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# Note: Methyl and *t*-Butyl Group Rotation in van der Waals Solids

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In this Note we report solid state <sup>1</sup>H nuclear magnetic resonance (NMR) spin-lattice relaxation experiments and single crystal X-ray diffractometry with solid 2-*t*-butyl-1,4-benzoquinone (TBBQ) (Fig. 1). The spin-lattice relaxation is caused by the modulation of <sup>1</sup>H-<sup>1</sup>H spin-spin interactions by the rotations of the *t*-butyl groups and their constituent methyl groups.<sup>1,2</sup> The parameters that characterize the rotations, in turn, contribute to a better understanding of the anisotropies in the intramolecular and intermolecular potentials in these types of van der Waals solids composed of small organic molecules. The compound was purchased from Sigma-Aldrich (98%, mp 327-331 K). <sup>1</sup>H and <sup>13</sup>C high resolution NMR and gas chromatography-mass spectrometry indicated the compound was pure to the limits of detection for these techniques and the compound was used as is. A single crystal was taken directly from the supplier's sample and the crystal and molecular structure was determined using X-ray techniques as described elsewhere.<sup>1</sup> The reference number for the Cambridge Structural Database, where parameters characterizing the monoclinic structure can be found, is 1539154. The structure is shown in Fig. 1a and the two molecules in the asymmetric unit can be seen in Fig. 1b on an expanded scale.

Solid state <sup>1</sup>H NMR spin-lattice relaxation rates  $R$  (the inverse of the spin-lattice relaxation time  $T_1$ ) were measured as a function of temperature  $T$  between 96 and 300 K at NMR frequencies

of  $\omega/(2\pi)=22.5$  and 53.0 MHz. Details of the experimental procedure, including temperature control and measurement can be found elsewhere.<sup>1</sup> The relaxation was always exponential within experimental uncertainty and  $\ln R$  versus  $T^{-1}$  is shown in Fig. 2. This data is fitted to a well-established model<sup>2</sup> based on the Bloch-Redfield-Wangsness model of spin-lattice relaxation<sup>3</sup> as first extended to *t*-butyl plus methyl group rotation by Dunn and McDowell.<sup>4</sup> There are seven terms (indexed by  $k$ ) in the expression for  $R$ ; one for the *t*-butyl group rotation ( $k=T$ ), one each for the rotations of the three methyl groups ( $k=1, 2, 3$ ), and one each for the superimposed rotations of each methyl group and the *t*-butyl group ( $k=T+1, T+2, T+3$ ). The seven contributions to the relaxation at 53.0 MHz are indicated in Fig. 2. Each term is of the form  $R_k=A_k J(\omega, \tau_k)$  where  $J(\omega, \tau_k)=(2/\omega)[\sin\{\varepsilon \arctan(\omega \tau_k)\}]/[(1+\omega^2 \tau_k^2)^{\varepsilon/2}]$  is the Davidson-Cole spectral density.<sup>5,6</sup> Here,  $\tau_k$  is an NMR correlation time (for the  $k$ -th rotation) that can be taken as the mean time between hops in a semiclassical methyl and *t*-butyl group hopping process. Four of the  $\tau_k$  involve the four rotors in a *t*-butyl group ( $k=T, 1, 2, 3$ ) and the other three  $\tau_k$  are the superposition terms ( $k=T+1, T+2, T+3$ ).<sup>2</sup> There are two adjustable parameters for each of the four individual rotations.<sup>2</sup> These are a preexponential factor<sup>2,7</sup>  $\tau_{\infty k}$  and an NMR activation energy<sup>2,8,9</sup>  $E_k$  in an Arrhenius relation  $\tau_k=\tau_{\infty k} \exp(E_k/kT)$ .  $E_k$  is usually 0-20% smaller than the barrier height.<sup>8,9</sup> The seven values of  $A_k$  in the seven  $R_k=A_k J(\omega, \tau_k)$  characterize the many intra-*t*-butyl  $^1\text{H}$ - $^1\text{H}$  spin-spin interactions that are modulated by the rotations and are all related to a single adjustable parameter that accounts for *t*-butyl–non-*t*-butyl (both intramolecular and intermolecular)  $^1\text{H}$ - $^1\text{H}$  interactions.<sup>2</sup> For the present textbook case this is unnecessary; the seven  $A_k$  are calculated with no adjustable parameters<sup>2</sup> and this fits the data very well. This means that the modulation of *t*-butyl–non-*t*-butyl  $^1\text{H}$ - $^1\text{H}$  interactions by *t*-butyl and methyl group rotation plays a negligible role in the relaxation process.

We have discussed the meaning of  $\varepsilon < 1$  in the Davidson-Cole spectral density extensively:<sup>10</sup> it implies a distribution of activation energies with  $E$  being the upper-limit cutoff. When  $\varepsilon=1$ , the Davidson-Cole spectral density reduces to the unique- $\tau$  random-motion spectral density  $J(\omega, \tau_k)=2 \tau_k/(1+\omega^2 \tau_k^2)$ .<sup>5</sup> The structure (Fig. 1) indicates that all *t*-butyl groups have one methyl group in the plane of the aromatic ring. The data is reasonably well fitted assuming that the correlation time for *t*-butyl group rotation  $\tau_T$  (that is,  $k=T$ ) and the correlation time for rotation of the in-plane methyl group  $\tau_1$  are the same ( $\tau_T=\tau_1$ ) and that the correlation times  $\tau_2$  and  $\tau_3$  for the two out-of-plane methyl groups are nearly the same. The slight difference between  $\tau_2$  and  $\tau_3$

would result from one of two causes between which, given the small difference, we cannot discriminate. If all *t*-butyl groups are taken to be dynamically equivalent then the two out-of-plane methyl groups will see slightly different intermolecular interactions. Or, the two out-of-plane methyl groups in the two molecules in the asymmetric unit (molecules A and B in Fig. 1) see slightly different intermolecular potentials.

We assume a single value of  $\varepsilon$  for the seven terms in  $R_k=A_kJ(\omega, \tau_k)$ . A global fit of the relaxation rate  $R$  versus temperature  $T$  at the two NMR frequencies determines that  $\varepsilon=0.90\pm 0.04$ ,  $E_T=E_1=24.9\pm 2.5$  kJ mol<sup>-1</sup> for the *t*-butyl group and the in-plane methyl group, and  $E_2=14.1\pm 1.4$  kJ mol<sup>-1</sup> and  $E_3=12.5\pm 1.3$  kJ mol<sup>-1</sup> for the out-of-plane methyl groups. The parameters  $\tau_{\infty 2}$  and  $\tau_{\infty 3}$  can be modeled by  $\tau_{\infty k}=x_k(2\pi/3)(2I/E_k)^{1/2}$  [ $k=2,3$ ]. The model, with  $x_k=1$  results from a somewhat simplistic model for the preexponential factor that assumes that between hops the methyl group is vibrating as a harmonic oscillator at the bottom of the rotational potential.<sup>7</sup> The parameter  $I$  is the moment of inertia of a methyl group. The parameter  $x_k$  is simply a fitting parameter that accounts for departure from this simple model. In this case  $x_2=1.0$  and  $x_3=1.5$  with uncertainties of approximately  $\pm 50\%$  since  $\tau_{\infty k}$  is multiplied by  $\exp(E_k/kT)$  to get  $\tau_k=\tau_{\infty k}\exp(E_k/kT)$  and  $E_k$  in the exponential has an uncertainty of approximately  $\pm 10\%$ . The correlation times  $\tau_T=\tau_1$  characterize the geared rotation of a *t*-butyl group and its in-plane methyl group so  $E_T=E_1$  is not so much an activation energy for the two individual rotations as it is for the coupled rotation. As such, it is difficult to model  $\tau_{\infty T}=\tau_{\infty 1}$  but if the same model is used here as was used for  $\tau_{\infty 2}$  and  $\tau_{\infty 3}$  (with  $I$  now being the moment of inertia of a *t*-butyl group), then  $\tau_{\infty T}=\tau_{\infty 1}=0.25\pm 0.13$ . The values for all these parameters are similar to the parameters found for similar planar organic van der Waals molecular solids.<sup>2, 11</sup> Most important, a value of  $\varepsilon = 0.9$  implies a very small distribution of activation energies with only a few percent of the rotors having activation energies less than the cutoff values given above.<sup>10</sup> The origin of this may be rotors near crystallite surfaces.<sup>10</sup> Calling  $E_k$  the activation energy for the  $k$ th rotation is very reasonable.

The results presented here indicate that the model used to determine the activation energies and other properties of the rotations of *t*-butyl groups and their constituent methyl groups in planar aromatic molecules that make up van der Waals solids is very robust.

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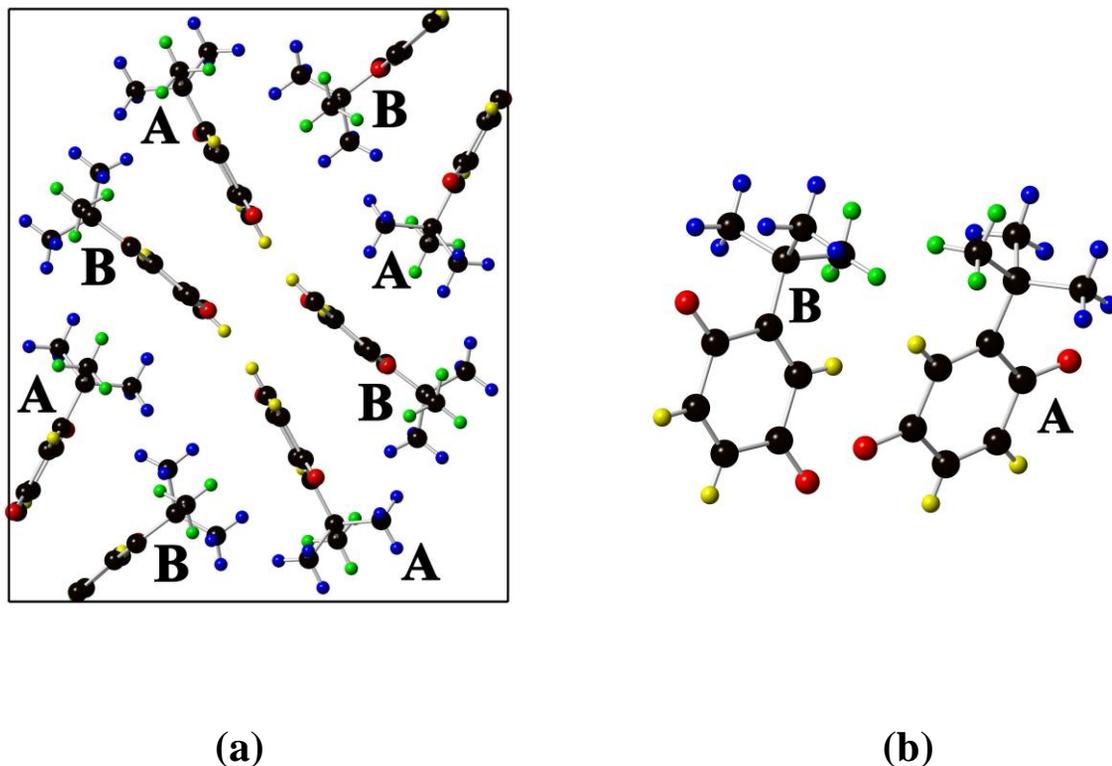


Fig. 1. (a) The crystal structure of 2-*t*-butyl-1,4-benzoquinone (TBBQ) in the 100 plane. The lines indicate the unit cell. There are eight molecules in the unit cell ( $Z=8$ ) and two molecules A and B in the asymmetric unit ( $Z=2$ ) as indicated. (b) A different view of the two molecules in the asymmetric unit. C atoms are black, O atoms are red, *t*-butyl group in-plane methyl group H atoms are green, *t*-butyl group out-of-plane methyl group H atoms are blue, and ring H atoms are yellow. The reference number for the Cambridge Structural Database, where parameters characterizing the monoclinic structure can be found, is 1539154.

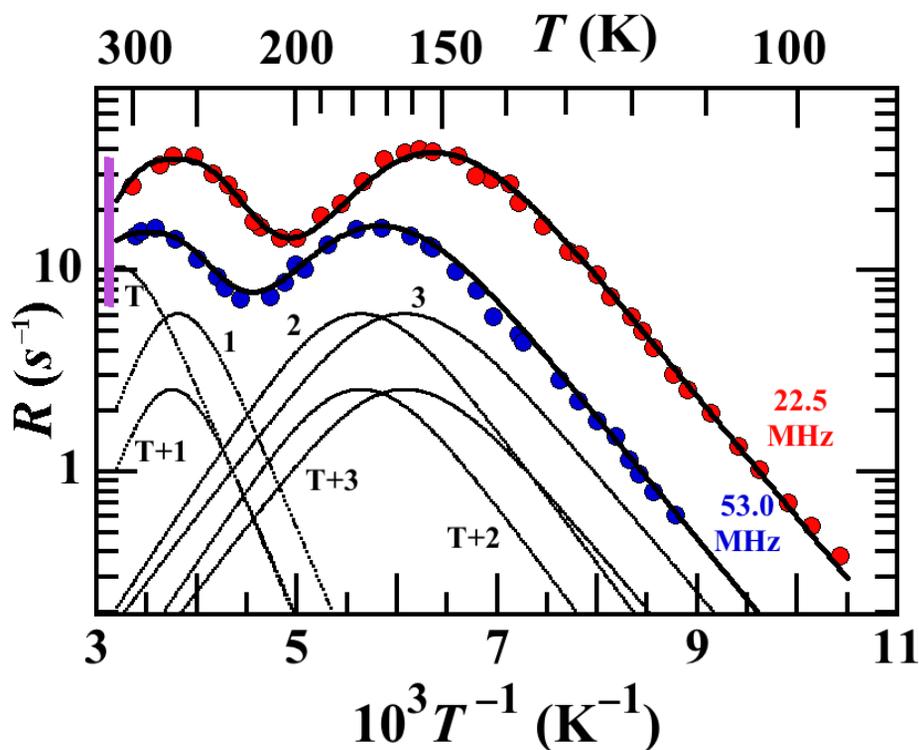


Fig. 2. The solid state  $^1\text{H}$  NMR spin-lattice relaxation rate  $R$  versus inverse temperature  $T^{-1}$  at 22.5 and 53.0 MHz in 2-*t*-butyl-1,4-benzoquinone (TBBQ). The uncertainty bars are within the size of the symbols. The single fit for both frequencies is discussed in the text. The seven components of the relaxation rate for 53.0 MHz are indicated and discussed in the text. The vertical purple line at 330 K indicates the melting point.