Brief Reports

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Thermally activated methyl and *t*-butyl group reorientation in solids

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We reinterpret proton spin-lattice relaxation measurements in solid 1,4-di-*t*-butylbenzene (1,4-DTB) [P. A. Beckmann, F. A. Fusco, and A. E. O'Neill, J. Magn. Reson. **59**, 63 (1984)] in light of a recent study of solid 1,3-DTB [P. A. Beckmann, A. I. Hill, E. B. Kohler, and H. Yu, Phys. Rev. B **38**, 11098 (1988)]. We investigate the relationship between the spectral density that characterizes the intramolecular reorientation of the *t*-butyl groups and their constituent methyl groups in DTB, and the *t*-butyl group environment which dictates the symmetry of the local electrostatic potential. For both isomers, if one assumes a sixfold potential, then a spectral density characteristic of a distribution of correlation times (or a nonexponential correlation function) is required, but if one assumes a lower, threefold symmetry due to crystal effects (for both isomers) or due to intramolecular effects (for the 1,3-isomer), then the relaxation-rate data can be interpreted in terms of a unique correlation time for intramolecular reorientation. For the case where only methyl groups are reorienting (i.e., either no *t*-butyl group reorientation or no *t*-butyl groups at all) one can only use the model which characterizes the reorientation in terms of a distribution of correlation times (or a nonexponential correlation function). Recent work in methyl-substituted phenanthrenes [K. G. Conn, P. A. Beckmann, C. W. Mallory, and F. B. Mallory, J. Chem. Phys. **87**, 20 (1987)] is used to make the latter point.

The number of parameters (correlation times, activation energies, etc.) that describe methyl and *t*-butyl group reorientation in molecular solids depends on the symmetry of the groups' environment. At temperatures above about 50 K, where methyl group rotation is thermally activated[1] (i.e., no tunneling), the reorientation of a methyl group is characterized by a correlation time τ, or, via $\tau=\tau_\infty e^{E/kT}$, by an activation energy E and a preexponential factor τ_∞.[1-3] A *t*-butyl group can have, in principle, four different correlation times τ, one characterizing the reorientation of each of the three methyl groups and one characterizing the reorientation of the whole *t*-butyl group.[4] In this Brief Report we wish to point out, via a few examples, that nuclear-spin relaxation-rate data can sometimes be interpreted in more than one way, depending on the choice of local symmetry, and that this choice can have important ramifications for the more general nuclear-spin relaxation problem. Specifically, we reinterpret (successfully in one case and unsuccessfully in other cases) published proton nuclear-spin–lattice relaxation-rate data as a function of temperature and Larmor frequency in a few molecular solids.

For a large class of aromatic solids with *t*-butyl groups, the *local single-molecule* symmetry (considering only nearest neighbors on a ring) is one of two types.[4,5] In one case, there is a plane of symmetry resulting from protons on either side of the *t*-butyl group on the ring [e.g., 1,3- and 1,4-di-*t*-butylbenzene (DTB)].[4,6] In this case, the intramolecular electrostatic potential is sixfold and all three methyl groups are equivalent. This is an *A*-type *t*-butyl group and the three methyl groups and the *t*-butyl group will reorient with the same correlation time τ_a. In the other case, there is a lower symmetry where a hydrogen atom is on one side of the *t*-butyl group and another atom or group (often OH) is on the other side (e.g., some of the *t*-butylhydroxybenzenes[5,7]). In this case, two equivalent methyl groups are above and below the ring and are characterized by one correlation time (τ_c) and the third, adjacent to the ring proton, reorients with a different characteristic correlation time τ_b. The *t*-butyl group also reorients with τ_b. This is a *B*-type *t*-butyl group. Other symmetries are possible[4] but these two are the most physically appealing and have been found to be prevalent. The symmetry can be lower than these two cases because of the *crystal* symmetry.[4]

Nuclear-spin relaxation is a very useful technique for studying reorientation processes in organic molecular solids. The observed relaxation rate R is given by $R=\sum_i A_i J_i$ where the J_i are normalized spectral densities and the A_i are constants independent of the dynamics.[4,8] The number of terms in the sum depends on the interaction and on the number of independent motions. In all the

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examples considered here, the proton-proton dipole-dipole interactions cause the nuclear-spin relaxation. This interaction is bilinear in the nuclear-spin operators and therefore leads to two terms, one for single spin flips and one for double spin flips.[8] For an A-type t-butyl group, the resulting relaxation rate R vs T^{-1} where T is the temperature, gives rise to a single maximum in R when $\tau_a\omega \sim 1$ (Ref. 4) where ω is the Larmor angular frequency. For a B-type t-butyl group, there are normally two R maxima corresponding to the two correlation times τ_b and τ_c.[7] The situation is slightly more complicated because there are cross terms due to the fact that the methyl and t-butyl reorientations are superimposed. These details are discussed elsewhere.[4] If, however, τ_b and τ_c are very close, the two R maxima can coalesce into one.[4]

For systems with reasonably large backbones and one or more relatively isolated methyl groups (e.g., the methyl substituted phenanthrenes and other similar molecules[3]) there is a single R vs T^{-1} maximum for each chemically inequivalent methyl group and the situation is much simpler.

The form of the spectral density $J(\omega,\tau)$ is an important problem in the study of dynamical processes in solids. For a simple random (Poisson) process the correlation function is an exponential $g=e^{-|t|/\tau}$ and the spectral density is $J=2\tau/(1+\omega^2\tau^2)$.[8] When coupled with an Arrhenius relationship $\tau=\tau_\infty e^{E/kT}$, this leads to an R vs T^{-1} plot with characteristic linear $\ln R$ vs T^{-1} regions at high and low temperatures.[8] In fact, this form for J leads to high- and low-temperature slopes in $\ln R$ vs T^{-1} which are identical in magnitude to E/k. For 1,4-DTB,[6] there is only one R maximum and the ratio of the low- to high-temperature slopes is $\epsilon=0.9$. This is a *significant* departure from unity. Employing *both* the A-type t-butyl group model *and* the random-motion spectral density will not fit the data. In cases such as this where there is only one R maximum with no flat region in the vicinity of the R maximum, the next step usually taken is to assume a distribution of correlation times τ_a. The most successful of these has been a Davidson-Cole distribution[9] which has ϵ, a measure of the distribution of correlation times[8] (or activation energies), as an additional parameter. The published fit of the R vs T^{-1} data in 1,4-DTB[6] comes from using the A-type model and a Davidson-Cole distribution. In light of the recent study of 1,3-DTB,[4] we have refitted the 1,4-DTB data assuming a B-type t-butyl group and random-motion spectral densities, $J=2\tau/(1+\omega^2\tau^2)$. The resulting fit is virtually identical to the A-type fit[6] assuming a distribution of correlation times so there is no need to provide a new figure. The new fit gives $E_b=19$ kJ mol^{-1}, $E_c=16$ kJ mol^{-1}, $\tau_{\infty b}=5\times10^{-14}$ s, and $\tau_{\infty c}=1.2\times10^{-13}$ s (and $\epsilon\equiv1$). This is to be compared with $E_a=18$ kJ mol^{-1}, $\tau_a=7.6\times10^{-14}$ s, and $\epsilon=0.89$ in the published A-type fit.[6] This reinterpretation suggests that the crystal packing reduces the environment from being sixfold, which is the molecular symmetry, to threefold. The physical situation is the same for the 1,3-isomer in that either model will fit the data.[4] Either interpretation makes physical sense. The case of a distribution of correlation times could result from the presence of several t-butyl group environments due to the crystal structure[10] or it could result from widespread crystal imperfections in the powdered sample.

It is important to note that this reinterpretation will not work in the case of single methyl groups. For example, the reorientation of the 9-methyl group in 9-methylphenanthrene (9-MP) and 3,9-dimethylphenanthrene (3,9-DMP) has been interpreted using a single Davidson-Cole spectral density with $\epsilon=0.57$ (9-MP) and 0.68 (3,9-DMP).[3] These values of ϵ imply large distributions of correlation times or very nonexponential correlation functions. A single Davidson-Cole spectral density requires four adjustable parameters; E, ϵ, τ_∞, and a weight factor.[3] The fitted values of τ_∞ and the weight factor for these methyl substituted phenanthrenes are very close to the values predicted by simple models.[3] Although the t-butyl classifications are not relevant here, it is of interest to ask whether a small number of random-motion spectral densities can be used in place of a single Davidson-Cole spectral density. Using the random-motion spectral density, we have attempted to refit the data with first two and then three terms and it does not work (i.e., the fits are very poor). Four crystallographic sites were not attempted although, if enough terms are employed, eventually the data could be fitted since all the Davidson-Cole spectral density is doing is mimicing a distribution of random-motion spectral densities. However, each additional random-motion spectral density introduces three new parameters (E, τ_∞, and a relative weight factor) so even if a four-term fit was successful, it would have twelve adjustable parameters (with constraints on the relative weights) and this seems a poorer model than a single Davidson-Cole fit with its four parameters.

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