

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, $\theta \sim 19^\circ$, 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.

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

The results of minimizations on the ^{13}C hfs of $(\text{CH}_3)_3^{13}\text{C}$ and $(\text{CD}_3)_3^{13}\text{C}$ and the ^1H hfs of $(\text{CH}_3)_3^{12}\text{C}$ and $(\text{CH}_3)_3^{13}\text{C}$ 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 $(\text{CD}_3)_3^{13}\text{C}$ 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 INDO⁶ 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 INDO⁶ 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 Meakin⁹ 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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John B. Lisle, Lawrence F. Williams, David Eldon Wood*

Department of Chemistry, University of Connecticut
Storrs, Connecticut 06268

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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 G⁷ 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 peroxide¹⁰ ($a(\text{H}) = 22.78$ G at -100°). Because of signal strength limitations, only the methyl ^{13}C coupling could be measured without isotopic enrichment ($|a(^{13}\text{C}_p)| = 12.44$ G at -100°).¹¹ This coupling should be negative (spin polarization) and should display a negative temperature coefficient for its absolute value (cf. $d|a(\text{H})|/dT$ for methyl¹²). Instead, a *positive* coefficient was observed of 6 mG/ $^\circ\text{C}$ 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-

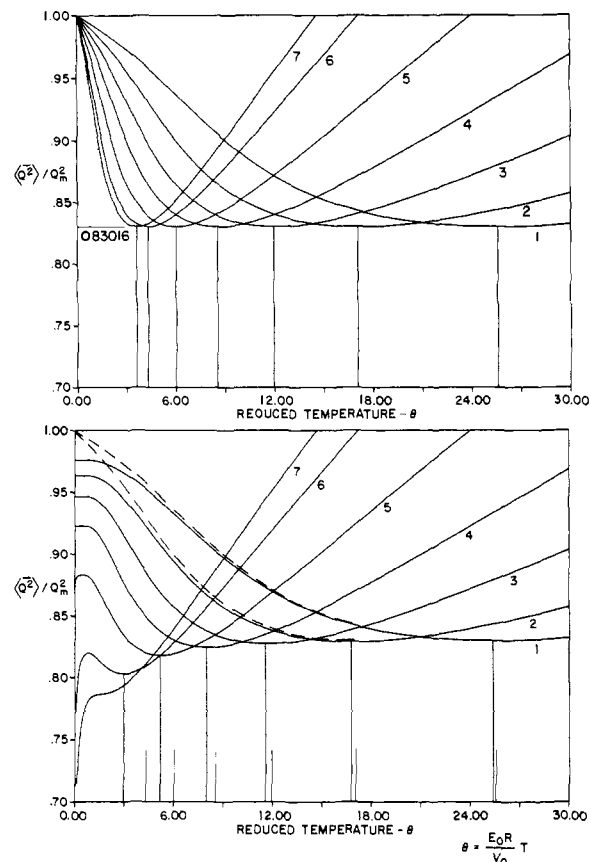


Figure 1. The quadratic coefficient $F_2(\theta, E_0)$ calculated in the classical approximation (top) and quantum mechanically (bottom) as a function of θ for $E_0 = 30, 20, 14, 10, 7, 5,$ and 4.25 (curves 1 through 7, respectively). The classical approximation (e.g., dashed curves for $E_0 = 30$ and 20) breaks down at low θ 's (zero-point effect) and at low E_0 's. θ_{\min} for each quantum-mechanical curve (marked by vertical lines) is less than the corresponding classical value (short vertical lines). The ratios $E_0 R / \theta_{\min}$ are: 2.330 (classical), 2.347 (1), 2.369 (2), 2.406 (3), 2.486 (4), 2.685 (5), and 3.346 (6) $\text{cal mol}^{-1} \text{deg}^{-1}$.

dent on the out-of-plane bending angle. For radicals with inversional symmetry, the angular dependence of these couplings can be expressed by an even-power expansion

$$a(\alpha) = a_0 + a_2\alpha^2 + a_4\alpha^4 + \dots \quad (1)$$

where α is the angle between the inversion plane and the internuclear direction from the central carbon to the α atom. Several authors have considered the vibrational and thermal averaging of $a(\alpha)$ for planar radicals in which the out-of-plane vibrations were assumed to be governed by a harmonic potential function.¹³ For inverting bent radicals, the treatment is conceptually analogous but it involves necessarily a double-minimum potential. We chose a potential of the form $V(q) = -aq^2 + bq^4$ ($a, b > 0$).¹⁴

The Hamiltonian for the out-of-plane vibrational mode

$$\mathcal{H}(q) = P_q^2/2\mu - aq^2 + bq^4 \quad (2)$$

can be converted to a dimensionless coordinate system by suitable linear transformations on the displacement coordinate and its conjugate momentum¹⁵ (transformation I, ref 15b). They yield the reduced Hamiltonian

$$\mathcal{H}(Q) = (\text{scale factor})[P_q^2 - Q^2 + BQ^4] \quad (3)$$

with a one-parameter potential function defined by either B or by the reduced barrier to inversion $E_0 = 1/4B$ or by the reduced coordinate at the two minima $Q_m = \pm(1/2B)^{1/2}$. In this Hamiltonian, the terms depending on the reduced mass and the vibrational frequency have been factored out.

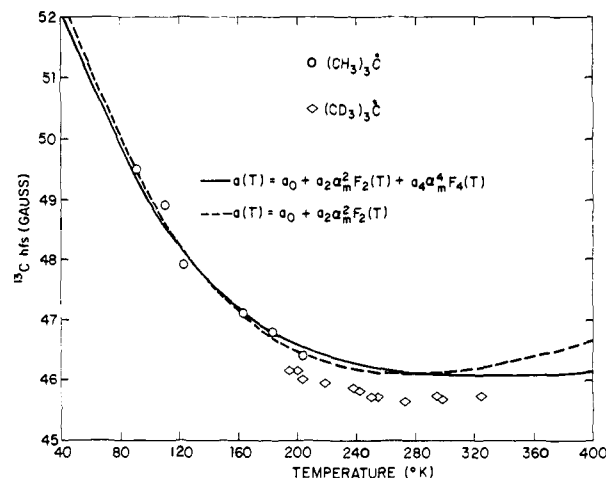


Figure 2. Experimental (from ref 1) and calculated temperature dependence of the trigonal- ^{13}C coupling for the $\text{C}(\text{CH}_3)_3$ radical. Only the points denoted by circles were used in the least-squares fitting.

The spatial and energy scale factors can be added to the calculations at the end.

The general procedure followed in our analysis involved the following steps: (a) The angular dependence of eq 1 was expressed in terms of the dimensionless coordinate Q with the substitution $\alpha = (\alpha_m/Q_m)Q$ where α_m determines the minima of the true potential function (equilibrium geometry):

$$a(Q) = a_0 + a_2\alpha_m^2 Q^2/Q_m^2 + a_4\alpha_m^4 Q^4/Q_m^4 + \dots \quad (4)$$

(b) The reduced Hamiltonian was solved¹⁶ for the reduced eigenvalues E_i and the expectation values $\langle Q^n \rangle_i$ ($n = 2, 4$) as a function of B (or E_0). (c) The thermal averages

$$\langle Q^n \rangle / Q_m^n = F_n(\theta, E_0) = \frac{\sum \langle Q^n \rangle_i \exp[-E_i/\theta]}{Q_m^n \sum \exp[-E_i/\theta]} \quad (5)$$

were calculated ($n = 2, 4$) as a function of the reduced barrier E_0 and the reduced temperature. The latter is related to the actual temperature by a scale factor, $\theta = (E_0 R / V_0)T$, where V_0 is the actual barrier to inversion. (d) The classical limits of eq 5 were obtained by replacing the summations with integrals, $\langle Q^n \rangle_i$ with Q^n , E_i with $-Q^2 + BQ^4$, and by numerical integration of the resulting integrals. (e) The functional forms of $a(T)$ can then be obtained in the quantum mechanical or classical formulations from

$$a(\theta) = a_0 + a_2\alpha_m^2 F_2(\theta, E_0) + a_4\alpha_m^4 F_4(\theta, E_0) + \dots \quad (6)$$

The resulting curves must, of course, be scaled in the direction of the temperature axis in accordance with the scale factor relating θ to T , i.e., $E_0 R / V_0$ for each case.

The classical calculations for the quadratic coefficient $F_2(\theta, E_0)$ show (Figure 1) that, if the angular dependence $a(\alpha)$ can be approximated by a parabola, the anomalous temperature coefficient of $a(T)$ follows as a natural consequence of the double-minimum potential. It is apparent that these curves differ from each other only by a scale factor. Furthermore, it can be shown numerically that

$$E_0 R / \theta_{\min} \approx V_0 / T_{\min} = 2.330 \text{ cal mol}^{-1} \text{deg}^{-1} \quad (7)$$

from which an estimate for the barrier to inversion can be obtained immediately if the temperature at which the coupling constant achieves its minimum is known. T_{\min} for the *tert*-butyl (Figure 2) is approximately 275 K corresponding to a barrier to inversion of 640 cal/mol (224 cm^{-1}) in this approximation.

The quantum mechanical curves of $F_2(\theta, E_0)$ (Figure 1) show that the classical approximation breaks down at low

temperatures (zero-point effect) and for low barriers to inversion. Curve 7 (two vibrational states below the barrier top) no longer displays a negative temperature coefficient.¹⁷ The latter is thus a *sufficient but not necessary* symptom of bent radical structure. The ratio of eq 7 is not constant and is greater than 2.330 which is approached asymptotically as E_0 increases. Our complete least-squares calculations indicate that reduced potentials with $E_0 \leq 10$ (curves 4 through 7) cannot be used to fit the experimental points for *tert*-butyl (Figure 2). In that case, the use of 2.330 rather than the appropriate quantum mechanical value involves an error of less than 3% justifying our further use of the classical approximation.

The simplest least-squares fitting (classical theory) involves the approximation of a quadratic $a(\alpha)$ ($V_0 = 640$ cal/mol) and $a(T) = a_0 + a_2\alpha_m^2 F_2(T)$ in which $F_2(T)$ can be easily calculated (Figure 1). The least-squares fit to Wood's data gives $a_0 = 8.8$ G and $a_2\alpha_m^2 = 44.9$ G (Figure 2). The resulting value of the ¹³C coupling for a nonvibrating planar *tert*-butyl (8.8 G) is low compared to the INDO calculations.¹⁸ The latter can be fitted for $0 \leq \alpha \leq 30^\circ$ with a root mean square deviation of 4 G by $a(\alpha) = 38.9 + 0.150\alpha^2 = 820.1 (0.0475 + 1.835 \times 10^{-4}\alpha^2) = A^C \rho^C(\alpha)$ (α in degrees). The second expression is obtained by extracting the empirical proportionality constant built into the INDO program¹⁹ ($A^C = 820.1$ G) relating the ¹³C coupling to the unpaired C 2s spin density. A comparison of the least-squares results with the INDO quadratic $\rho^C(\alpha)$ gives $A^C = 185$ G and $\alpha_m = 36^\circ$ in this approximation.

The INDO results indicate the importance of the *quartic* term since they can be fitted much better by $a(\alpha) = 34.0 + 0.211\alpha^2 - 8.846 \times 10^{-5}\alpha^4$ (root mean square (dev) = 0.7 G). Unfortunately, there are now too many parameters for a meaningful least-squares treatment. A systematic variation of V_0 and α_m using the INDO quartic $\rho^C(\alpha)$ followed by a least-squares determination of A^C indicates that reasonable root mean square deviations between theory and experiment can be obtained only for $450 \leq V_0 \leq 700$ cal/mol and $17^\circ \leq \alpha_m \leq 22^\circ$ leading to $375 \leq A^C \leq 489$ G ($15.6 \leq a_0 \leq 20.3$ G). The curve for $V_0 = 550$ cal/mol, $\alpha_m = 19.5^\circ$ (tetrahedral angle), and $A^C = 435$ G (Figure 2) shows that the effect of the quartic term is to make the minimum shallower and to move T_{\min} toward higher values. The discrepancy between our range for A^C and the INDO A^C is noteworthy and can no doubt be attributed to the neglect of zero-point effects, which can be appreciable even for shallow double-minimum potentials (Figure 1), in the INDO parametrization.¹⁹ The details of this study as well as further applications (e.g., the CF₃ radical) will be reported elsewhere.

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P. J. Krusic,* P. Meakin

Contribution No. 2309, Central Research and Development
Department, E. I. duPont de Nemours and Company
Wilmington, Delaware 19898
Received August 20, 1975

An Electron Spin Resonance Study of the Substituent Effects Causing Nonplanarity in Alkyl Radicals. Electronegativity vs. π -Conjugative Destabilization

Sir:

The geometries of simple organic radicals (CXYZ) are strongly substituent dependent. Thus, while the methyl radical is planar or nearly so,¹ the trifluoromethyl² and *tert*-butyl³ are pyramidal albeit with different barriers to inversion. Pauling⁴ has explained these structural variations in free radicals in terms of electronegativity concepts, noting that the s character of the singly occupied orbital on carbon, and hence the nonplanarity of the radical, should increase as the polarity of the C-X bond increases in the direction C⁺-X⁻. Recently, Bingham and Dewar⁵ have presented theoretical arguments which demonstrate that conjugative destabilization associated with the presence of two or three donor dominant substituents should also give rise to nonplanar geometries.^{5b} This latter proposal receives considerable support from the observation that two donor substituents induce pyramidal to a far greater extent than would be expected on the basis of the effect of one alone.⁶ We report now the ESR data for several radicals derived from fluoroacyl halides which, taken together with published results, clearly show that conjugative destabilization and not electronegativity is the primary electronic factor which gives rise to nonplanar radical structures.

Ultraviolet irradiation in the ESR cavity of dilute solu-