Communications to the Editor

A Method for Determining the Conformational Preference of Nonrigid Radicals by Electron Paramagnetic Resonance[1]

Sir:

Many workers have used hybridization ratios to determine bond angles from EPR spectral parameters.[2] However, it has not always been realized that there is an implicit assumption in this method that the radical is not undergoing vibrational motion and that neglect of this can lead to serious errors in interpretation.[3] We show herein that proper inclusion of vibrational effects in the case of the *tert*-butyl radical gives results diametrically opposed to those from the simple application of the hybridization method.[4]

It is well known that given a vibrational potential function and the hfs corresponding to this vibration, the hfs of a radical can be calculated at any desired temperature by standard methods.[5] Simply stated, our method is to find a potential function which accurately reproduces the observed hfs of the radical at all temperatures. We then obtain barriers to inversion, equilibrium geometries, vibrational frequencies, etc., from this potential function. For the application of this method to *tert*-butyl radical we used INDO[6] spin densities which have been shown by Beveridge and Miller[5a] to give good results for the hfs of isotopically substituted methyl radicals. As in the case of the methyl radical the a_2'' bending mode (umbrella mode) of *tert*-butyl will have the largest effect on the hfs as a result of the relatively large change in hfs and the low frequency of this vibration. The specific procedure which we follow is the following. (a) The valence s orbital spin densities for ^{1}H and ^{13}C in *tert*-butyl radical were calculated at 1° intervals of θ by INDO, where θ is defined as the angle between the plane of the methyl groups and one of the C–C bonds. Each value of θ was converted via an integral transform into a normal coordinate, X, such that the moment of inertia for the a_2'' binding mode is constant in X. Each isotopically substituted *tert*-butyl radical has, of course, a different transformation. The INDO spin densities were then fitted to a tenth-order polynomial in X in order to allow evaluation at any value of X desired. (b) For arbitrary initial values of the parameters in a potential function, sufficient vibrational wave functions were found by a direct integration method to ensure insignificant populations in the highest level at the highest temperature for which the hfs were desired. Expectation values of the spin densities, $\rho_{N\nu}$, were evaluated for each of the vibrational states, ν. The hfs at each temperature for which experimental values were known for nucleus N were then calculated via the expression

$$a_N(T) = \textstyle\sum_\nu c\rho_{N\nu} \exp(-E_\nu/kT)/\sum_\nu \exp(-E_\nu/kT) \quad (1)$$

where k is the Boltzmann constant, and the summation is over all occupied vibrational states. The sum of the squared differences between calculated and experimental hfs were then evaluated for this potential function, c being the proportionality constant between spin density and hfs which was chosen to minimize this sum. (c) The variable metric method for minimization[7] was then used to find values of the parameters in the potential function which minimized the sum of the squared differences, thus achieving a least-squares fit of the potential function parameters to the experimental data.

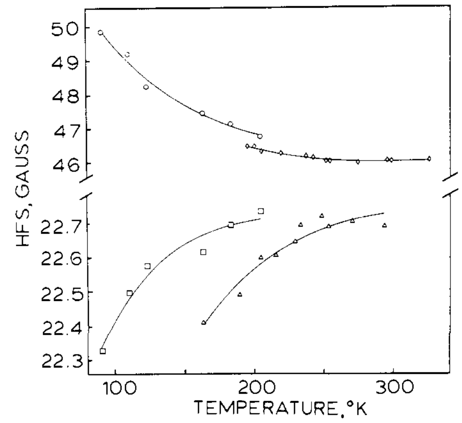

Figure 1. Solid lines are calculated hfs vs. temperature using the parameters in Table I. Experimental measurements are the points: ○ = ^{13}C hfs in $(CH_3)_3{}^{13}C$, ref 3b; ◇ = ^{13}C hfs in $(CD_3)_3{}^{13}C$, ref 3a; □ = ^{1}H hfs in $(CH_3)_3{}^{13}C$, ref 3b; △ = ^{1}H hfs in $(CH_3)_3{}^{12}C$ this work. The hfs taken from previous papers have been corrected for a Fremy's salt ^{14}N hfs of 13.091 G from the value of 13 G used previously. The displacement of the lower temperature curves from the higher temperature ones appears to be a systematic error introduced by the evaluation of isotropic hfs from anisotropic spectra rather than from a reduced mass effect. This latter explanation was proposed earlier[3a] but is now ruled out because of the nearly classical nature of the *tert*-butyl radical vibrations.

In order to reproduce the anomalous temperature dependence of the *tert*-butyl radical hfs (i.e., negative for ^{13}C in the trigonal position and positive for ^{1}H, at low temperatures) it was necessary to have a minimum of two vibrational levels below the barrier to inversion due to the alternation in expectation values of the spin density between even and odd wave functions. We also found that as a result of the large moment of inertia and the rather soft potential function required to obtain reasonable fits to the data for *tert*-butyl radical, the classical approximation gave essentially identical results with those of the quantum mechanical treatment. This entails evaluating the eq 1 above as an integral rather than as a discrete summation, and inasmuch as

Table I. Parameters for Temperature Dependence of *tert*-Butyl Radicals

Radical	hfs fitted	Barrier (cal/mol)	θ_{min}	Potential function parameters[a] p_1	p_2	p_3	rms deviation (G)	c(G)
$(CH_3)_3{}^{12}C$	^{1}H[b]	428	26.2	1.340736	20.77960	0.07079774	0.0243	705.6
$(CH_3)_3{}^{13}C$	^{1}H[c]	309	19.8	1.024161	15.92141	0.09050398	0.0273	629.6
$(CH_3)_3{}^{13}C$	^{13}C[c]	496	18.7	0.5795945	8.243019	0.08486169	0.1362	407.3
$(CD)_3{}^{13}C$	^{13}C[d]	535	22.8	0.5377621	10.89976	0.03464242	0.0358	323.8

[a] Equation 2. [b] From isotropic spectra of isobutane x-irradiated in adamantane-d_{16}, this work. [c] From anisotropic spectra in ref 3b. [d] From isotropic spectra in ref 3a.

it greatly speeded up the computations the results of the classical treatment are reported herein. Several different functional forms of the potential were tried and each resulted in relatively good fits to the data. Although the barriers and minima found by the use of different potential functions do vary, the general features of a low barrier, ~0.5 kcal/mol, and nearly tetrahedral geometry, $\theta \sim 19°$, were always obtained. In order to compare our results more easily with those of other workers we report herein our minimizations using the usual even-power expansion in X for the potential functions. This particular form of the X^2, X^4, X^6 expansion was chosen to keep the potential always positive for simplicity in the calculation of the wave functions.

$$V(X) = p_1((X/p_2 - 1)(X/p_2 + 1))^2 + p_3X^6 \qquad (2)$$

The results of minimizations on the ^{13}C hfs of $(CH_3)_3{}^{13}C$ and $(CD)_3{}^{13}C$ and the ^{1}H hfs of $(CH_3)_3{}^{12}C$ and $(CH_3)_3{}^{13}C$ are plotted in Figure 1 and the relevant parameters are collected in Table I. The barriers found range from 309 to 535 cal/mol and the angles at minimum potential, θ_{min}, range from 18.7 to 26.2°. These four different results correspond of course to four separate experimental determinations and their accuracy depends on the accuracy of the respective measurements as well as the assumptions used in the calculations. We believe that the best data for measuring the barrier height, both with respect to the least amount of scatter and better coverage of the critical region wherein the slope of the temperature dependence changes sign, are those from the ^{13}C hfs in the $(CD_3)_3{}^{13}C$ radical. However, it is clear that these numbers should be taken only as a guide because of their potential function dependence. When accurate vibrational frequencies become available for the *tert*-butyl radical via some other form of spectroscopy then one can make cross comparisons which will be very useful in establishing the limitations of this method.

There are several interesting features which have arisen out of this work. Firstly, the multiplication factor c, which converts INDO ^{13}C spin densities to hfs, is only ca. half the value used in the INDO[6] program of 820.1 G. This result is very similar to that of Beveridge and Miller[5a] who used 413.7 G to fit the ^{13}C hfs of methyl radical. This seems to confirm these author's contention that considerable discrepancies between calculated and observed values may result from neglecting vibrational averaging. This leads directly to the second point; namely that the ^{13}C hfs of a rigid, planar *tert*-butyl should be ~16 G and that of a rigid, planar methyl radical should be ~23 G. Thus it is clear that the present parameterization of ^{13}C hfs in the INDO[6] program is considerably in error. Thirdly, the geometry of the *tert*-butyl radical cannot be specified as being so many degrees nonplanar, as is implied by use of the hybridization method;[4] instead it is a very nonrigid structure which at any normal temperature is undergoing a very wide-ranging vibration, although it does have a measurable barrier to inversion.

Recent photoelectron spectroscopy results by Koenig et al.[8] on the *tert*-butyl radical also indicate its nonplanar equilibrium geometry. In addition, Krusic and Meakin[9] have obtained much the same results as we have found by a similar but independent treatment of the temperature dependence of the *tert*-butyl radical hfs.

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Barrier to Pyramidal Inversion in the *tert*-Butyl Radical by Electron Spin Resonance

Sir:

The pyramidal structure of the *tert*-butyl radical, cogently proposed by Wood Sprecher, and collaborators,[1] has not yet gained wide acceptance.[2] Additional evidence for the substantial deviation from planarity in this radical has been obtained very recently from its photoelectron spectrum.[3] The nonplanar structure of the *tert*-butyl radical has important chemical implications since it implies that β-halo-*tert*-butyl and related radicals may also be nonplanar.[4] In that case, the stereoselectivity observed in the reactions of these radicals need not be the result of halogen bridging,[5] a concept made necessary by the notion of simple alkyl radicals as planar species, but a natural consequence of rotational isomerism in a bent radical structure.[6]

The ESR arguments for the nonplanarity of the *tert*-butyl radical rest mostly on the large magnitude of the tertiary ^{13}C coupling constant (49.5 G at −182° vs. 38.3 G[7] for methyl at −177°)[8] and its *negative temperature coefficient* which decreases in magnitude with increasing temperature with indications of a minimum at about 0°.[1] We wish to present a quantum mechanical and classical vibrational analysis which explains this unusual temperature dependence and leads to an essentially tetrahedral equilibrium geometry and a barrier to inversion of about 600 cal/mol for this radical.[9] The classical theory leads to a simple equation from which approximate values for inversion barriers can be estimated. We also report solution ESR measurements of the primary-^{13}C coupling in the *tert*-butyl radical.

The ESR spectrum of the *tert*-butyl radical was obtained by photolysis of a cyclopropane solution containing tri-*tert*-butylphosphine and di-*tert*-butyl peroxide[10] (a(H) = 22.78 G at −100°). Because of signal strength limitations, only the methyl ^{13}C coupling could be measured without isotopic enrichment ($|a(^{13}C_p)|$ = 12.44 G at −100°).[11] This coupling should be negative (spin polarization) and should display a negative temperature coefficient for its absolute value (cf. $d|a(H)|/dT$ for methyl[12]). Instead, a *positive* coefficient was observed of 6 mG/°C at −100°. The anomalous temperature coefficient for the tertiary ^{13}C splitting in Wood's work is thus paralleled by a temperature coefficient of anomalous sign for the primary ^{13}C splitting.

The temperature dependence of the trigonal-^{13}C coupling constant and of the couplings to α atoms in alkyl radicals is caused primarily by the effects of out-of-plane vibrations at the radical center since these couplings are strongly depen-