J. Phys. Chem. A **2004,** *108,* 7591−7595

Dependence of α-Proton Hyperfine Couplings on Free Radical Geometry

Paul A. Erling and William H. Nelson*

Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303

Received: April 23, 2004; In Final Form: June 22, 2004

The α-proton hyperfine coupling is a major source of information useful for identifying the chemical and physical structure of free radicals. Use of the isotropic component for estimating spin distributions has been particularly widespread. However, the proportionality between the measured isotropic component and the unpaired spin is known to depend on radical geometry. Using DFT-based computational methods, this work explores the geometry dependence with the model structure $^{\bullet}C_{\alpha}H_{\alpha}(R1)(R2)$, where R1 and R2 are all combinations of H, Me, COOH, NH_2, and OH. Results indicate that symmetrical bending of all bonds to C_{α} from planar to tetrahedral geometries (1) leads to a change in the isotropic component, dependent on the identity of R1 and R2, which can exceed 200%, (2) leads to very small change in the most-positive dipolar component (less than 6%), and (3) preserves the property that the vector associated with the most-positive dipolar component indicates the direction of the $C_{\alpha}H_{\alpha}$ bond (within 6° or less). Other geometrical features, associated with possible constraints from surrounding molecules, also affect the isotropic coupling and emphasize the need to account for the surroundings when computing optimized structures.

Introduction

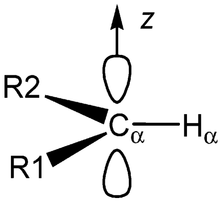
Hyperfine couplings from magnetic resonance spectroscopy are a major source of information useful for identifying the chemical and physical structure of free radicals. The basic idea is that structural characteristics determine the distribution of unpaired spin in radicals; in turn, the spin distribution determines the observable magnetic resonance spectrum. It is important, therefore, to have a reliable, quantitative description of radicals that provides the connection between the molecular structure and the observable hyperfine interactions. Early in the history of using EPR spectroscopy to study organic radicals, a high level of experimental and theoretical activity was undertaken with the goal of meeting this need. A key result of this activity was the description of the α-proton hyperfine interaction, that between unpaired spin centered on a carbon atom and the nucleus of a hydrogen atom bonded directly to the carbon (Scheme 1). Largely through the theoretical efforts of McConnell and co-workers, it was recognized that the isotropic component of the α-coupling is roughly proportional to the unpaired spin on the carbon[1] and that the most positive dipolar component of the coupling was parallel with the CH bond.[2]

For free radicals in solution, rapid tumbling averages the dipolar component to zero so that only the isotropic component of the coupling is observable. Since one of the most flexible methods for producing radicals of known structure is to use solutions, a large set of studies for validating and using the McConnell relationships focused on the isotropic relation, usually referred to as the "McConnell relation", shown as eq 1:

$$a_{\alpha,\mathrm{iso}} = Q^{\alpha}_{\mathrm{iso}}\rho_{\pi} \tag{1}$$

In the equation, Q_{iso} is a "constant" and ρ_{π} is the unpaired spin localized on the carbon in the molecular π-orbital. Since it was also recognized early on that "Q" is not truly a constant, much effort was spent in learning the range of values for Q and in detecting systematic molecular characteristics which might provide predictable Q values. Fessenden and Schuler[3] reported a comprehensive set of measurements from which the values and concepts became essentially the standard for applying the McConnell relation in analytical problems. In their work with methyl radicals ($^{\bullet}CH_3$), where ρ_{π} was taken to be 1.0, the measurement of $a_{\mathrm{iso}} = -23.0$ G indicated $Q_{\mathrm{iso}} = -23.0$ G (or -64.5 MHz).

SCHEME 1. Standard $\bullet C_{\alpha}H_{\alpha}$ Fragment



It was also recognized that the theoretical development of the McConnell relation was built on the case where the bonding system of the central carbon was planar, while there was no reason to expect planarity in all cases. In this connection, Dobbs et al.[4,5] reported a systematic set of measurements, coupled with a geometry-based analysis using ^{13}C couplings, aimed at describing the way in which α-proton couplings depended on nonplanarity, or bending, at the center of spin. A qualitative result of their work is that nonplanarity at C_{α} can produce a severe effect on the isotropic coupling: for example, for the methyl radical as reported above, $a_{\alpha,\mathrm{iso}} = -23.0$ G; for the difluoromethyl radical ($^{\bullet}CHF_2$), in which ^{13}C couplings indicate a significantly bent C_{α} bonding system, $a_{\alpha,\mathrm{iso}} = +22.2$ G,[6] a difference of ~200%.

For radicals trapped in solids, particularly those in single crystals, it is possible to measure both the isotropic and dipolar components of the hyperfine interaction. Moreover, single-crystal methods have been very important to studies focused on identifying damage to molecules by ionizing radiation. From

---

* Corresponding author: Ph 404-651-2708; Fax 404-651-1427; e-mail wnelson@gsu.edu.

10.1021/jp0482159 CCC: $27.50

this background, Bernhard[7] developed an idea initially due to Gordy,[8] that the dipolar component of the α-coupling is much less sensitive to bending than the isotropic component. On the basis of Gordy's simplified two-center model for the orbital of the unpaired electron, Bernhard proposed a McConnell-like relation between ρ_π and the positive component of the dipolar coupling as shown in eq 2. On the basis of an analysis of experimental data, Bernhard proposed the value 38.7 MHz for Q_{dip}. Thus, couplings where "ρ_π" values computed from eqs 1 and 2 are significantly different indicate bending at the center of spin.[9]

$$b_{+,\mathrm{dip}} = Q^{\mathrm{H}}_{\alpha,\mathrm{dip}}\rho_\pi \qquad (2)$$

In principle, it is possible to compute hyperfine couplings directly from the molecular structure. Successful computation of isotropic values imposes two requirements onto the computations: (a) an accurate representation of the radical geometry and (b) a high-quality basis set of orbitals. In fact, one "figure of merit" for modern computational methods is their success in accurately computing isotropic hyperfine couplings, typically that of the methyl radical. With the rapid advancement of computational methods, efforts to compute accurate hyperfine couplings from geometry-optimized radical structures have appeared frequently.[10]

Reasons for the increased interest in computation of hyperfine couplings are that current quantum-chemistry program suites not only provide reasonable results for isotropic hyperfine values but also compute the anisotropic values and relate their characteristic directions to the molecular framework. These computations have the benefit that they directly connect the radical structure with the observable hyperfine couplings. Consequently, it is no longer necessary—in principle—to use spin distributions to connect structures with observable hyperfine couplings.

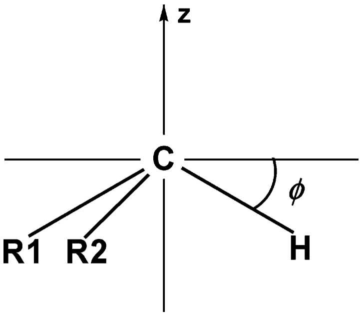
It is important to note, however, that a straightforward geometry optimization finds the lowest-energy conformation for an isolated molecule. However, particularly for radicals trapped in solids, interactions with their neighbors can prevent the radicals from taking on the optimum gas-phase structure. Consequently, in some cases, the geometry dependence of isotropic couplings has reappeared as an issue.[11]

Therefore, we decided on a systematic set of computations aimed at characterizing the main geometry dependencies of the α-proton hyperfine interaction. Our goal was to examine in more detail the geometry dependence of the α-proton hyperfine coupling characteristics: the value of the isotropic coupling, the value of the most-positive dipolar component, and the correlation between the direction of the $C_\alpha H_\alpha$ bond and the vector associated with the most-positive dipolar component. In essence, the objective is to revisit the McConnell−Chesnut,[1] McConnell−Strathdee,[2] Dobbs et al.,[4,5] and Gordy−Bernhard[7,8] efforts making use of the more sophisticated computational methods now available to explore the effect of nonplanarity on α-coupling properties.

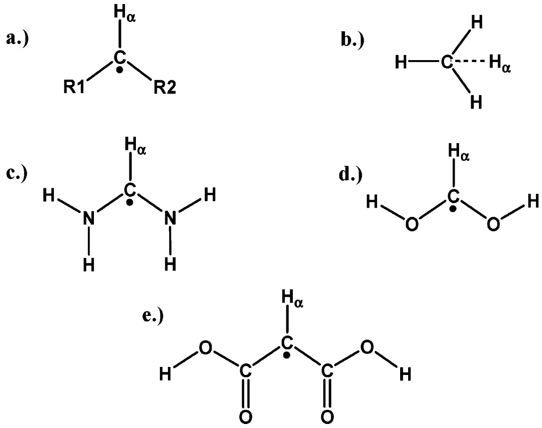
Methods

To explore the geometry dependence of the α-proton interaction, we chose the methyl-like structure $^{\bullet}C_\alpha H_\alpha(R1)(R2)$, where R1 and R2 were all combinations of the groups H, Me, COOH, NH_2, and OH—for a total of 15 different versions. Hyperfine couplings were calculated for each version with the three bonds to C_α bent equally from the horizontal as indicated by the bending angle ϕ in Scheme 2. This bending, like that of an umbrella as it folds, describes the planar and tetrahedral cases when $\phi = 0°$ and $\phi = 19.5°$, respectively. (We note that the bond angles $R1C_\alpha R2$, etc., are different for each value of ϕ in this mode of bending.)

SCHEME 2. Schematic Diagram Defining the Umbrella Angle ϕ



SCHEME 3. Schematic of the Planar Case (Umbrella Angle $\phi = 0$) Showing (a) the Generalized Methyl-like Structure, (b) the Conformation of Protons in the Methyl Groups Relative to the $\bullet C_\alpha H_\alpha(C1)(C2)$ Plane, and (c)−(e) Conformations Used for the OH, NH_2, and COOH Groups[a]



[a] For $\phi = 0$, all atoms in structures (c)−(e) were coplanar.

Since our goal was to examine hyperfine couplings in artificially bent structures, the actual structures were not geometry-optimized. Rather, to create reasonable structures, we used typical values for the respective bond angles (120° for $R1C_\alpha R2$, etc., in the planar structure), and we used bond lengths based on previous optimizations for radicals: $C_\alpha H_\alpha$, 1.09 Å; $C_\alpha C_{\mathrm{Me}}$, 1.48 Å; $C_\alpha C_{\mathrm{carboxyl}}$, 1.45 Å; $C_\alpha O_{\mathrm{hydroxyl}}$, 1.36 Å; $C_\alpha N_{\mathrm{amino}}$, 1.39 Å; $C{=}O_{\mathrm{carboxyl}}$, 1.22 Å; $C{-}O_{\mathrm{carboxyl}}$, 1.36 Å. In addition, we chose conformations of the R1 and R2 groups for the planar geometry as shown in Scheme 3. Except for the hydrogens of methyl groups, all atoms were coplanar in these structures; the methyl conformation was chosen as indicated in Scheme 3b. These choices create a symmetric arrangement of all atoms relative to the $C_\alpha H_\alpha$ bond for the planar structure when R1 = R2. (We note that these conformations may not correspond to actual structures found experimentally. In particular, the case where R1 = R2 = COOH is the well-known radical from malonic acid crystals,[12] and the two COOH's are probably perpendicular to each other in that case.[13])

Because of the nonoptimized character of the structures, we have not shown the actual computed hyperfine coupling values since they could only approximate the experimental values. Instead, we have presented the results as values relative to those of the corresponding planar structures; this presentation most

TABLE 1: Gaussian-Reported Total Atomic Spin Distributions for the Indicated (R1)(R2) Structures in Planar ($\phi = 0°$) and Near-Tetrahedral ($\phi = 20°$) Geometries[a]

(R1)(R2)	(H)(H)		(H)(Me)		(H)(COOH)		(H)(OH)		(H)(NH_2)	
	0°	20°	0°	20°	0°	20°	0°	20°	0°	20°
C_α	1.074	1.036	1.007	0.975	0.885	0.901	0.876	0.817	0.801	0.740
R1	−0.025	−0.012	−0.020	−0.020	−0.023	−0.061	−0.014	0.009	−0.011	0.005
R2	−0.025	−0.012	−0.039	−0.008	−0.062	−0.014	0.150	0.173	0.222	0.254

(R1)(R2)	(Me)(Me)		(Me)(COOH)		(Me)(OH)		(Me)(NH_2)		(COOH)(COOH)	
	0°	20°	0°	20°	0°	20°	0°	20°	0°	20°
C_α	0.927	0.906	0.808	0.838	0.844	0.800	0.768	0.719	0.768	0.808
R1	−0.039	−0.022	−0.024	−0.015	−0.041	−0.009	−0.038	−0.013	−0.073	−0.063
R2	−0.039	−0.022	−0.038	−0.034	0.136	0.151	0.209	0.231	−0.073	−0.063

(R1)(R2)	(COOH)(OH)		(COOH)(NH_2)		(OH)(OH)		(OH)(NH_2)		(NH_2)(NH_2)	
	0°	20°	0°	20°	0°	20°	0°	20°	0°	20°
C_α	0.643	0.674	0.535	0.554	0.797	0.731	0.744	0.681	0.722	0.659
R1	0.014	0.003	0.034	0.028	0.105	0.113	0.086	0.091	0.126	0.140
R2	0.163	0.205	0.256	0.322	0.105	0.113	0.160	0.178	0.126	0.140

[a] The values for R1 and R2 are those reported for the atoms directly bonded to C_α. (Although the values include a small amount of s-orbital spin, the 0° vs 20° comparison provides a reasonable indication of any redistribution due to bending.)

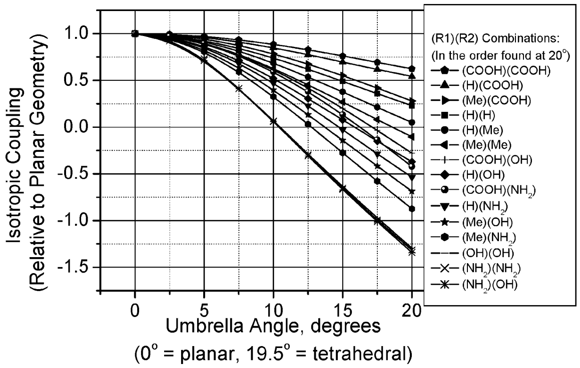


Figure 1. Variation of $a_{\alpha,\mathrm{iso}}$ for bending the ${}^\bullet C_\alpha H_\alpha$(R1)(R2) systems from planar to tetrahedral geometries (in 2.5° steps). Note the near congruency of the curves for the systems with R1 and R2 all versions of OH and NH_2; note also the change of approximately 225% in $a_{\alpha,\mathrm{iso}}$ for these systems.

clearly shows how the α-coupling properties vary as the structure folds. All computations listed below were performed using DFT capabilities in the Gaussian suite of programs with the B3LYP functional and the 6-311G(2df,3p) basis.[14] On the basis of other studies, this functional appears to give results in good correspondence with experiment. Also, the reasonably high-level basis set minimizes errors which might arise from a too-restricted version.

Results and Discussion

Effect of Umbrella-like Bending at C_α. *Isotropic Coupling.* Figure 1 shows the dependence of the H_α isotropic coupling on the umbrella angle. Particularly obvious is the high degree to which the coupling changes with the bending angle and that the dependence is a strong function of the specific identity of the R1 and R2 groups. For example, in the cases where R1 and R2 are combinations of NH_2 and OH groups (nearly congruent on the graph), the coupling undergoes a change of more than 200% as the structure changes from planar to tetrahedral. (This is similar to the change quoted above for the difluoromethyl radical.) Notable also is that any structure in which R1 or R2 is either an NH_2 or an OH group is more sensitive to bending than those with neither group. Table 1 shows the total Mulliken atomic spin distributions as reported by Gaussian for each structure in the planar ($\phi = 0°$) and near-tetrahedral ($\phi = 20°$) cases. The relatively small differences between the values for the two geometries rule out redistribution of spin as the primary cause for the bending sensitivity of the α-proton hyperfine couplings.

On the basis of the idea that changes in $a_{\alpha,\mathrm{iso}}$ originate from rehybridization of the C_α-centered orbital system, Dobbs et al.[5] proposed a plausible, but empirical, relationship for describing the bending sensitivity. Their initial relation is shown as the leftmost expression of eq 3a. In eq 3, ρ_T is the total unpaired spin in the C_α-centered lone-electron orbital (LEO); a and b respectively are the s- and p-character of the LEO; $\rho_s = a\rho_T$ and $\rho_p = b\rho_T$ respectively are the net s- and p-components of spin in the LEO. Also, c_s and c_p are parameters derived from experimental data: $c_p = -22.4$ G from methyl radical measurements and $c_s = 429$ G from difluoromethyl radical measurements.[5] Using standard orbital hybridization considerations (with the approximation that the C_α hybrids bonding to H_α, R1, and R2 are all identical), eq 3a can be converted to the corresponding relationship between the umbrella angle (ϕ) and the coupling as given by eq 3b.

$$a_{\alpha,\mathrm{iso}} = c_s\rho_s + c_p\rho_p = c_s a\rho_T + c_p b\rho_T = \rho_T(c_s a + c_p b) \quad (3a)$$

$$a_{\alpha,\mathrm{iso}} = \rho_T(c_s a + c_p b) = \rho_T[(c_s - c_p)(2\tan^2\phi) + c_p] \quad (3b)$$

Unfortunately, the spread of results in Figure 1 shows that this simple relation cannot describe all cases. Although the reasons for this breakdown may be several, one is that structures containing either NH_2 or OH groups have nonnegligible unpaired spin on the N or the O. For example, in the case where R1 and R2 are both NH_2, the computed ρ_π spin is ~0.12 on each nitrogen. This raises the prospect that the total H_α coupling is actually a combination of the "normal" α-coupling mechanism and the hyperconjugative β-coupling mechanism. (This point was recognized also by Bernhard.[7]) In particular, Whiffen[15] noted that the case where unpaired spin resides on both sides of a β-proton can lead to a remarkably large total β-coupling. This is because the "effective" spin is more nearly the square of the sum of the two spin amplitudes rather than the simple sum of the two densities: $\rho_{\mathrm{eff}} = (\sqrt{\rho_1} + \sqrt{\rho_2})^2$. For example, when both ρ_1 and ρ_2 are 0.12, ρ_{eff} evaluates to 0.48 using this relation. (According to our calculations, the difluoromethyl

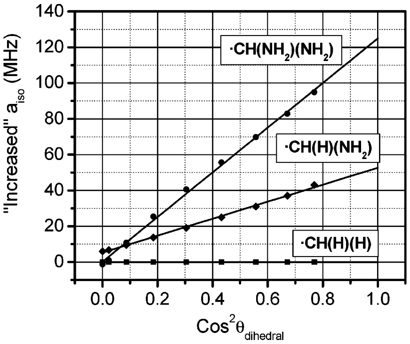


Figure 2. Variation of "increased a_{iso}" = ($\alpha_{\mathrm{R1R2}} - \alpha_{\mathrm{HH}}$) vs $\cos^2 \theta_{\mathrm{dihedral}}$ on bending for the $^{\bullet}C_{\alpha}H_{\alpha}$(R1)(R2) structures indicated. The data points for each case reflect the computed dihedral angle and isotropic coupling values on bending the structures from planar to tetrahedral geometries (in 2.5° steps). Note the significantly greater sensitivity to bending for $^{\bullet}C_{\alpha}H_{\alpha}(NH_2)(NH_2)$ vs $^{\bullet}C_{\alpha}H_{\alpha}(H)(NH_2)$. (The values for $^{\bullet}C_{\alpha}H_{\alpha}$(H)(H) are shown explicitly as 0 for all angles to indicate its role as the "baseline".)

radical should exhibit this behavior also since the value for ρ_F is ~0.07 on each fluorine in a geometry-optimized structure.)

To test the extent to which the "adjacent" spin might contribute to the total isotropic coupling with a $\cos^2 \theta$ dependence, we examined the behavior on bending of the structures $^{\bullet}C_{\alpha}H_{\alpha}$(H)(H), $^{\bullet}C_{\alpha}H_{\alpha}(H)(NH_2)$, and $^{\bullet}C_{\alpha}H_{\alpha}(NH_2)(NH_2)$. Specifically, there is no "adjacent" π-spin for $^{\bullet}C_{\alpha}H_{\alpha}$(H)(H); thus, we treated its behavior as reflecting the "intrinsic" bending behavior of the $^{\bullet}C_{\alpha}H_{\alpha}$ system. The $^{\bullet}C_{\alpha}H_{\alpha}(H)(NH_2)$ structure has only one site of adjacent spin, while $^{\bullet}C_{\alpha}H_{\alpha}(NH_2)(NH_2)$ has two adjacent sites and thereby the possibility of exhibiting the "Whiffen effect". Under the assumption that total isotropic couplings from the two amino-containing structures are simply the "intrinsic" α-couplings plus the β-contributions from bending, we fit the value "increased a_{iso}" = ($\alpha_{\mathrm{R1R2}} - \alpha_{\mathrm{HH}}$) to $\cos^2 \theta_{\mathrm{dihedral}}$ for each bending angle ϕ with the results shown in Figure 2. (The angle $\theta_{\mathrm{dihedral}}$ was computed directly from the atomic coordinates for each bending angle ϕ.)

The results clearly show the significantly increased sensitivity to bending of the diamino structure. Moreover, the slopes of the curves from the two amino-containing structures are different in the ratio 2.6:1. If the spins on the amino nitrogens are the same in both structures, the "Whiffen effect" predicts a ratio of 4:1 since $(\sqrt{a^2} + \sqrt{a^2})^2 = 4a^2$. However, the nitrogen-centered spins (at $\phi = 20°$; see Table 1) are different: the spin is 0.25 in the monoamino case and 0.14 on each in the diamino case. Using these two sets of values and the Whiffen relation, the couplings at $\phi = 20°$ should have the ratio 0.56/0.25 = 2.24, a value remarkably close to the ratio of slopes given above. Obviously, this overall analysis reflects significant assumptions; nevertheless, it also indicates the high probability that the computed α-couplings reflect a significant effect on bending from the hyperconjugative β-mechanism when there is spin on the adjacent atoms. Therefore, this behavior and the "Whiffen effect" predict the possibility that the naturally positive β-contribution can dominate the naturally negative α-contribution with increased bending. In any case, isotropic α-couplings should become more positive with increased bending.

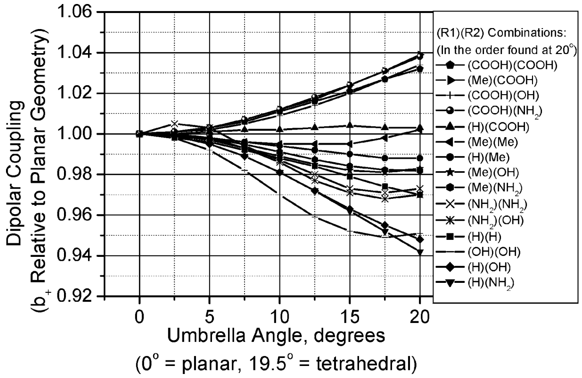


Figure 3. Variation of b_+, the most-positive dipolar component of the α-coupling, on bending the $^{\bullet}C_{\alpha}H_{\alpha}$(R1)(R2) systems from planar to tetrahedral geometries. Note the worst-case changes ranging from −6% to +4%.

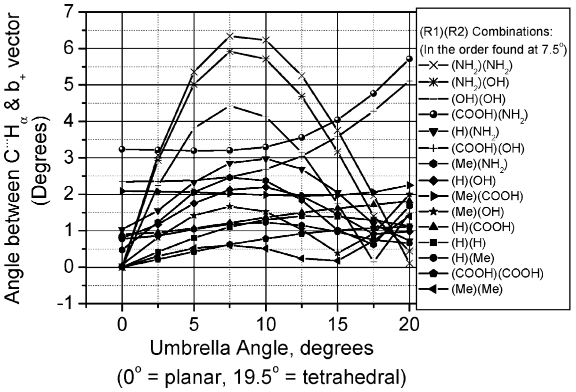


Figure 4. Angular difference (δu) between the vector associated with b_+ and the actual $C_{\alpha}H_{\alpha}$ vector on bending the $^{\bullet}C_{\alpha}H_{\alpha}$(R1)(R2) systems from planar to tetrahedral geometries. Note the worst-case difference of just over 6° and that most cases differ by less than 3°.

Anisotropic Coupling. Gordy and Bernhard used a simplified two-center model for the carbon-centered LEO containing the unpaired electron to conclude that the dipolar component of the α-coupling is much less sensitive to bending than the isotropic component. Moreover, of the three dipolar components (b_+, b_0, and b_-), they concluded that b_+, the "most-positive" component, was the least sensitive. Figure 3 shows the computed dependence of b_+ on the umbrella angle for the full set of structures considered here. In contrast to the change by 40% to over 200% exhibited by the isotropic coupling, these all lie within the range +4% to −6%. Therefore, these results reinforce the earlier Gordy−Bernhard conclusions and securely establish the value of dipolar couplings as reliable reporters of spin distribution.

As is mentioned above, one additional piece of information from the dipolar couplings is $\hat{V}_+$, the vector associated with b_+, which indicates the direction of the $C_{\alpha}H_{\alpha}$ bond in the planar structure. This property, first described by McConnell and Strathdee,[2] has played a central and important role in the identification of radical structures trapped in single crystals. For that reason, we analyzed the angular difference between $\hat{V}_+$ and the $C_{\alpha}H_{\alpha}$ bond direction as a function of the umbrella angle, with the results shown in Figure 4. The figure shows that δu, the angular difference, has the following characteristics: (1) $\delta u \sim 0$ at $\phi = 0$ (planar geometry) when R1 = R2, as is expected on grounds of the symmetry about the $C_{\alpha}H_{\alpha}$ bond; (2) $\delta u \neq 0$ at $\phi = 0$ for most cases when R1 and R2 are different, indicating that molecular asymmetry about the $C_{\alpha}H_{\alpha}$ bond is a factor; (3) δu changes most over the $0° \leq \phi \leq 20°$ range when R1 or R2 are either OH or NH_2, indicating an effect of the spin on the adjacent group.

Overall, however, the main result is that that the direction of $\hat{V}_+$ tracks the $C_{\alpha}H_{\alpha}$ bond direction with only minor deviation throughout the planar-to-tetrahedral range of bending. The worst cases come from the three combinations where R1 and R2 are NH_2 and/or OH. Even in these, the difference between the bond

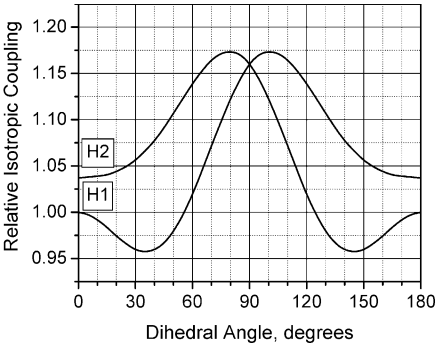


Figure 5. Variation of $a_{\alpha,\mathrm{iso}}$ for both α-hydrogen couplings in $^{\bullet}$C(H)(H)(COOH) as the plane of the COOH group is rotated relative to that of the CH_2 group. The smaller couplings at 0° and 180° are from the α-hydrogen nearer the carboxyl proton.

and $\hat{V}_+$ barely exceeds 6°; in fact, for all structures containing neither NH_2 nor OH, the two vectors are different by approximately 3° at the worst. Consequently, these calculations demonstrate that $\hat{V}_+$ is a reliable indicator of the $C_\alpha H_\alpha$ bond direction, even in the case of extreme bending.

Other Geometry-Related Effects. Factors other than bending also can affect the coupling values in radicals. For example, lengthening the $C_\alpha-H_\alpha$ bond increases the isotropic and reduces the dipolar couplings, while shortening the bond has the opposite effect. This, as well as bending, is important in description of vibrational effects: a bending vibrational mode for a planar structure reduces the magnitude of the isotropic value (it becomes "more positive" for all deviations from planarity, regardless of the direction of bending), while stretching in an anharmonic potential will increase the magnitude of the isotropic and reduce the magnitude of the dipolar components.[16]

We have a particular interest in cases where the geometry of molecules may be constrained by their surroundings, thereby making their hyperfine coupling values different from those computed for isolated molecules. Figure 5 emphasizes the extent to which environmentally imposed constraints on such a group can affect the hyperfine couplings. The figure shows the variation of $a_{\alpha,\mathrm{iso}}$ for the structure $^{\bullet}C_\alpha H_\alpha$ (H)(COOH) as the COOH group rotates about the CC bond relative to the CH_2 group. (In this structure the bonds to C_α are coplanar for all orientations of the COOH group.) The main point is that $a_{\alpha,\mathrm{iso}}$ changes by approximately 20%; therefore, the probability that the molecular environment will restrict reorientation of radicals reinforces the need to include the environment in geometry optimization computations. (The small difference in couplings to the two α-protons at 0° and 180° reflects their different geometrical relationships to the COOH groups in the somewhat artificial structure used for the computations. We note that McCalley and Kwiram[13] detected a definite, but smaller, difference, in the $^{\bullet}CH_2$(COOH) radical from malonic acid.)

Summary and Conclusions

In summary, therefore, the results presented here demonstrate clearly that the isotropic component of α-hydrogen hyperfine interactions is highly affected by nonplanarity of the bonding system at the center of spin. In addition, the results reinforce and strengthen previous conclusions that the dipolar component of α-couplings is only slightly affected by nonplanarity. A particularly important result is demonstration that the direction associated with the "most positive" dipolar coupling reliably indicates the $C_\alpha H_\alpha$ bond direction, even in the case of nonplanarity of the bonds to C_α. Finally, the results reinforce the need to account for the molecular environment in order to compute realistic geometry-optimized structures.

Acknowledgment. This work was supported by DHHS/NIH/NCI Grant CA36810 and by the Georgia State University Research Program Enhancement fund.

References and Notes

(1) McConnell, H. M.; Chesnut, D. B. *J. Chem. Phys.* **1958**, *28*, 107.

(2) McConnell, H. M.; Strathdee, J. *Mol. Phys.* **1959**, *2*, 129.

(3) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(4) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. D* **1969**, 1353.

(5) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 786.

(6) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1965**, *43*, 2704.

(7) Bernhard, W. A. *J. Chem. Phys.* **1984**, *81*, 5928.

(8) Gordy, W. *Theory and Applications of Electron Spin Resonance*; Wiley: New York, 1980.

(9) (a) Nelson, W. H. *J. Phys. Chem.* **1988**, *92*, 554. (b) Hosseini, A.; Lund, A.; Sagstuen, E. *Phys. Chem. Chem. Phys.* **2002**, *4*, 6086.

(10) (a) Ban, F.; Gauld, J. W.; Wetmore, S. D.; Boyd, R. J. The calculation of the hyperfine coupling tensors of biological radicals. In *Progress in Theoretical Chemistry and Physics*; Lund, A., Shiotani, M., Eds.; Kluwer: Dordrecht, 2003; Vol. 10; pp 239−265. (b) Improta, R.; Barone, V. *Chem. Rev.* **2004**, *104*, 1231.

(11) (a) Close, D. M.; Sagstuen, E.; Hole, E. O.; Nelson, W. H. *J. Phys. Chem. B* **1999**, *103*, 3049. (b) Close, D. M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 43.

(12) (a) McConnell, H. M.; Heller, C.; Cole, T.; Fessenden, R. W. *J. Am. Chem. Soc.* **1960**, *82*, 766.

(13) McCalley, R. C.; Kwiram, A. L. *J. Phys. Chem.* **1993**, *97*, 2888.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.01; Gaussian, Inc.: Pittsburgh, PA, 2003.

(15) Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223.

(16) (a) Barone, V. *Chem. Phys. Lett.* **1996**, *262*, 201. (b) Tachikawa, H.; Igarashi, M.; Ishibashi, T. *Chem. Phys. Lett.* **2002**, *352*, 113.