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## LETTERS

### Interpretation of $\beta$ -Hydrogen Hyperfine Splittings in the Electron Spin Resonance of the 3-Methyl-3-phenylbut-1-yl Radical<sup>1</sup>

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At low temperatures the  $PhCMe_2CH_2CH_2$  radical preferentially adopts a conformation in which the radical center and the phenyl substituent are gauche to each other when viewed along the  $C_{\beta}$ - $C_{\gamma}$  bond. The  $\beta$ -hydrogens are magnetically nonequivalent and the magnitudes of their hyperfine splitting represent an average over rotation about the  $C_{\alpha}$ - $C_{\beta}$  bond. On the basis of the equation  $a^{H_{\beta}} = 54 \langle \cos^2 \theta \rangle$  G, we have derived a simple, two-component rotational potential which supports the suggestion that there is a weak, attractive interaction between the singly occupied  $C_{\alpha} 2p_z$  orbital and the  $\pi$ -cloud of the phenyl substituent. The conformations of some related radicals are also discussed.

A recent report by Brumby<sup>3</sup> on preferred conformations and line broadening effects in the ESR spectra of primary alkyl and aralkyl radicals,  $R(CH_2)_n CH_2$  (R = Me, Ph;  $n \ge 1$ ), prompts us to present some novel results on a related series of aralkyl radicals, PhCMe<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>ĊH<sub>2</sub> ( $n \ge 1$ ).

At low temperatures PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> exists in both a gauche conformation,<sup>4</sup> 1, and a trans conformation,<sup>4</sup> 2, of which the



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 (2) (a) NRCC. (b) Strathclyde.
 (3) Brumby, S. J. Phys. Chem. 1983, 87, 1917-24.
 (4) Phenyl group vs. the CH<sub>2</sub> group.

preponderant conformer 1 has magnetically nonequivalent  $\beta$ hydrogens (see Figure 1 and Table I).<sup>5</sup> Both of these observations indicate that rotation about the  $C_{\beta}$ - $C_{\gamma}$  bond is slow on the ESR time scale at -117 °C. The barrier to this rotation is relatively high since there is still some broadening of the central lines of the triplets corresponding to the  $\beta$ -H splitting even at 25 °C, although the spectrum tends toward the triplet of triplets expected for free rotation (see Figure 1). For comparison, this type of behavior has been observed for the n-butyl radical at much lower temperature.<sup>3,6-9</sup> The preference for conformation 1 may be rationalized on steric or electronic grounds. Steric effects may favor this conformation because the effective bulk of a phenyl group is probably less than that of a methyl group. We believe

- (7) Kochi, J. K.; Krusic, P. J. J. Am. Chem. Soc. 1969, 91, 3940-2.
   (8) Krusic, P. J.; Kochi, J. K. J. Am. Chem. Soc. 1971, 93, 846-60.

<sup>(5)</sup> We are aware of only one other nonconjugated radical which has been reported to exist in two conformations, namely, CF<sub>3</sub>(Me<sub>3</sub>Si)CCH(SiMe<sub>3</sub>)CF<sub>3</sub>, see: Griller, D; Cooper, J. W.; Ingold, K. U. J. Am. Chem. Soc. **1975**, 97, 4269-75.

<sup>(6)</sup> Kochi, J. K. Adv. Free Radical Chem. 1974, 5, 189-317.

<sup>(9)</sup> Edge, D. J.; Kochi, J. K. J. Am. Chem. Soc. 1972, 94, 7695-702.



Figure 1. ESR spectra for PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> at -117, -30, and 25 °C in cyclopropane. Peaks due to 2 are marked by ×.

that there is also a weak attractive interaction between the singly occupied  $C_{\alpha} 2p_z$  orbital and the  $\pi$ -cloud of the proximate phenyl substituent. Such interactions have been suggested previously for

PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>ĊH<sub>2</sub> and PhC(CH<sub>2</sub>ĊH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>ĊH<sub>2</sub> (with support from INDO MO calculations),<sup>3</sup> and for PhCH<sub>2</sub>GèMe<sub>2</sub>.<sup>10</sup> The magnitudes of the  $\beta$ -H hyperfine splittings (hfs) in conformation 1 support our opinion.

In RCH<sub>2</sub>CH<sub>2</sub> radicals, the  $\beta$ -H hfs,  $a^{H_{\beta}}$ , is related to the dihedral angle,  $\theta$ , between the C<sub> $\beta$ </sub>-H bond and the axis of the singly occupied C<sub> $\alpha$ </sub> 2p<sub>z</sub> orbital by the equation

$$a^{\mathbf{H}_{\beta}} = A + B \cos^2 \theta \tag{1}$$

where A and B are constants ( $A \approx 3 \pm 2$  G,  $B \approx 49 \pm 5$  G).<sup>11</sup>

(10) Mochida, K.; Kira, M.; Sakurai, H. Chem. Lett. 1981, 645-8.

The value of  $a^{H_{\theta}}$  which is observed experimentally is, however, an average over quantum states and corresponds to an average value of  $\cos^2 \theta$ , denoted  $\langle \cos^2 \theta \rangle$ .<sup>12</sup> In the light of such averaging, it is not possible to use eq 1 to compute a physically meaningful value for  $\theta$  from the measured hfs.<sup>13</sup> Moreover,  $\langle \cos^2 \theta \rangle$  cannot be equated with  $\cos^2 \langle \theta \rangle$ , where  $\langle \theta \rangle$  is an average dihedral angle, were it hoped that  $\langle \theta \rangle$  might describe a physical structure.<sup>13</sup> Instead the derived quantity  $\langle \cos^2 \theta \rangle$  should be compared with values calculated by averaging  $\cos^2 \theta$  over the internal rotation about the  $C_{\alpha}-C_{\beta}$  bond.

For primary alkyl radicals it is usually assumed<sup>6,11</sup> that A is 0 and B is equal to twice the  $\beta$ -H hfs in CH<sub>3</sub>CH<sub>2</sub>,<sup>14</sup> namely, 2  $\times$  26.87  $\approx$  54 G. We write

$$a^{H_a} = B \langle \cos^2 \theta_a \rangle \tag{2}$$

$$a^{\mathrm{H}_{\mathrm{b}}} = B \langle \cos^2 \left( \theta_{\mathrm{a}} - 120^{\circ} \right) \rangle \tag{3}$$

or

$$a^{H_b} = B\left(\frac{3}{4} - \frac{1}{2}\langle\cos^2\theta_a\rangle - \frac{3^{1/2}}{4}\langle\sin 2\theta_a\rangle\right) \qquad (4)$$

by making use of trigonometric identities. For PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> in conformation 1 at -117 °C,  $a^{H_a} = 19.15$  G,  $a^{H_b} = 34.25$  G, <sup>15</sup> and eq 2 and 4 yield  $\langle \cos^2 \theta_a \rangle = 0.35_5$  and  $\langle \sin 2\theta_a \rangle = -0.14_3$ .

We must now introduce a trial potential and perform averaging over  $\cos^2 \theta$  and  $\sin 2\theta$ . In the simplest case, the preference for staggering the C<sub> $\alpha$ </sub>-H and C<sub> $\beta$ </sub>-H bonds is described by a sixfold potential

$$V(\phi) = V_6 \sin^2 3\phi \tag{5}$$

where  $\phi$  is the dihedral angle between the C<sub> $\beta$ </sub>-CMe<sub>2</sub>Ph bond and the axis of the singly occupied C<sub> $\alpha$ </sub> 2p<sub>z</sub> orbital (see 3 which has



been drawn for  $\phi = 60^{\circ}$ ). (Of course, because there are two  $C_{\beta}H$  bonds and one  $C_{\beta}$ -CMe<sub>2</sub>Ph bond, this component is not strictly sixfold.) Equation 5 cannot account for the observed hfs by itself because it leads to equivalent  $\beta$ -H's. In conformation 1 the phenyl group is not symmetrically disposed relative to the  $\beta$ -H's; it lies gauche to H<sub>a</sub> and trans to H<sub>b</sub>. Therefore, we introduce an additional twofold component in  $V(\phi)$ :

$$V(\phi) = V_2 \sin^2(\phi - \Psi) + V_6 \sin^2 3\phi$$
(6)

where  $\Psi$  is an adjustable phase angle which determines the position of the minimum for this component. Rather than average  $\cos^2 \theta$  and  $\sin 2\theta$  over each rotational state and then calculate an ensemble average of these values with Boltzmann weighting, we perform the classical average, which is sufficient for our purposes, namely

$$\begin{cases} \cos^2 \theta \rangle = \\ \int_0^{360} \cos^2 \left( \phi - 120^{\circ} \right) \exp\left[-\beta V(\phi)\right] d\phi / \int_0^{360} \exp\left[-\beta V(\phi)\right] d\phi$$
(7)

(11) (a) Ayscough, P. B. "Electron Spin Resonance in Chemistry"; Methuen: London, 1967. (b) Fischer, H. In "Free Radicals"; Kochi, J. K. Ed.; Wiley: New York, 1973; Vol II, Chapter 19.

(12) Stone, E. W.; Maki, A. H. J. Chem. Phys. 1962, 37, 1326-33.

(13) This restriction has frequently been overlooked and specific structures have been assigned to radicals containing one or two  $\beta$ -atoms on the basis of their  $a^{H\beta}$  values.

(14) In CH<sub>3</sub>ĊH<sub>2</sub> rotation about the  $C_{\alpha}$ - $C_{\beta}$  bond is essentially free so  $\langle \cos^2 \theta \rangle = \frac{1}{2}$ .

(15) A naive interpretation of these two  $\beta$ -H hfs via eq 1 leads to the impossible result that  $\theta_a = 53^{\circ}$  and  $\theta_b = 37^{\circ}$  with a consequent dihedral angle between the two  $\beta$ -H's of 90° rather than the necessary 120°.

R	temp, °C	<i>a</i> <sup>H</sup> <sub>α</sub> (2 H)	$a^{\mathrm{H}_{\beta}}(2 \mathrm{H})^{b}$	$a^{H_{\gamma}}$	ref
PhCMe <sub>2</sub>	-117	21.90 <sup>c</sup>	19.15 (1 H), <sup>c</sup> 34.25 (1 H) <sup>c</sup>		this work
	-117	21.75 <sup>d</sup>	22.75 <sup>d</sup>		this work
	25	21.88	24.80		this work
$PhCMe_2CH_2$	-113	21.92	28.60	0.70	this work
$PhCMe_2CH_2CH_2$	-113	21.85	29.50	<b>Q.8</b> 1	this work
$PhC(CH_2CH_2)$	-140	22.2	23.6 (1 H), 34.0 (1 H)		17
<u> </u>	-40	22.2	27.0		17
$PhC(CH_2CH_2)CH_2$	-120	22.1	28.3 (1 H), 30.5 (1 H)	1.0	17
	-40	22.4	28.5		17
PhCHMe	-117	22.1	27.95 <sup>e</sup>	0.9	this work
	-20	21.9	24.4 (1 H), 29.1 (1 H)	1.0	this work
PhCH <sub>2</sub>	-93	22.11	28.65	0.71	this work
PhCH <sub>2</sub> CH <sub>2</sub> <sup>f</sup>	-110	22.18	29.04	0.69	this work

TABLE I: ESR Hyperfine Splittings Constants for Some RCH<sub>2</sub>CH<sub>2</sub> Radicals<sup>a</sup>

<sup>*a*</sup>Hfs are given in Gauss. Radicals prepared in this work were generated by UV photolysis of mixtures of the appropriate bromide, triethylsilane, and di-*tert*-butyl peroxide in cyclopropane as solvent (see ref 23). <sup>*b*</sup>Unless otherwise noted. <sup>*c*</sup>Conformation 1. <sup>*d*</sup>Conformation 2. <sup>*e*</sup>Average value for the two  $\beta$ -H's. Spectrum resembles that of PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> at -30° (see Figure 1) and so barrier to rotation about C<sub> $\beta$ </sub>-C<sub> $\gamma$ </sub> bond is lower in PhCHMeCH<sub>2</sub>CH<sub>2</sub> than in PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, as expected. At higher temperatures the spectrum becomes complicated by the diastereotopic character of the  $\beta$ -H's. <sup>*f*</sup>Included for comparison. For other data on this radical, see ref 3, 7, and 9.



Figure 2. ESR spectra at -113 °C in cyclopropane of PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(A) and of PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(B).

where  $\theta = \phi - 120^{\circ}$  and  $\beta = (k_{\rm B}T)^{-1}$ . (sin  $2\theta$ ) is obtained in the same way. The calculated and measured values of these averages match for  $V_2 = 1.9 \pm 0.1$  kJ mol<sup>-1</sup>,  $V_6 = 4.5 \pm 2.0$  kJ mol<sup>-1</sup>, and  $\Psi = 40 \pm 5^{\circ}$ . The absolute minima of the rotational potential then occur at  $\phi = 60^{\circ}$  and 240°. There are relative minima at  $\phi = 0^{\circ}$  (180°) and 120° (300°) that are 0.6 and 1.6 kJ mol<sup>-1</sup>, respectively, above the absolute minima. There is some correlation between  $V_2$ ,  $V_6$ , and  $\Psi$ , but the available data do not allow a more precise analysis. The values of  $V_2$  and  $V_6$  appear to be reasonable in magnitude. A minimum energy conformation in which the axis

of the singly occupied  $C_{\alpha} 2p_z$  orbital nearly eclipses the  $C_{\beta}H_b$  bond has been proposed for *n*-butyl radicals trapped in an argon matrix at 4 K ( $\phi = 66.8^{\circ}$ ),<sup>16</sup> but INDO MO calculations place the minimum energy conformation at 18°.<sup>3</sup> We propose that the twofold component in eq 6 corresponds to an attractive interaction between the unpaired electron and the  $\pi$ -cloud of the phenyl substituent. A similar, albeit weaker, interaction could conceivably

<sup>(16)</sup> Adrian, F. J.; Bowers, V. A.; Cochran, E. L. J. Chem. Phys. 1975, 63, 919-23.

occur with the methyl group orbitals in *n*-butyl.

Two structurally related radicals, PhC(CH<sub>2</sub>CH<sub>2</sub>)CH<sub>2</sub>ĊH<sub>2</sub> and

PhC(CH<sub>2</sub>CH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, have been reported by Doyle et al.<sup>17</sup> to have inequivalent  $\beta$ -H hfs at low temperatures and so must adopt gauche conformations<sup>18</sup> analogous to **1**. Clearly, a similar attractive interaction should be present in both these radicals and, indeed, such an interaction has been suggested for the latter compound on the basis of INDO MO calculations.<sup>3</sup> Surprisingly, our analogue of Doyle et al.'s<sup>17</sup>  $\epsilon$ -phenyl-substituted radical, i.e., PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, has equivalent  $\beta$ -H's at all temperatures, as does the next member in our series, PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (see Table I). Line broadening in PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> is slight<sup>19</sup> even at -113 °C (see Figure 2). We suggest that the differences

between PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and PhC(CH<sub>2</sub>CH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> relate to the bulk of the group attached to  $C_{\gamma}$ , the PhCMe<sub>2</sub> group being the larger. This view is supported by the observation that the barrier to rotation about the  $C_{\beta}$ - $C_{\gamma}$  bond is lower, as judged from the temperatures at which line broadening occurs, in Ph

#### A Theory of Chemical Kinetics

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The chemical kinetics of the simple first-order reversible reaction  $A \rightleftharpoons B$  is considered by assuming many intermediate states between the reactant A and the product B. An Arrhenius type of relation for rate constants is obtained with a full account of the dynamics by comparing the phenomenological rate equations to a set of equations arising from the Smoluchowski equation. Also, it is shown that the Smoluchowski equation with an arbitrary force field can be put into a set of rate equations for the successive first-order reversible reaction.

The kinetics of the first-order successive reversible reactions

$$A_1 \xrightarrow[k_1]{k_1} A_2 \xrightarrow[k_2]{k_2} \dots \xrightarrow[k_{n-1}]{k_{n-1}} A_n \qquad (I)$$

where  $A_i$  (i = 1, 2, 3, ..., n) is a chemical species, and  $k_i$  and  $k'_i$  are the rate constants for the forward and backward reactions, respectively, is written by the phenomenological rate equations

$$d(a_1(t))/dt = -k_1a_1(t) + k'_1a_2(t)$$

$$d(a_j(t))/dt = -(k'_{j-1} + k_j)a_j(t) + k_{j-1}a_{j-1}(t) + k'_ja_{j+1}(t)$$
(1)

$$d(a_n(t))/dt = -k'_{n-1}a_n(t) + k_{n-1}a_{n-1}(t)$$

where  $a_j(t)$  is the concentration of  $A_j$  at the time t. The above chemical reaction describes how the starting chemical species  $A_1$ = A may become the final product  $A_n$  = B through the intermediate species  $A_j$  (j = 2, 3, 4, ..., n - 1). Hence this reaction scheme can be used for considering the diffusion phenomena. In fact, it is well-known that, for an irreversible reaction where  $k_i$ = k and  $k'_i = 0$ , the requirement of the initial condition of  $a_i(0)$   $\dot{C}(CH_2\dot{C}H_2)CH_2\dot{C}H_2$  than in PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>. That is, for steric reasons the PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> radical prefers a trans conformation<sup>20</sup> analogous to **2**,<sup>21</sup> whereas PhC(CH<sub>2</sub>CH<sub>2</sub>)-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (and PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) adopt gauche conformations<sup>22</sup> analogous to **1**.<sup>3</sup>

In summary, from an analysis of the measured  $\beta$ -H hfs in conformation 1 of PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, we have obtained a simple potential for internal rotation about the C<sub> $\alpha$ </sub>-C<sub> $\beta$ </sub> bond. This potential is comprised of a sixfold component, which corresponds to the interaction between C<sub> $\alpha$ </sub>-H and C<sub> $\beta$ </sub>-H bonds, and a twofold component, which represents the interaction between the singly occupied C<sub> $\alpha$ </sub> 2p<sub>2</sub> orbital and the  $\pi$ -cloud of the phenyl substituent. Similar interactions probably occur in the analogous conformations of other  $\omega$ -substituted primary alkyl radicals if C<sub> $\alpha$ </sub> and the  $\pi$ -cloud are proximate.

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 $= a^{(0)} \delta_{1,i}$ , where  $\delta_{i,j}$  is the Kroneker  $\delta$ , leads to  $a_i(t)/a^{(0)}$  as given by the Poisson distribution which is often used in the statistical treatment. In considering the diffusion phenomena, we often use the Smoluchowski equation

$$\frac{\partial w}{\partial t} = D \frac{\partial}{\partial x} \left[ \frac{\partial w}{\partial x} - f(x) w \right]$$
(2)

where w(x,t) is a distribution function, D is the diffusion constant, x is the position of a Brownian particle, and  $f(x) = F(x)/k_{\rm B}T$ where F(x) is the mechanical force relating to the potential energy function V(x) by the equation

$$F(x) = -d(V(x))/dx$$
(3)

 $k_{\rm B}$  is the Boltzmann constant and T is the absolute temperature. The first term on the right of eq 2 arises from the random motion of the particle due to collisions by the surrounding molecules and the second from a force field f(x). On putting  $(\partial w/\partial t) = 0$  in eq 2, we find the Maxwell-Boltzmann distribution function

$$w^{(eq)} = N \exp\left[-\frac{V(x)}{k_{\rm B}T}\right] \tag{4}$$

<sup>(17)</sup> Doyle, M. P.; Raynolds, P. W.; Barents, R. A.; Bade, T. R.; Danen, W. C.; West, C. T. J. Am. Chem. Soc. 1973, 95, 5988-6000.

<sup>(18)</sup> Ph group or Ph $C(CH_2CH_2)$  group vs. the  $\dot{C}H_2$  group.

<sup>(20)</sup>  $PhCMe_2CH_2$  group vs. the  $CH_2$  group.

<sup>(21)</sup>  $Me_3CCH_2CH_2CH_2$  also adopts a trans conformation.<sup>3</sup>

 <sup>(22)</sup> PhC(CH<sub>2</sub>CH<sub>2</sub>)CH<sub>2</sub> group or PhCH<sub>2</sub>CH<sub>2</sub> group vs. the CH<sub>2</sub> group.
 (23) Hudson, A.; Jackson, R. A. J. Chem. Soc., Chem., Commun. 1969, 1323-4.