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The relationship between crystal structure and methyl and *t*-butyl group dynamics in van der Waals organic solids

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We report x-ray diffractometry in a single crystal of 2-*t*-butyl-4-methylphenol (TMP) and low-frequency solid state nuclear magnetic resonance (NMR) proton relaxometry in a polycrystalline sample of TMP. The x-ray data show TMP to have a monoclinic, $P2_1/c$, structure with eight molecules per unit cell and two crystallographically inequivalent *t*-butyl group ($C(CH_3)_3$) sites. The proton spin-lattice relaxation rates were measured between 90 and 310 K at NMR frequencies of 8.50, 22.5, and 53.0 MHz. The relaxometry data is fitted with two models characterizing the dynamics of the *t*-butyl groups and their constituent methyl groups, both of which are consistent with the determined x-ray structure. In addition to presenting results for TMP, we review previously reported x-ray diffractometry and low-frequency NMR relaxometry in two other van der Waals solids which have a simpler structure. In both cases, a unique model for the reorientational dynamics was found. Finally, we review a similar previously reported analysis in a van der Waals solid with a very complex structure in which case fitting the NMR relaxometry requires very many parameters and serves mainly as a flag for a careful x-ray diffraction study.
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INTRODUCTION

When used together, x-ray diffraction and nuclear magnetic resonance (NMR) relaxometry can provide valuable information concerning motion in van der Waals solids composed of organic molecules with internal rotational degrees of freedom.[1,2] We report here a study with solid 2-*t*-butyl-4-methylphenol (TMP, Fig. 1) and compare the results with three related systems. An x-ray study provides a time-averaged map of the electron density which can be translated into both the structure of the molecules in question and how the molecules form the crystal lattice.[3] Nuclear spin-lattice relaxation rate R measurements as a function of NMR frequency $\omega/2\pi$ and temperature T (NMR relaxometry) provide information on the time dependence of local magnetic fields on the NMR time scale.[4] This is a convenient time scale for methyl (CH_3) and *t*-butyl, ($C(CH_3)_3$) reorientation.[2] The three methyl groups can reorient [for example, about the C(7)–C(8), the C(7)–C(9), and the C(7)–C(10) bonds in Fig. 1] and these motions can be superimposed on the reorientation of the *t*-butyl group [for example, about the C(2)–C(7) bond in Fig. 1].

X-ray diffractometry and NMR relaxometry involve very different time scales; x-ray-electron scattering occurs at the 10^{-19} s time scale and low-frequency NMR relaxometry, in the present case, observes motions in the 10^{-10}–10^{-5} s range. For TMP, the x-ray diffraction studies see a unique orientation for each of two crystallographically distinct types of *t*-butyl groups (Figs. 1 and 2) implying that a (different) threefold orientational potential energy profile dominates for both types. In the present case, the structure and the dynamics are sufficiently complex that fitting the NMR relaxometry data does not result in a unique dynamical model. We investigate the use of the observed molecular and crystal structure to provide constraints on fitting the NMR relaxometry data. For comparison, we provide two previous examples where the interpretation of the NMR relaxometry data is unique. Both cases correspond to one *t*-butyl site per unit cell. In TMP there are two distinct *t*-butyl sites and two dynamical models survive scrutiny. Finally, we review one case where the structure is too complex for NMR relaxometry to be of much help, other than to raise a flag which then can result in a careful x-ray diffraction study.[1]

NUCLEAR SPIN RELAXATION: THEORY REVIEW

In proton-dense systems like those discussed here, the spin-lattice (longitudinal or Zeeman) relaxation results from

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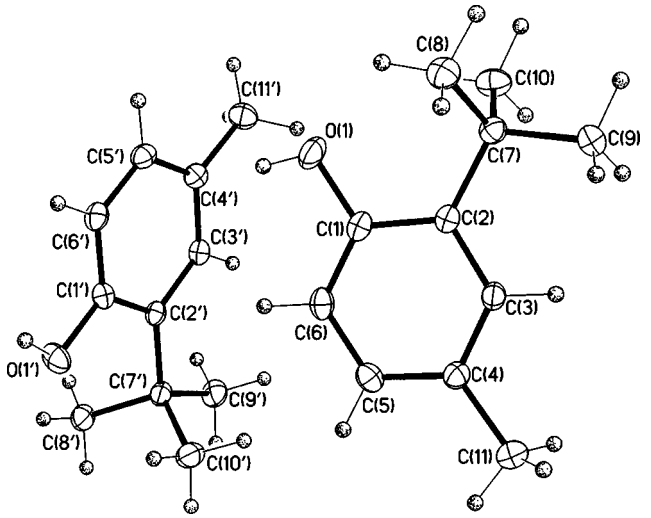

FIG. 1. The two crystallographically inequivalent molecules of 2-*t*-butyl-4-methylphenol.

proton spin–proton spin dipolar interactions being modulated by methyl group and *t*-butyl group motion. Intramethyl spin–spin interactions dominate but inter-methyl, intra-*t*-butyl spin–spin interactions are significant.[5–7] Rapid spin–spin (or transverse) relaxation ensures a common spin temperature and the effect of spin–spin interactions that are not modulated by the motion is to slow the exponential relaxation process. The proton spin–lattice relaxation rate is given by[5]

$$R=\sum_{q=1}^{Q}\left[\Delta_q\sum_{j=1}^{M}\left\{R_{jq}^{\alpha}+\sum_{i=1}^{3}R_{ijq}^{\beta}\right\}\right], \tag{1}$$

$$R_{jq}^{\alpha}=A^{\alpha}h(\omega,\tau_{jq}^{t}), \tag{2}$$

$$R_{ijq}^{\beta}=A^{\beta}[\tfrac{2}{9}h(\omega,\tau_{ijq}^{m})+\tfrac{2}{9}h(\omega,\tau_{jq}^{t})+\tfrac{19}{36}h(\omega,\tau_{ijq}^{tm})], \tag{3}$$

$$\frac{1}{\tau_{ijq}^{tm}}=\frac{1}{\tau_{jq}^{t}}+\frac{1}{\tau_{ijq}^{m}}, \tag{4}$$

$$h(\omega,\tau)=J(\omega,\tau)+4J(2\omega,\tau), \tag{5}$$

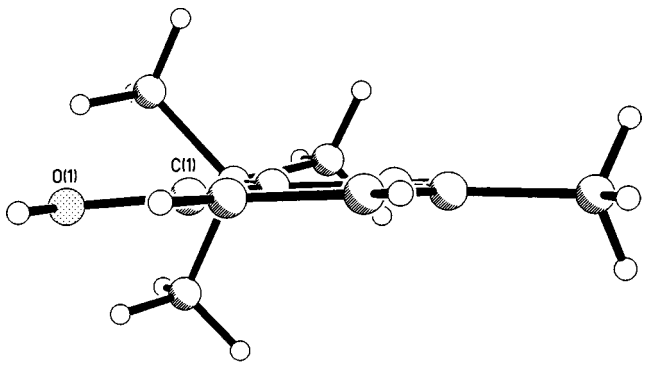

FIG. 2. One of the two inequivalent molecules of 2-*t*-butyl-4-methylphenol viewed in the plane of the aromatic ring. The *t*-butyl group is oriented with one methyl group 9.2° out of the aromatic plane. (For the *t*-butyl group in the other molecule, this angle is 1.7°.)

$$J(\omega,\tau)=\frac{2\tau}{1+\omega^2\tau^2}, \tag{6}$$

$$\tau=\tau_{\infty}\exp\left(\frac{E}{kT}\right). \tag{7}$$

The NMR resonance frequency is $\omega=B/\gamma$ for magnetic field B and proton magnetogyric ratio γ. TMP crystallizes with two crystallographically independent molecules and therefore, $Q=2$ in Eq. (1). Δ_q is the fraction of molecules of each type ($\Delta_1+\Delta_2+\cdots=1$ with $\Delta_1=\Delta_2=0.5$ for TMP) and there are M ($=1$ for TMP) *t*-butyl groups in the molecule. The reorientation of the jth *t*-butyl group in the qth molecule is characterized by the mean time between hops τ_{jq}^{t} and the reorientation of the ith methyl group in the jth *t*-butyl group in the qth molecule is characterized by the mean time between hops τ_{ijq}^{m}.

R_{ijq}^{β} in Eq. (3) accounts for the relaxation due to the modulation of the six spin–spin interactions among the three protons in a methyl group (three spins each engaged in two pairwise interactions) and A^{β} can be calculated from the geometry of a methyl group.[5] These interactions are modulated by both methyl and *t*-butyl reorientation and as a consequence there is a term in Eq. (3) involving the superposition time given by Eq. (4). R_{jq}^{α} in Eq. (2) accounts for the intra-*t*-butyl, intermethyl spin–spin interactions among the nine protons in a *t*-butyl group. The calculation[5–7] of A^{α} involves approximations since the spin–spin vectors are changing both in length and direction as a *t*-butyl group and its resident methyl groups reorient, unlike methyl group reorientation where only the direction of the spin–spin vectors is changing. The experiments are performed on polycrystalline samples and the calculations of A^{α} and A^{β} properly account for the averaging of the angles between the rotation axes and the magnetic field.[8] The model also accounts for rapid spin diffusion (spin–spin relaxation rate $R_2\gg R$) among all protons by incorporating the appropriate ratios n^{α}/N and n^{β}/N in Eqs. (2) and (3) where n^{α} and n^{β} are the number of protons involved in the motion and $N=16$ is the number of protons in the molecule. At the same time, however, this model [Eqs. (1)–(7) along with the calculations of A^{α} and A^{β}] does neglect those dipolar interactions between protons in a *t*-butyl group and other protons that are modulated by the various rotations. These interactions are accounted for in a phenomenological manner by labeling the calculated values of A^{α} and A^{β}, $\overline{A^{\alpha}}$, and $\overline{A^{\beta}}$ and fixing $A^{\beta}/\overline{A^{\beta}}=A^{\alpha}/\overline{A^{\alpha}}$ with A^{β} or $A^{\alpha}=(A^{\beta}/\overline{A^{\beta}})\overline{A^{\alpha}}$ as the single fitting parameter. Indeed, it is simplest to think of the parameter $A/\overline{A}\equiv A^{\beta}/\overline{A^{\beta}}=A^{\alpha}/\overline{A^{\alpha}}$ as the single fitting parameter. This single parameter simply raises and lowers the entire R versus T curve. A fitted value of $A/\overline{A}<1.0$ (within experimental error) completely rules out the dynamical model since the interactions accounted for by A^{β} and A^{α} are definitely present. Dipolar interactions between protons in a *t*-butyl group and other protons can, however, increase $A/\overline{A}$ by 10–30%. A fitted value of $A/\overline{A}>1.4$ would, however, also rule out the model unless the geometry were very unusual and there were many protons on a neighboring molecule very close to the

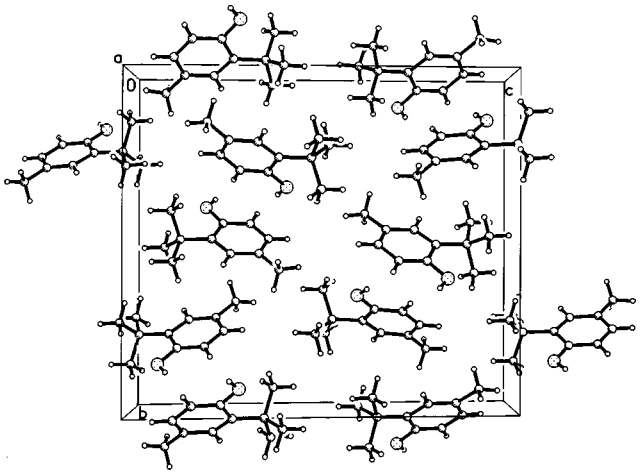

FIG. 3. The unit cell of solid 2-*t*-butyl-4-methylphenol.

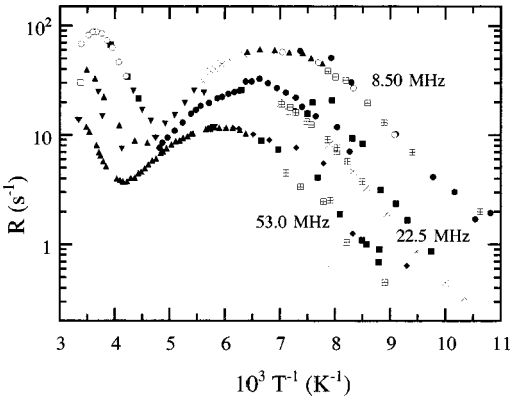

FIG. 4. Proton spin-lattice relaxation rate R vs temperature T in 2-*t*-butyl-4-methylphenol at three NMR frequencies as shown. At each frequency, a different day's set of experiments is shown with a different symbol; eight sets (days) at 8.50 MHz, seven sets at 22.5 MHz, and five sets at 53.0 MHz.

t-butyl group. In any event, the modeling is set up such that the fitted value of $A/\overline{A}$ is a reasonably strong test of a model.

The spectral density in Eq. (6) assumes the motion is random and describable by Poisson statistics.[4] This form of J is the Fourier transform of an exponential correlation function (the probability of no hops in a time t assuming a hop at time $t=0$). The mean hop rate is modeled by a canonical ensemble or an Arrhenius relationship (depending on your educational background) in Eq. (7) where E is the activation energy and τ_∞ is the ''mean time between hop attempts.'' It is convenient to scale τ_∞ according to $\overline{\tau_\infty}$, the mean time between hop attempts in a simple harmonic model,[9] and use $\tau_\infty/\overline{\tau_\infty}$ as a convenient fitting parameter.

EXPERIMENTS

The sample was purchased from Aldrich Chemical and the quoted purity was 99%. It was a dark gray solid with a reported mp of 324–325 K. It was purified by sublimation at 323 K/0.005 mm pressure which resulted in a colorless, polycrystalline material with mp 325.4–326.0 K.

Crystallographic data for TMP: $C_{11}H_{16}O$, monoclinic, $P2_1/c$, $a=6.2618(4)$, $b=16.6852(10)$, $c=18.9674(12)$ Å, $\theta=94.1670(10)°$, $V=1976.5(2)$ Å^3, $Z=8$, $Z'=2$, $T=173(2)$ K. Of 11 027 reflections collected, 3847 were independent and used to refine 217 parameters. At convergence, with all nonhydrogen atoms anisotropic and hydrogen atoms in idealized locations, $R=5.02\%$, $wR2=16.03\%$. The relative positioning of the two independent molecules is shown in Fig. 1. Figure 2 shows one of the two molecules viewed in the plane of the aromatic ring and Fig. 3 shows the packing in the unit cell. There is no appreciable hydrogen bonding involving the OH groups.

R values were measured using a standard inversion-recovery procedure as outlined elsewhere.[2] Experiments were performed from 90 to 310 K at 8.50, 22.5, and 53.0 MHz corresponding to magnetic fields of 0.200, 0.528, and 1.24 T. The observed relaxation rates are shown in Fig. 4 in which, for a given frequency, a different symbol is used for each of the 20 days of experiments. The uncertainly in each measured R value ranges between $\pm 5\%$ and $\pm 10\%$ and this is consistent with the scatter from measurement-to-measurement *on each day*. There is a pronounced thermal history effect at low temperatures which becomes clear by comparing the day-to-day measurements on different days. This implies some differences in the sample from day-to-day which probably results from the fact that the sample is stored at room temperature between each day's experiments and this is close to the melting point. This phenomenon has been discussed elsewhere in some detail[10] and it does not effect our fitting the data or the conclusions of this paper. Figures 5 and 6 show the data just using three different symbols for the three frequencies.

RELAXATION DATA FITS

R versus T shows two well separated maxima in R and this suggests a minimum of two distinct motions each characterized by a mean time between hops $\tau=\tau_\infty \exp(E/kT)$. We are not guided, at first, by the x-ray diffraction work here.

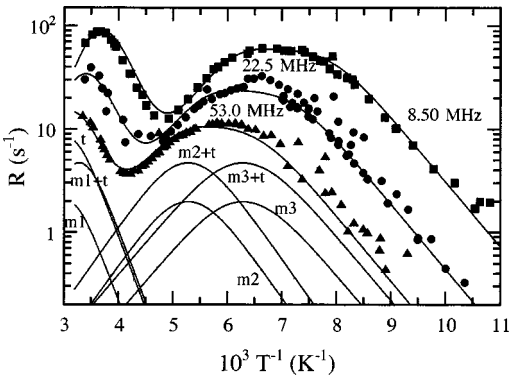

FIG. 5. Proton spin–lattice relaxation rate R vs temperature T in 2-*t*-butyl-4-methylphenol at three NMR frequencies as shown. A *single* fit to all three frequencies is shown. This fit uses the one-site model with the seven adjustable parameters indicated in Table I. The various contributions to R at 53.0 MHz are indicated: the (rotation of the) nearly in-plane methyl group ($m1$), the *t*-butyl group (t), the superposition of the two motions ($m1+t$), one out-of-plane methyl group ($m2$), the other out-of-plane methyl group ($m3$), and the two superimposed motions of these two methyl groups and the *t*-butyl group ($m2+t$ and $m3+t$).

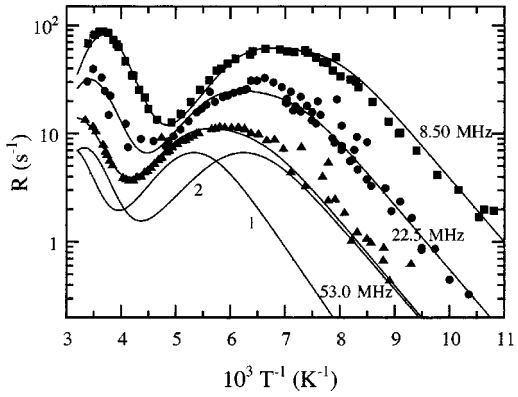

FIG. 6. Proton spin-lattice relaxation rate R vs temperature T in 2-*t*-butyl-4-methylphenol at three NMR frequencies as shown. A *single* fit to all three frequencies is shown. This fit uses the two-site model with the nine adjustable parameters indicated in Table I. The contribution to R from the dynamics of the *t*-butyl groups at the two sites (labeled 1 and 2) is indicated for 53.0 MHz.

Rather we seek the simplest fits of the data and *then* ask whether they are unique and consistent with the x-ray results. The parameters are the activation energies E, the constant $A/\overline{A}$ and the ''mean time between hopping attempts'' parameter $\tau_\infty/\overline{\tau_\infty}$. To start, we assume a unique crystallographic site in the molecule for *t*-butyl groups (which is not the case) and assume that the nearly in-plane methyl group and the entire *t*-butyl group reorient at one rate (i.e., characterized by one τ) and that the two out-of-plane methyl groups reorient at a different rate. This is a five-parameter fit and fits the data very badly.

The simplest one-site model that fits the data well assumes that the nearly in-plane methyl group and the entire *t*-butyl group reorient at one rate (as above) but that the two out-of-plane methyl groups reorient with rates that are not only different from the *t*-butyl group and the in-plane methyl group, but also different from each other. The fit is shown in Fig. 5 and the seven independent parameters are indicated in Table I. Although the uncertainties in E are about ± 1 kj mole^{-1}, the difference between 12 and 14 kj mole^{-1} for the two out-of-plane methyl groups is significant. The uncertainty in $A/\overline{A}$ is about $\pm 5\%$ and the uncertainties in the $\tau_\infty/\overline{\tau_\infty}$ values are about $\pm$ a factor of 2 or 3 (since the activation energy appears in the exponential). That the fitted value of $A/\overline{A}$ is 1.1 and that all the $\tau_\infty/\overline{\tau_\infty}$ values are within a factor of 10 of unity simply suggests the assumptions concerning what is reorienting are reasonable.

TABLE I. Relaxation rate parameters for 2-*t*-butyl-4-methylphenol.

Model	Rotors	E kJ/mole	$A/\overline{A}$	$\tau_\infty/\overline{\tau_\infty}$
One site	*t*-butyl and methyl 1	27	1.1	1.0
	methyl 2	14		1.5
	methyl 3	12		1.5
Two site	*t*-butyl 1 and methyl 11	32	1.1	0.15
	methyls 12 and 13	14		0.15
	t-butyl 2 and methyl 21	30		1.5
	methyls 22 and 23	11		2.6

TABLE II. A comparison among systems.

Molecular solid	X-ray sites	NMR sites	NMR τ's	Ref.
Polymorph A of 2,6-di-*t*-butylnaphthalene	1	1	1	1
3-*t*-butylchrysene	1	1	2	2
2-*t*-butyl-4-methylphenol	2	1	3	
		2	4	
Polymorph E of 2,6-di-*t*-butylnaphthalene	12	>4	>4	1

Finally, we seek the simplest two-site model. We assume two crystallographically distinct *t*-butyl sites in the crystal (as is the case). There is a variety of possible models but the simplest one that fits the data (i.e., having the fewest number of adjustable parameters) is that for each of the two types of *t*-butyl groups, the nearly in-plane methyl group and the entire *t*-butyl group reorient at one rate (as in the one-site model) and the two out-of-plane methyl groups reorient at a different rate. The fit is shown in Fig. 6. The two curves labeled 1 and 2 each have a high-temperature R maximum resulting from the reorientation of the *t*-butyl group and its (nearly) in-plane methyl group and a low-temperature R maximum resulting from the reorientation of the two out-of-plane methyl groups. The nine independent fitting parameters are indicated in Table I.

DISCUSSION

In van der Waals organic solids like 2-*t*-butyl-4-methylphenol, the x-ray data provide a clear picture of the equilibrium structure of the molecules and how they pack together to form the solid. The goal of this long-term project is to relate this structure with models for the dynamics of the *t*-butyl groups and their constituent methyl groups obtained by analyzing nuclear spin relaxation rate data. The x-ray data for TMP show two crystallographically inequivalent *t*-butyl group sites; in one, the *t*-butyl group is oriented at 1.7° out of the plane of the ring and in the other the *t*-butyl group is oriented at 9.2° out of the plane of the ring (Fig. 2).

We have presented two models based on the NMR relaxometry data. Simply stated, the first says that the two crystallographically distinct sites are equivalent from the dynamical perspective but that whereas the nearly in-plane methyl group and the *t*-butyl group reorient at one rate, the two out-of-plane methyl group reorient at two different rates. This is not unreasonable given that the two out-of-plane methyl groups see slightly different environments (see Figs. 2 and 3). In this case there are three distinct reorientation rates. The second model says that the motion for the two crystallographically distinct types of *t*-butyl groups is different. For each, the nearly in-plane methyl group and the *t*-butyl group reorient at one rate and the two out-of-plane methyl groups reorient at another rate. Thus there are four distinct reorientation rates.

We compare this analysis in TMP with three other systems in Table II.[1,2] The molecules are drawn in Fig. 7. Poly-

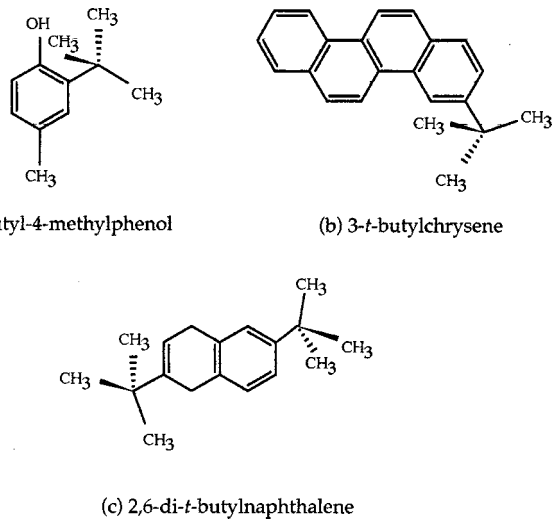

FIG. 7. The molecule used in this study and two others with which it is compared.

morph A of 2,6-di-*t*-butylnaphthalene is the simplest system investigated to date[1] and provides a textbook example for the simplest possible dynamical model. Even though there are four molecules per unit cell and two *t*-butyl groups per molecule, the presence of inversion centers results in a unique crystallographic environment for *t*-butyl groups. The proton spin relaxation measurements are characterized by the simplest possible dynamical model; the three methyl groups and the *t*-butyl group *all* reorient at the same rate. In addition the analysis is unambiguous about concluding that all four rotors are involved in the motion. The next entry in Table II is 3-*t*-butylchrysene.[2] The local intramolecular environment of the *t*-butyl group in 3-*t*-butylchrysene is the same as it is in 2,6-di-*t*-butylnaphthalene, namely a ring proton on both sides (Fig. 7). The x-ray data[2] shows a structure with four molecules per unit cell but with a crystallographically unique *t*-butyl group site (as in polymorph A of 2,6-di-*t*-butylnaphthalene) yet the nuclear spin relaxation rate data clearly show two distinct reorientation rates. The *t*-butyl group and the in-plane methyl group reorient at one rate and the two out-of-plane methyl groups reorient at the other rate. In both these cases the dynamical model used to interpret the relaxation rate data is both unique and consistent with the x-ray diffraction data. In both these cases the x-ray data show a crystallographically unique *t*-butyl group site. The difference between the two systems (one NMR τ for one, two for the other) is a measure of the *difference* in the anisotropy of the *intermolecular* interactions experienced by the *t*-butyl groups.

In 2-*t*-butyl-4-methylphenol (TMP), there are two sites and we can interpret the relaxation rate data assuming a single site (with the unique *t*-butyl group motion involving three distinct reorientation rates) or with two sites (with the motion of each of the two *t*-butyl groups involving two distinct reorientation rates). See Table II. Finally, polymorph E of 2,6-di-*t*-butylnaphthalene, like polymorph A discussed above, provides an extreme case, only in the opposite sense. The structure[1] in polymorph E is very complicated with 12 molecules per unit cell and 12 crystallographically distinct *t*-butyl group sites, though many of the differences may be slight. However, there are *many* distinct reorientation rates. The relaxation rate data is, not surprisingly, most unusual and an example fit showed that there were more than four inequivalent sites.[1] The data could have been beautifully fit with say five or six sites but with many possible dynamical models. This would be over analyzing the data. Indeed, the best fit (the fewest number of parameters) assumed a continuous distribution of reorientation rates but the phenomenological distribution function used offers no insight into modeling the motion or relating it to the structure. The point is that this case is out of reach of the nuclear spin relaxation rate experiments. All that can be said is that there are a minimum number of reorientation rates. At the same time, however, it was the NMR relaxometry experiments that raised the flag that the structure was complicated. What turned out to be an interesting structure could then be investigated in detail by x-ray diffraction.[1]

SUMMARY

We have presented x-ray diffraction data and proton spin-lattice relaxation rate data in solid 2-*t*-butyl-4-methylphenol. We are able to interpret the relaxation rate data with two dynamical models, both of which are consistent with the x-ray data. We have compared this study with other cases. In two cases, a simpler structure results in a unique dynamical model and in another case the structure is so complex that the proton spin relaxation rate technique offers little in understanding the dynamics beyond providing a minimum number of reorientation rates needed to fit the data. The power of the x-ray experiments is that they provide very clear boundary conditions for the set of possible dynamical models. The power of the spin-lattice relaxation measurements are that they are very sensitive to both which rotors are actually reorienting (on the NMR time scale) and when different rotors have quite small differences in the parameters describing their reorientation. To put it another way, NMR relaxometry provides information on *local angular anisotropies* in the intramolecular and intermolecular potentials.

This project continues in three directions: First, we are looking for similar systems with two crystallographically inequivalent *t*-butyl group sites. Second, we are pursuing deuteron spin relaxation experiments which are less sensitive to intermolecular interactions but provide different information[11–13] about intramolecular interactions (than do proton relaxation experiments). Third, we are investigating systems with fluoromethyl (CF_3) groups. The rotational motion is simpler (just one rotor rather than four) but with both F-19 and H-1 atoms in the molecule, the relaxation is nonexponential and more information is available.[14,15] Also, x-ray studies can see fluorine atoms much more easily than they can see hydrogen atoms.

ACKNOWLEDGMENTS

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