Physics Faculty Research and Scholarship

Physics

1991

Solid State Proton Spin Relaxation and *t*-Butyl and Methyl Group Reorientation in 1-Bromo-2,4,6-Tri-*t*-Butylbenzene

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We have used the solid state proton spin relaxation technique to investigate the barriers for methyl and *t*-butyl group reorientation in polycrystalline 1-bromo-2,4,6-tri-*t*-butylbenzene. The barriers in the range of 15–19 kJ/mol (3–5 kcal/mol) are compared with those found in related molecules. It is shown that the neighboring ring bromine atom has an effect on the barrier for *t*-butyl group reorientation similar to that of a neighboring hydrogen atom despite the significantly larger van der Waals' radius of a bromine atom. This most likely occurs because of the relatively long carbon–bromine bond, the distorted ring geometry, and the relatively high polarizability of bromine. In addition, the barriers for methyl group reorientation, about 16 kJ/mol, seem to be largely intra-*t*-butyl in origin.

INTRODUCTION

Solid state proton spin relaxation (SSPSR) experiments are very good for investigating the dynamics of alkyl groups and for determining internal rotation barriers in alkylbenzenes. In this paper, we investigate the temperature dependence of the Zeeman spin–lattice relaxation rate R at three Larmor frequencies in polycrystalline 1-bromo-2,4,6-tri-*t*-butylbenzene (1). The molecule is shown in Fig. 1. We discuss dynamical models for the motion of the *t*-butyl groups and their constituent methyl groups. One important set of parameters to come out of the experiments is the barriers for the superimposed internal motions. We compare the models and barriers obtained here for 1 with those obtained from previous studies using other molecules, including the representative molecules 1,4-di-*t*-butylbenzene (2) and 1-hydroxy-4-methyl-2,6-di-*t*-butylbenzene (3) shown in Fig. 1. This comparison allows us to conclude that the bromine atom affects the dynamical properties of the 2- and 6-*t*-butyl groups in 1 in much the same manner as does a hydrogen atom. That is, the dynamics of the 2- and 6-*t*-butyl groups in 1 are essentially indistinguishable from the dynamics of the 4-*t*-butyl group. Alkyl groups and their constituent methyl groups in alkylbenzenes reorient in barriers in the range 10–30 kJ/mol (2–7 kcal/mol) and these barriers are generally too low to measure by high resolution liquid state nuclear magnetic resonance spectroscopy.[1,2] Microwave spectroscopy is a good technique to measure CH_3 barriers in isolated molecules.[3] However, in the determination of internal rotation barriers, only smaller molecules or molecular groups such as CH_3 are generally investigated by microwave spectroscopy.[3] We know of no technique other than SSPSR for measuring *t*-butyl group and constituent methyl group barriers in *t*-butylbenzenes and related molecules.

EXPERIMENTS

The proton Zeeman relaxation rates R were measured at nuclear Larmor frequencies of $\omega/(2\pi) = 8.50$, 22.5, and 53.0 MHz using standard solid state pulsed nuclear magnetic resonance (NMR) techniques.[4,5] The data are shown in Fig. 2. The uncertainties in R are about 5%, but are best estimated by the scatter in adjacent data points. Temperature T was controlled with a flow of reheated, cold nitrogen gas and measured with a calibrated copper–constantan thermocouple.

The sample of 1-bromo-2,4,6-tri-*t*-butylbenzene (1) was prepared by the silver nitrate-promoted bromination of 1,3,5-tri-*t*-butylbenzene.[6] Its purity was assessed as > 99% by 400 MHz NMR spectroscopy ($CDCl_3$) and by gas chromatography-mass spectrometry.

THEORY REVIEW

In the free molecule, the *t*-butyl group in many *t*-butylbenzenes has an equilibrium position with one methyl group in the plane of the ring adjacent to a ring atom and the other two methyl groups in and out of the plane.[7] This may not necessarily be the case in the solid state, but the vast majority of SSPSR experiments are consistent with this geometry. It is the case for 3 where the crystal structure has been determined.[8] The benzene ring has twofold symmetry, the *t*-butyl group has threefold symmetry, and the reorientation process for the *t*-butyl group and its constituent methyl groups is a complicated motion involving four coupled rotors. An intramolecular reorientation process is described in terms of a correlation time τ which is the inverse of a mean reorienta-
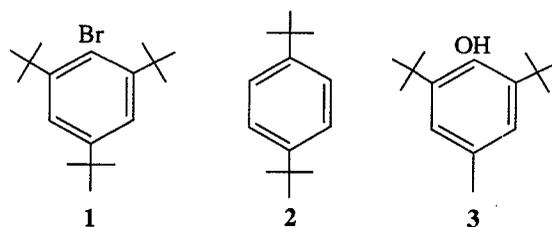

FIG. 1. Schematic drawings of (1) 1-bromo-2,4,6-tri-*t*-butylbenzene; (2) 1,4-di-*t*-butylbenzene; and (3) 1-hydroxy-4-methyl-2,6-di-*t*-butylbenzene.
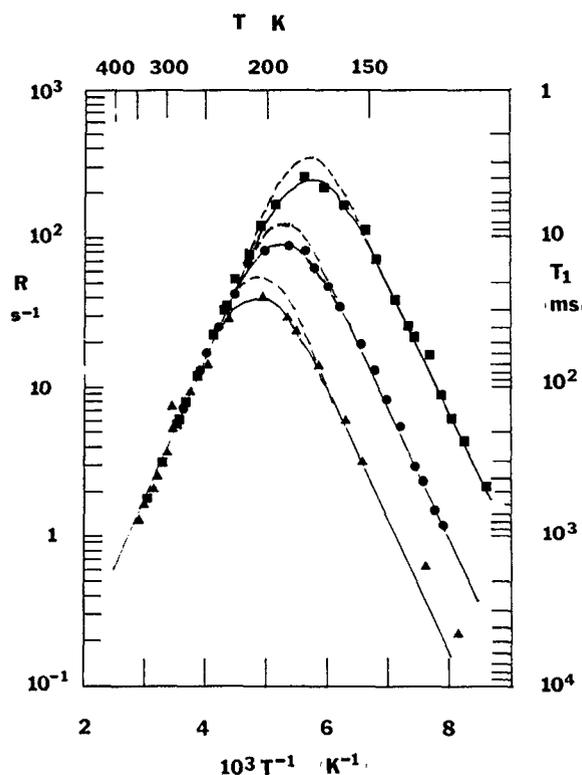
T K

400 300   200   150

FIG. 2. The temperature T dependence of the proton Zeeman relaxation rates R at Larmor frequencies of 8.5 (■), 22.5 (●), and 53 Mhz (▲) in polycrystalline 1-bromo-2,4,6-tri-*t*-butylbenzene (1). The dashed lines indicate fits for the $3A$, $3M$, and $3T$ models and the solid lines indicate fits for the $3B$ and $2B + A$ models.

tion rate in a random hopping model.[9] The parameter τ must be suitably defined for other models.[10]

If a *t*-butyl group reorients in a threefold potential, as might be expected for the 2- and 6-*t*-butyl groups in 1 and 3, the *t*-butyl group and the in-plane methyl group (next to the 3- and 5-hydrogen atoms in 1 and 3) reorient in some complicated geared fashion. (This assumes that the intermolecular potential is negligible compared with the intramolecular potential.) This motion is described by one correlation time τ_b. The two out-of-plane methyl groups (next to the bromine atom in 1 or the OH group in 3) reorient at a different (usually greater) mean rate τ_c^{-1}, since they tend to be freer. This model for *t*-butyl group motion is called the B model. It was first proposed in 1979[11] for 3 in a SSPSR study and has been used successfully in interpreting SSPSR data in many related molecules.[4,11-15] Of considerable interest is a recent deuteron magnetic resonance study[16] (using 3) which supports the model.

For the 4-*t*-butyl group in 1 and both *t*-butyl groups in 2, the *t*-butyl group might reorient in a sixfold potential if only intramolecular potentials are considered. If so, a more appropriate quantum mechanical description involves a more complicated cooperative motion among the four rotors. The three methyl groups are equivalent in this case and the entire dynamical process is described by a single mean reorientation rate. No classical geometrical picture will suffice here as it will for the B model outlined above. Thinking in terms of

the restrictions placed on the quantum mechanical wave functions by the sixfold symmetry of the electrostatic potential, one can think of six time-averaged, equivalent half-methyl groups. In this case, $\tau_b = \tau_c$ and both are relabeled τ_a for convenience. This special case of the B model is called the A model. It was first proposed in 1981[15,17] to interpret SSPSR data in 2 and has since been used to interpret SSPSR data in other molecular solids.[4,12-14,18,19] One might expect 1 to be characterized by a $2B + A$ model (i.e., two B-type *t*-butyl groups and one A-type, *t*-butyl group).

For completeness, we mention two other models. In the M model, the *t*-butyl groups are immobile on the nuclear magnetic resonance time scale and the three methyl groups reorient with the same correlation time τ_m. If the *t*-butyl group correlation time is τ_t, then for the M model, $\tau_t \gg \tau_m$ in the temperature region where $\omega\tau_m \sim 1$. Finally, in the T model, the *t*-butyl groups are reorienting rapidly on the nuclear magnetic resonance time scale ($\tau_t \ll \tau_m$, where $\omega\tau_m \sim 1$). Neither of these motions seem very realistic and eliminating them with great certainty is straightforward as shown in the next section.

The correlation times are modeled by Arrhenius relationships

$$\tau_i = \tau_{\infty i} \exp\left(\frac{E_i}{kT}\right), \quad i = a,b,c,m,t \tag{1}$$

for preexponential factor $\tau_{\infty i}$ and activation energy E_i. The relationship between the activation energy measured in a SSPSR experiment and a reorientation barrier is model dependent, but realistic models suggest that at high temperatures where thermally activated hopping is the dominant motion, Eq. (1) is an excellent approximation to the mean hopping time and the activation energy E_i is very close to the barrier.[20] One theoretical calculation[21] suggests that in the energy range being considered here, the observed SSPSR activation energy and the reorientation barrier are very close, although this is not obvious *a priori*. We will take the E_i to be barrier heights and quote results in the 10–20 kJ/mol range to $\pm$ 1–2 kJ/mol.

In fitting data, E_i and $\tau_{\infty i}$ are parameters. It is hard to have a feel for the value of $\tau_{\infty i}$, so we will compare the fitted value with a theoretical value $\tilde{\tau}_{\infty i}$ obtained from a simple model where the rotor reorients in a deep ($E_i \gg kT$) threefold potential. (A barrier of 15 kJ/mol corresponds to 1800 K.) In this model, the rotor spends most of its time at the bottom of the well. The mean hopping frequency τ_i^{-1} [the inverse of Eq. (1)] comes from the canonical ensemble and is the product of the attempt frequency $\tau_{\infty i}^{-1}$ and the probability of being in an excited state at the top of the well $\exp(-E_i/kT)$. In this case,[22]

$$\tilde{\tau}_{\infty i} = \left(\frac{2\pi}{3}\right)\left(\frac{2I}{E_i}\right)^{1/2}, \tag{2}$$

where I is the moment of inertia which, for a methyl group, is $I = 5.3 \times 10^{-47}$ kg m^2. We do not claim this is a realistic model, but it is found, surprisingly, that experimentally determined values of $\tau_{\infty i}$ are generally within an order of magnitude of $\tilde{\tau}_{\infty i}$ for methyl reorientation (i.e., $i = m$ or c). It is difficult to understand why it should apply at all to *t*-butyl-

+ methyl reorientation (i.e., $i = a$ or b), but in any event, we use it only as a benchmark. Modeling τ_∞ is an important ongoing problem, but is not of concern in this work. Values of $\tau_{\infty c}$ or $\tau_{\infty m}$ not within, say, two orders of magnitude of $\tilde{\tau}_{\infty a}$ or $\tilde{\tau}_{\infty m}$ should be treated with suspicion.

The observed Zeeman relaxation rate in an SSPSR experiment is discussed extensively and presented in detail elsewhere.[12] R is given by

$$R = \sum_i A_i q(\omega,\tau_i) \qquad (3)$$

with

$$q(\omega,\tau_i) = J(\omega,\tau_i) + 4J(2\omega,\tau_i) \qquad (4)$$

and

$$A_i = \sum_j a_j \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^2 \hbar^4}{r_j^6}. \qquad (5)$$

The A_i are measures of the number and the strengths of the proton spin dipole–dipole interactions (whose modulation causes the relaxation) and $J(\omega,\tau_i)$ is the spectral density discussed below. Specific examples of Eq. (5) and the values of the numerical factors a_j, which are typically in the range from 0.1 to 1, appropriate for the A and B models are given elsewhere.[4] The nuclear Larmor angular frequency $\omega = \gamma B$, where $\gamma = 2.675 \times 10^8$ kg^{-1} s A, is the magnetogyric ratio of the nucleus (proton) and B is the magnetic field intensity. Other constants are $\mu_0/(4\pi) = 10^{-7}$ m kg s^{-2} A^{-2}, where μ_0 is the permeability of free space and $\hbar = 1.054 \times 10^{-34}$ m^2 kg s^{-1}. The parameter r is the appropriate proton–proton separation, e.g., within a methyl group, $r = 0.1797$ nm. The number of terms in the sum in Eq. (3) depends on the dynamical model.

The spectral density characteristic of random motion is[9]

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

An observed maximum in R vs T^{-1} occurs when $\omega\tau$ is of the order of unity. The precise value of $\omega\tau$ at the maximum depends on the number and relative strengths of the terms in R.[14] In principle, Eqs. (3)–(6) are not really correct for the superimposed reorientation of a t-butyl group and its constituent methyl groups. In practice, however, they can often be used successfully to interpret the data so long as the relaxation is exponential (in which case cross correlations are not important) and, pragmatically, they fit the data well. The main reason they work is that powder averaging mimics isotropic motion; i.e., an isotropic spatial average often has the same effect in the dynamical model as an isotropic time average even when the latter is not appropriate from a fundamental point of view. Understanding these matters on a more fundamental basis is an important ongoing project.

The spectral density in Eq. (6) requires that the magnitude of the slope of ln R vs T^{-1} in an SSPSR experiment be the same at high and low temperatures (i.e., the straight-line parts in Fig. 2) if only one correlation time is involved in the motion. This is the case for the M, T, and A models. The slopes can be different if more than one correlation time is involved and that is the case for the B model (or any combi-

nation of two or more models for molecules that have chemically inequivalent t-butyl groups such as 1). The data in Fig. 2 have different slopes at low and high temperatures, so the M, T and A models will not work with Eq. (6). In this case, we use[23]

$$J(\omega,\tau) = \frac{2}{\omega} \frac{\sin[\epsilon \arctan(\omega\tau)]}{(1 + \omega^2\tau^2)^{\epsilon/2}}. \qquad (7)$$

This is the Davidson–Cole spectral density which, in addition to the parameters E_i and $\tau_{\infty i}$ in Eq. (1) and A_i in Eq. (3), has the parameter $0 < \epsilon \leqslant 1$ which is a measure of a distribution of correlation times.[10] When $\epsilon = 1$, the Davidson–Cole spectral density in Eq. (7) reduces to the Lorentzian spectral density in Eq. (6). We will ultimately reject the A (by itself), M, and T models, so there is no need to justify Eq. (7) in great detail. It is phenomenological and is discussed extensively[10] and used[4,15,23] elsewhere.

DATA ANALYSIS

The procedure for fitting the data and the subsequent fitting parameters have been discussed elsewhere.[12,23] We present five fits of the data.

The simplest dynamical model, unphysical as it may be, is the M model. It assumes that all nine methyl groups are reorienting with the same τ_m and that the t-butyl groups are static on the nuclear magnetic resonance time scale. Equation (3) becomes[23]

$$R_M = \frac{n}{N} A_m q(\omega,\tau_m), \qquad (8)$$

where $n = 9$ is the number of methyl groups and $N = 29$ is the total number of protons in the molecule. (This makes A_m independent of molecule.) We refer to the theoretical value of A_m as $\tilde{A}_m$ and it is given by $\tilde{A}_m = 1.14 \times 10^9$ s^{-2} (Ref. 23). (In Ref. 23, $\tilde{A}$ is one-third of this value and n is the number of protons in methyl groups rather than the number of methyl groups. This revised definition is more convenient.) For 1, we call this a $3M$ model since it assumes three M-type t-butyl groups. The best fit is shown as the dashed line in Fig. 2. As in all fits reported here, the high and low temperature linear ln R vs T^{-1} regions are fitted.[12,23] Not only is the fit poor in the vicinity of the R maximum, but the ratio $A_m/\tilde{A}_m$ (i.e., fitted to theoretical) is 2.1. This implies that the intramethyl dipole–dipole interactions account for less than one-half the observed relaxation. Given the geometry of the molecule, this is not possible and effectively rules out this model. The other fitted parameters for this fit are $\epsilon = 0.89$ in Eq. (7) and $\tau_{\infty m} = 2.4 \times 10^{-14}$ s which gives $\tau_{\infty m}/\tilde{\tau}_{\infty m} = 0.19$. Although $\epsilon = 0.85$ is close to unity in the sense that the implied distribution of activation energies is very narrow,[24] the experiments are very sensitive to this parameter.

The second fit is for the T model. We have not performed the calculation, but the form of R will be as given in Eq. (8), only $\tilde{A}_t$ will be significantly smaller than $\tilde{A}_m$ discussed above since the rapid t-butyl group reorientation will further average the intramethyl dipole–dipole interactions. The fit will be identical to that for the M model, only the fitted value of $A_t/\tilde{A}_t$ will be significantly greater than the value of 2.1 determined above and this model can be ruled

out. This result is consistent with the calculation[11] of values of the maximum in R for 3 and with the detailed calculations[24] which have been done for ethyl groups.

The third fit assumes there are three A-type t-butyl groups; the dynamics of all three t-butyl groups and their constituent methyl groups are characterized by the single correlation time τ_a as discussed in the theory review. In this case,[4,12]

$$R_A = \frac{n}{N}[A_a q(\omega,\tau_a) + A_{aa}q(\omega,\tau_a/2)]. \tag{9}$$

There is only one correlation time τ_a. The second term in Eq. (9) arises because the motion of the methyl groups is superimposed on that of the t-butyl groups. The theoretical values of the A constants are $\tilde{A}_a = \tilde{A}_{aa} = 2.40 \times 10^{10}$ s^{-2}. That $\tilde{A}_a = \tilde{A}_{aa}$ to better than 0.5% is a coincidence.[4,12] The fit assuming three A-type, t-butyl groups is called the $3A$ model for 1 and it is very similar to that obtained for the $3M$ model (dashed line in Fig. 2). The fitted value of $A_a/\tilde{A}_a = A_{aa}/\tilde{A}_{aa} = 1.4$. (The ratio A_a/A_{aa} is fixed at $\tilde{A}_a/\tilde{A}_{aa} = 1$ in the fits.) It is highly unlikely, but not impossible that the extra 40% of relaxation intensity arises from dipole–dipole interactions not included in the model.[12] However, the fit for this $3A$ model, like the $3M$ and $3T$ models, is poor.

The fourth fit, shown by the full line in Fig. 2 is for a $3B$ model; there are two correlation times τ_b and τ_c for each of the three identical t-butyl groups. The relaxation rate is given by[4,12]

$$R_B = \frac{n}{N}[A_b q(\omega,\tau_b) + A_{bb}q(\omega,\tau_b/2) + A_c q(\omega,\tau_c)$$
$$+ A_{bc}q(\omega,\tau_{bc})] \tag{10}$$

with $\tau_{bc} = (\tau_b^{-1} + \tau_c^{-1})^{-1}$. The bb and bc terms arise because the motion of the methyl groups is superimposed on that of the t-butyl groups. The theoretical A values are $\tilde{A}_b = 1.73 \times 10^{10}$ s^{-2}, $\tilde{A}_{bb} = 8.02 \times 10^9$ s^{-2}, $\tilde{A}_c = 6.75 \times 10^9$ s^{-2}, and $\tilde{A}_{bc} = 1.60 \times 10^{10}$ s^{-2} and the ratios A_j/A_k are fixed at the theoretical ratios $\tilde{A}_j/\tilde{A}_k$. The fit is very good. The ratio of the fitted to the calculated[4,12] A values is 1.05 ± 0.08 and the activation energies via Eq. (1) are $E_b = 19 \pm 1$ and $E_c = 16 \pm 1$ kJ/mol.

The $3B$ model fits the data quite well and the resulting fitted values of A_i are in the ranges expected. However, we note that a fifth model with two B-type, t-butyl groups (presumably positions 2 and 6) and one A-type, t-butyl group (presumably position 4) also fits the data very well. In this case,

$$R_{2B+A} = \tfrac{2}{3}R_B + \tfrac{1}{3}R_A \tag{11}$$

with R_B given by Eq. (10) and R_A given by Eq. (9). We refer to this as a $2B + A$ model for 1. The differences between the fits for the $3B$ and $2B + A$ models are minor and the same full line in Fig. 2 will suffice for both, but in fact, the $2B + A$ model fits the data slightly better. The ratio of the fitted to calculated A values is $A_a/\tilde{A}_a \equiv A_{aa}/\tilde{A}_{aa} \equiv A_b/\tilde{A}_b \equiv A_{bb}/\tilde{A}_{bb} \equiv A_c/\tilde{A}_c \equiv A_{bc}/\tilde{A}_{bc} = 1.00 \pm 0.08$ and the activation energies are $E_a = 17 \pm 2$, $E_b = 19 \pm 2$, and $E_c = 15 \pm 2$ kJ/mol. (Again, the values of A_j/A_k were set equal to $\tilde{A}_j/\tilde{A}_k$ for all j,k.) If two of the three E values are fixed at a value in the ranges given, the uncertainty on the third is much smaller than the 10%–15% indicated. The indicated uncertainties reflect the manner in which the three E values can be changed simultaneously in the fit.

DISCUSSION

If quite different correlation times are present, more than one local maximum in R vs T^{-1} is observed.[11,14,15,25,26] In 3, e.g., maxima in R vs T^{-1} at 31 MHz are observed at 125 K when $\omega\tau_c$ is of order unity and at 300 K when $\omega\tau_b$ is of order unity.[11] In this case, the hydroxy group makes the intramolecular potential threefold and the activation energies $E_c = 11$[11,27] and $E_b = 34$ kJ/mol[28] are very different. The same situation occurs for the t-butyl groups in 1-hydroxy-2,6-t-butylbenzene[15] (3 without the 4-methyl group), where $E_c = 16$ kJ/mol and $E_b = 33$ kJ/mol. The situation for 1, however, with $E_c = 15$–16 kJ/mol (depending on the model) and $E_b = 19$ kJ/mol is like 2, in which case $E_c = 16$ kJ/mol and $E_b = 19$ kJ/mol.[13] (All these activation energies have uncertainties in the 3%–15% range, depending on the details of the SSPSR experiments and the model which links observed SSPSR activation energies to reorientation barrier heights. An uncertainty of ± 1–2 kJ/mol is a reasonable average uncertainty to use for the purpose of discussion.)

In the substituted benzenes we have studied to date, the t-butyl groups either have H on both sides[4,12,14,15,17–19,28] (as in 2) or H on one side and OH on the other[11,14,15,17,26–28] (as in 3). The present experiments with 1 were performed in an attempt to better understand the relationship between the t-butyl and methyl group barriers and the ring constituents. The van der Waals radius of bromine (0.20 nm) is much larger than those of oxygen (0.14 nm) and hydrogen (0.12 nm) and it might therefore be expected on the basis of an idealized geometry that E_b and E_c would be very different (for the 2- and 6-t-butyl groups) in 1 as it is in all cases with H, OH neighbors like 3. The observation, however, is that the situation is much more like the t-butyl groups in 2 which has H, H neighbors.

The apparent similarity between bromine and hydrogen in their effects on neighboring t-butyl groups may appear surprising at first sight, especially since OH, while closer in size to H, has a larger effect on neighboring t-butyl group in 3 than does bromine in 1. However, a number of effects are undoubtedly in operation in these highly sterically congested systems. First, the C–Br bond (0.19 nm) in 1 is longer than the C–H bonds (0.11 nm) in 1–3 or the C–O bond (0.14 nm) in 3. Thus, even though the Coulomb field for the bromine atom is more extensive (i.e., bromine is "larger"), the center of the atom is further away from the ring. Second, the bromine atom is more easily polarized than an atomic group such as OH (i.e., bromine is "softer"). These two effects are known to play an important role in governing the conformational properties of organic substrates, including substituted cyclohexanes.[29–31] Third, the t-butyl groups in 1 can relieve steric interactions with the bromine atom by bending away from the bromine atom and out of the plane of the benzene ring or, alternatively, the bromine atom, rather than the t-

butyl groups, might bend out of the plane of the benzene ring. Fourth, substituents generally distort a benzene ring from the ideal hexagonal geometry. The effect of the steric bulk of t-butyl groups is generally to expand the external ring angles at the point of attachment and therefore to reduce the internal angle at the same site substantially below 120°. This is the case in 3.[8] Hydrogen exerts no effects at the sites to which it is attached, but bromine *expands* the internal ring angles at the site to which it is attached. (See, e.g., the structure of 2-methyl-3-bromo-hydroxybenzene.[8]) If anything, the bromine atom in a substituted bromobenzene acts as though it is slightly "smaller" than a hydrogen atom.

Independent of the problem of how to describe the complicated motion of a t-butyl group in terms of its environment, it is of interest to investigate the rotation barriers for those methyl groups in and out of the plane of the ring in these systems. We have determined that this barrier is about 15 kJ/mol, independent of whether or not these methyl groups are reorienting faster than, or at rates comparable with the t-butyl group. For comparison, the barrier for intramolecular reorientation in ethane, a classic example, is about 12 kJ/mol; about 4 kJ/mol for each of the three eclipsed bonds in the 60° reorientation transition state.[32] (This barrier has been measured recently with very high precision.[33]) We are not aware of any measurements or calculations in the literature on the height of the barrier to methyl group reorientation in a t-butyl group, but there are many examples of microwave measurements of CH_3 barriers in isopropyl and ethyl or similar environments although not in alkyl substituted benzenes. (See Refs. 34 and 35 for recent measurements and Ref. 3 for many examples prior to 1985.) The barriers are all about 12–14 kJ/mol and are relatively insensitive to the details of the geometry of the rest of the molecule. The observed barriers of $E_c = 16$ kJ/mol for 1 and 2, and 11 kJ/mol[11,27] for 3 are in the same range of this result though the differences are interesting. Methyl group reorientation barriers in this range as measured by the SSPSR technique occur in several other t-butyl substituted benzenes[4,12,13–15, 18] as well as in isopropyl[36] and ethyl[24] substituted benzenes. The relative importance of intra-t-butyl and other interactions (both intramolecular and intermolecular in the present case) is not known, but it can be stated very clearly that the intermolecular component and the intramolecular, non-intra-t-butyl component of the potential are, at the most, quite small.

ACKNOWLEDGMENTS

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