresponding to magnetic fields of 0.200, 0.528, and 1.24 T). The data is shown as $\ln R$ versus T^{-1} in Fig. 3 since the theoretical models for R all predict linear $\ln R$ versus T^{-1} relationships when $\omega \tau \ll 1$ (high temperature) and when $\omega \tau \gg 1$ (low temperature), as observed. *Low* NMR frequencies are used in these NMR *relaxation* studies to bring the mean hop rates τ^{-1} in resonance with the NMR angular frequencies ω at reasonable temperatures. This is to be contrasted with the *high* NMR frequencies used in NMR *spectroscopy* measurements so chemical shifts and other interactions can be better resolved.

R values were measured using an inversion-recovery pulse sequence and R was determined from a three-parameter Simplex fit of the observed time-dependence of the proton magnetization $M(t) = M(\infty)[1 - (1 - \sin \alpha)\exp(-Rt)]$. The adjustable parameter α accounts for imperfections in the inverting $\alpha = \pi$ pulse. The relaxation was always found to be exponential. For a few experiments at the lowest, highest, and middle temperatures,

very lengthy experiments were performed to check the exponentiality of the relaxation. In a few cases, the equilibrium magnetization $M(\infty)$ was accurately determined and $\ln[M(\infty) - M(t)] = -Rt + \text{a constant}$ was fitted using a linear regression to ensure agreement with the non-linear Simplex fitting routine. Temperature was controlled by a flow of cold nitrogen gas that could be heated to obtain the desired temperature. Temperature was measured with a silver-soldered copper-constantan thermocouple that was imbedded in the sample 2 mm outside the end of the NMR coil. The many thermocouples used in the laboratory are carefully calibrated every few years using standard temperature references. They have not varied over a 25 year period. There is typically a 0.5 K gradient along the 15 mm of sample in the coil. Absolute temperatures are measured to ± 2 K and temperature differences are monitored to ± 0.2 K.

The data in Fig. 3 show an interesting thermal history effect. Most of the R values, involving many days of experimentation fall on a smooth curve with little scatter. They are indicated by \square , \square , and \square for the three NMR frequencies. On four days, however, significantly different R values were obtained as indicated by \square (8.50 MHz), \blacktriangle and \blacktriangle (22.5 MHz) and \square (53.0 MHz). Some of these latter measurements are five - eight times the uncertainties different from the "regular" values and they form their own consistent, smooth curves.

4. Results

The X-ray results (Figs. 1 and 2) show that all molecules are equivalent and that the repeating structure is half a molecule. There are two maxima in $\ln R$ versus T^{-1} in Fig. 3 and therefore (at least) two distinct dynamical processes. We assume that the high-temperature $\ln R$ versus T^{-1} is dominated by the reorientation of the *t*-butyl groups and their in-plane methyl groups characterized by the NMR activation energy E_{DCb} . The slope of this high-temperature $\ln R$ versus T^{-1} obtained from an appropriately weighted linear least squares fit is $16.27 \pm 0.04 \text{ kJ mole}^{-1}$, the uncertainty being $\pm 3\%$. *This is independent of any other parameterization of the data.* However, when the entire data set is fitted to the chosen model, there is a contribution to R at high temperature from a second process and the final fitted value is $E_{DCb} = 15.8 \pm 1.6 \text{ kJ mole}^{-1}$, the uncertainty being $\pm 10\%$.

Eqns. 1-4, 11, and 12 predict that

$$\frac{R_{w_1}}{R_{w_2}} = \frac{x_{w_2} \bar{\omega}_2^{1+\varepsilon}}{x_{w_1} \bar{\omega}_1} \quad (13)$$

at low temperatures where $w t_i \gg 1$ for all t_i (for $i = b, c, m$). The low temperature $\ln R$ versus T^{-1} slopes are well defined and they are the same at all three NMR frequencies.

This gives $\varepsilon = 0.60 \pm 0.03$ in Eqn. 13 and therefore in Eqns. 10 and 11. *This is independent*

of any other parameterization of the data. Whereas the spectral density in Eqn. 11 with Eqn. 12 predicts a high-temperature slope of E_{DC}/kT (in the same way that the unique correlation time spectral density in Eqn. 8 with Eqn. 5 predicts a slope of E/kT), it predicts a low-temperature slope of $-\varepsilon E_{DC}/kT$ (as opposed to simply $-E/kT$ as predicted by the unique correlation time spectral density). As such, we are able to conclude that the low-temperature $\ln R$ versus T^{-1} data is characterized by an NMR activation energy of 15.8 kJ mole⁻¹, exactly the same activation energy (within experimental uncertainty) required to characterize the high-temperature $\ln R$ versus T^{-1} data. Since there are two additional activation energies to determine, E_{DCc} and E_{DCm} , we begin by assuming they are the same (and equal to E_{DCb}). We have inherently assumed that $e_b = e_c = e_m = \varepsilon$ which seems reasonable if ε characterizes a distribution of molecular sites as discussed in the Conclusions Section.

The additional parameters to determine are $t_{\nabla DCb}/\tilde{t}_{\nabla DCb}$ for the *t*-butyl groups and their in-plane methyl groups, $t_{\nabla DCc}/\tilde{t}_{\nabla DCc}$ for the *t*-butyl groups' out-of-plane methyl groups, $t_{\nabla DCm}/\tilde{t}_{DCm}$ for the 9-methyl groups, K/\tilde{K} for the *t*-butyl groups, and $K^{intra}/\tilde{K}^{intra}$ for the 9-methyl groups. The crystal structure shows no unusually close intermolecular H-H contacts and we assume $K/\tilde{K} = K^{intra}/\tilde{K}^{intra} = 1$. Setting these parameters to their theoretically predicted value provides a good fit of the data and essentially eliminates them as adjustable parameters. With these conditions, we find that $t_{\nabla DCb}/\tilde{t}_{\nabla DCb} = 0.61$

and $\tilde{t}_{\nabla DCc}/\tilde{t}_{\nabla DCc} = t_{\nabla DCm}/\tilde{t}_{DCm} = 0.050$ produces the fit shown in Fig. 3. With $E_{DCb} = E_{DCc} = E_{DCm} = 15.8 \pm 1.6 \text{ kJ mole}^{-1}$ fixed at $15.8 \text{ kJ mole}^{-1}$, these values of $t_{\nabla DCk}/\tilde{t}_{\nabla DCk}$ ($k = b, c, m$) have uncertainties of approximately $\pm 10\%$ but if the activation energies are permitted to take on their extreme values (i.e., $\pm 10\%$) then these values of $t_{\nabla DCk}/\tilde{t}_{\nabla DCk}$ ($k = b, c, m$) could change by up to two orders of magnitude. Such is the affect of an Arrhenius equation where the activation energy appears in the exponential. We conclude the values of the $t_{\nabla DCk}/\tilde{t}_{\nabla DCk}$ ($k = b, c, m$) are reasonable. Note that $t_{\nabla DCc}/\tilde{t}_{\nabla DCc} = t_{\nabla DCm}/\tilde{t}_{DCm}$, $E_{DCc} = E_{DCm}$, and $K/\tilde{K} = K^{intra}/\tilde{K}^{intra}$ imply that the out-of-plane methyl groups in the *t*-butyl groups and the two 9-methyl groups are dynamically identical, within the uncertainties in these parameters. This is consistent with the molecular geometry (Fig. 1). It also suggests that *intermolecular* spin-spin interactions can be neglected. This is consistent with the crystal structure (Fig. 2). Finally, Fig. 3 shows the result, at 53.0 MHz, of turning the 9-methyl groups off.

Noting the overall fit is perhaps less important than noting the relative height of the two maxima in $\ln R$ versus T^{-1} . For two maxima with this spacing in T^{-1} , the considerably higher, low-temperature $\ln R$ versus T^{-1} maximum is a clear indication that we are seeing a motion that is in addition to the motion of a *t*-butyl group and its three constituent methyl groups. The $\ln R$ versus T^{-1} observed here can be compared with a system where there are no methyl groups not in *t*-butyl groups [1]. Finally, a better fit of the relaxation

rate data presented in Fig. 3 can certainly be obtained by relaxing the condition $E_{DCb} = E_{DCc} = E_{DCm}$ (which will affect all other parameters) but this seems an unjustified over analysis of the data, given the achieved level of "goodness of fit."

In summary, only four adjustable parameters are required to provide a reasonable fit of the entire R versus T^{-1} data set at three NMR frequencies. Two of these are $E_{DC} = 16$ kJ mole⁻¹ for all five reorientations in the half-molecule (the fundamental unit) and $\varepsilon = 0.6$ which characterizes a narrow, but highly asymmetric distribution of values of E with E_{DC} the upper limit cutoff. The detail of the rest of the data can be reasonably well fitted with only two additional parameters. These are two "attempt periods" (Arrhenius preexponential factors); one for the *t*-butyl groups and their constituent in-plane methyl groups and the other for the 9-methyl groups and the out-of-plane methyl groups in the *t*-butyl groups. Models that predict these pre-exponential factors are not very sensitive to the shape of the hindering barrier [8] and in the present case, the two fitted values are in the expected ranges. Most studies do not bother to compare fitted values of parameters like this to model predictions (Eqn. 6).

5. Conclusions

We have observed the temperature and NMR frequency dependence of the ¹H spin-lattice relaxation rate in 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene. We have

combined a model for the relaxation resulting from the reorientation of *t*-butyl groups and their constituent methyl groups and a model for relaxation resulting from the reorientation of single methyl groups. This compound has both types of rotors. We have determined the molecular and crystal structure by X-ray diffraction. There are 4 molecules per unit cell but they are all identical. Indeed, the repeating unit is half a molecule. The ^1H nuclear spin relaxation results from the modulation of the ^1H - ^1H spin-spin interactions by the reorientations and we find that the assumption that only intra *t*-butyl spin-spin interactions, and, for the 9 methyl groups, only intramethyl spin-spin interactions, are involved, is consistent with the data.

Seeking the simplest possible model that is consistent with the data, we find that the reorientation of the *t*-butyl groups, their three constituent methyl groups, and the 9-methyl groups are all characterized by the same NMR upper-limit cutoff activation energy of $15.8 \pm 1.6 \text{ kJ mole}^{-1}$. The model suggests that this activation energy characterizes the "perfect crystal" environment. The model does predict a small distribution of activation energies to values smaller than this cutoff value. Given that NMR activation energies can be between zero and 20% smaller than rotational barriers V for methyl groups with activation energies in this range [9, 10], we conclude that the "perfect crystal" barrier for these motions is $V = 17.4 \pm 3.2 \text{ kJ mole}^{-1}$. The dynamical model for the rotors in this system is elegant in its simplicity. This barrier is not a meaningful parameter for the in-

plane methyl groups in the *t*-butyl group since they are locked into a geared reorientation with the *t*-butyl group. Or, put another way, the *t*-butyl group and the in-plane methyl group must be considered a single superimposed reorienting unit. Usually, in systems like that studied here, the out-of-plane methyl groups in the *t*-butyl group have a lower barrier than the *t*-butyl group and its in-plane methyl group, the latter being determined by intermolecular interactions. In this case, however, they can be all taken to be the same. That the 9-methyl groups have the same barrier as the *t*-butyl groups' out-of-plane methyl groups (within the uncertainties quoted) is not surprising given that the intramolecular environments are very similar and that there are no unusually close intermolecular neighbors.

The molecular and crystal structure (determined using a small single crystal) suggests that all molecules are in the same environment. This suggests that the ^1H nuclear spin-lattice relaxation rate should be modeled by an exponential correlation function $g(t) = \exp(-t/\tau)$ for mean time between hops (or correlation time) τ . This leads to the Poisson (also called the Debye or the BPP or the unique-correlation time) spectral density. However, the proton spin-lattice relaxation rate measurement are performed with a large polycrystalline sample. Fitting the relaxation rate data requires the use of a *single* parameter *in addition to* those found in the Poisson model. This parameter is uniquely determined by the NMR frequency dependence of the relaxation rate at low temperatures.

The simplest model that involves this parameter is the Davidson-Cole spectral density which finds widespread use in the modeling of both nuclear spin relaxation and dielectric relaxation experiments [7]. One interpretation of this model is that there is a distribution of reorientational barriers with the additional parameter characterizing the width of the (highly asymmetric) distribution. One possible source of this distribution is that the crystallites in the fine powder that results from recrystallization have a significant number of molecules on or near crystal surfaces or at or near crystal imperfections. The distribution of mean times between hops that corresponds to the Davidson-Cole model is consistent with this suggestion in that there is a logarithmic singularity at the perfect-crystal barrier. We are actively perusing this possibility by measuring ^1H spin-lattice relaxation rates in a series of samples made up of crystallites of different size ranges.

The general model of nuclear spin relaxation for spin-1/2 systems, the Bloch-Wangsness-Redfield model [4, 11-14], which provides the basic relaxation equations, is very robust. It seems to work in all cases where it is tested. Here, we have extended this model to a case that has different kinds of rotors, in this case, *t*-butyl groups with their constituent methyl groups, and other non-*t*-butyl group methyl groups. We are continuing this study in systems that have non-*t*-butyl group rotors with quite different barriers than those studied here.

This work presents both X-ray diffraction and NMR relaxation studies. The structure determined from X-ray diffraction studies places considerable constraints on the models used to fit the NMR relaxation experiments. We have previously included ab initio electronic structure calculations of methyl group barriers in clusters of molecules based on the X-ray structures for the case of methyl groups [6]. We are currently extending these electronic structure calculations to the much more difficult and computationally demanding case of reorientation barriers for *t*-butyl groups and their constituent methyl groups.

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Supplementary Information

CCDC 699537 contains the supplementary crystallographic data for 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Figure Captions

Fig. 1. The molecule 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene with the molecular structure found in the crystal. Bromine atoms are indicated by the two large dark grey spheres, the oxygen atom is indicated by the slightly smaller dark grey sphere, carbon atoms are indicated by small black spheres and hydrogen atoms are indicated by small white spheres. (a) shows a projection where all the atoms are visible. (b) shows a "top down" projection that indicates the symmetry. The methyl groups at the extreme ends are in-plane *t*-butyl methyl groups and their neighboring two methyl groups are out-of-plane *t*-butyl methyl groups. The 9-methyl groups are in the center.

Fig. 2. The crystal structure of 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene showing the 001 plane. The dashed line indicates the unit cell in the *x* (up-down) and *y* (right-left) directions.

Fig. 3. The ^1H spin-lattice relaxation rate R , on a logarithmic scale, as a function of inverse temperature T^{-1} at 8.50 (\square), 22.5 (\square), and 53.0 MHz (\square). Additional data at 8.50 (\square), 22.5 (\blacktriangle , \blacktriangleleft), and 53.0 MHz (\square) show single-day experiments indicating a dependence of R on thermal history in the range 105 – 130 K ($7.7 < 1000/T < 9.5 \text{ K}^{-1}$). All uncertainties are within the size of the symbols. A single fit to Eqn. 1 for all three NMR frequencies is shown. For 53.0 MHz, the two contributions to R in Eqn. 1 are shown separately.