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The use of alpha hyperfine coupling tensors as a measure of unpaired spin density and free radical geometry

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The dipolar elements (B_x, B_y, B_z) of the α-hydrogen hyperfine coupling tensor ($^\alpha$A) are used to calculate unpaired spin density (ρ) and bond lengths (R_H) by using the two center dipole equations derived by Gordy (Ref. 1). B_z is used as a measure of ρ in the equation $B_z = Q_z^{\text{dip}}\rho$ with $Q_z^{\text{dip}} = 38.7$ MHz. The $^\alpha$H–C bond length of electron gain π radicals and alkyl radicals are found to be 0.05–0.10 Å shorter than in comparable nonradicals while in electron loss π radicals the bond lengths are longer by 0.04–0.09 Å. The two center dipole formalism appears to be useful as an analytical method for distinguishing electron loss π radicals from electron gain π radicals. It is suggested that the isotropic component of $^\alpha$H hfc is affected by spin density β to the $^\alpha$H of interest, accounting for a significant portion of the variability in Q_{CH}^H in the McConnel (Ref. 2) equation, $^\alpha A = Q_{\text{CH}}^H\rho$.

INTRODUCTION

Hyperfine interaction between the nucleus of an α hydrogen and an unpaired electron provides considerable information regarding the spatial distribution of the unpaired electron relative to the nucleus. This has placed the α hydrogen hyperfine coupling tensor $^\alpha$A among the most important pieces of information that can be obtained when trying to deduce the structure of an organic free radical. Because of this one can find on the order of 1000 $^\alpha$A tensors published in the literature. Of these about 100 have been determined by ENDOR. Though the $^\alpha$A's determined by ENDOR are subject to inaccuracies, on the whole they are more accurate and more reliable than those calculated from ESR data. The ENDOR determined $^\alpha$A's form a data base that makes it possible to explore in more detail the relationship between $^\alpha$A and free radical structure. The structural parameters of interest are unpaired electron population (commonly referred to as spin density), degree of radical bending, and length of α hydrogen bonds.

McConnell and co-workers recognized that α hydrogen hyperfine coupling ($^\alpha$H hfc) serves as an indicator % $^\alpha$H–C bond orientation and unpaired spin density.[1,2] Both experimentally and by MO calculations it was demonstrated that for the three principal values, the minimum $^\alpha A_z$ occurs when $\mathbf{H}_0$ is parallel to the $^\alpha$H–C bond, the intermediate $^\alpha A_x$ occurs when $\mathbf{H}_0$ is parallel to the LEO axis (lone-electron orbital symmetry axis) and the maximum $^\alpha A_y$ occurs when $\mathbf{H}_0$ is normal to the $^\alpha$H–C bond and the LEO axis. The isotropic component $^\alpha a$ was found to be negative and, therefore, the corresponding dipolar elements B_x, B_y, and B_z are such that the B_z is most positive and B_y is most negative. The magnitude of $^\alpha a$ was suggested to vary directly as the LEO spin density ρ:

$$^\alpha a = Q_{\text{CH}}^H\rho. \tag{1}$$

Variations in Q_{CH}^H from one free radical type to another have been reported by a number of investigators. Such reports generally utilize β hyperfine coupling ($^\beta a$) stemming from an adjacent methyl group, as a reporter of spin density. Equation (2) is employed:

$$^\beta a = \rho(B_0 + B_2\cos^2\phi), \tag{2}$$

where the torsion angle ϕ, between the LEO and the $^\beta$H–C bond, changes as the methyl group rotates and gives an average of $\cos^2\phi = 1/2$. The constants B_0 and B_2 are usually in the range of 0–14 MHz and 110–130 MHz, respectively.[3] Using the methyl hfc as a measure of ρ, Fessenden and Schuler[4] noted variations in Q_{CH}^H for the series of radicals $\dot{\text{C}}\text{H}_3$, $\dot{\text{C}}\text{H}_2\text{CH}_3$, $\dot{\text{C}}\text{H}(\text{CH}_3)_2$, and $\dot{\text{C}}(\text{CH}_3)_3$. Each methyl group added withdraws $\sim 8\%$ spin density from the radical center and Q_{CH}^H increases from 64.5 MHz for $\dot{\text{C}}\text{H}_3$ to 73.4 MHz for $\dot{\text{C}}\text{H}(\text{CH}_3)_3$.

Taking advantage of the relative constancy of B_0 and B_2 in Eq. (2), Fisher[5,6] has used methyl hfc to measure ρ in a series of alkyl radicals and then calculated Q_{CH}^H for a variety of substituents. These results led to the suggestion that electron withdrawing substituents affect the degree of spin polarization (hence the value of Q_{CH}^H) through an inductive effect. An increase in inductive electron withdrawing power was proposed to decrease spin polarization (smaller Q_{CH}^H), e.g., for the $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$ radical $Q_{\text{CH}}^H = 45.6$ MHz.

Dobbs et al. have studied a series of oxy substituted alkyl radicals and found that distortions from planarity occur about the radical center.[7,8] They propose that this is a consequence of an electron-donating mesomeric effect of the oxy substituents. Bending is accompanied by the LEO changing from a pure $2p$ orbital in a planar radical to an sp^n hybrid. This shifts $^\alpha a$ to less negative values, to the point where in strained cyclic systems with two oxy substituents $^\alpha a$ depends on too many variables other than ρ to be used as a direct and simple indicator of ρ. Other factors, such as substituent type and radical geometry, must be taken into account.

Ngo et al. have pointed out that the dipolar elements of $^\alpha$A can serve as a measure of spin density.[9] They have observed that the difference between the maximum and minimum elements $(B_z - B_y)$ yields values of ρ comparable to those calculated from $^\alpha a$. Gordy extended this concept, and from a two-center dipole approximation derived a set of equations for B_x, B_y, and B_z that were used to estimate val-

ues of ρ and then in turn calculate Q_{CH}^H for a series of alkyl radicals.[10]

In the work reported here, we apply the semiempirical equations derived by Gordy to a series of $^\alpha A$ tensors. For the sake of accuracy and reliability only tensors determined by ENDOR have been used. We find that Gordy's equations are valuable analytical tools that are easy to apply.

Gordy's two-center dipole equations

The equations for the three dipolar components of $^\alpha A$ are given below:

$$B_y = -K\rho(R_H^2 + R_p^2)^{-3/2}, \tag{3}$$

$$B_x = K\rho(2R_p^2 - R_H^2)(R_H^2 + R_p^2)^{-5/2}, \tag{4}$$

$$B_z = K\rho(2R_H^2 - R_p^2)(R_H^2 + R_p^2)^{-5/2}. \tag{5}$$

These are derived for a planar radical with the unpaired electron in a $2p$ orbital,[10] as shown in Fig. 1. The unpaired electron is located at two effective centers, a distance R_p above and below the radical plane on the LEO axis of symmetry. The $^\alpha H$ is located a distance R_H from the LEO node (the carbon nucleus). Under these conditions, with R_H and R_p in units of Å and $B_{x,y,z}$ in units of MHz, the value of K is 78.8 MHz/Å^3. Only two of these three equations are linearly independent since the dipolar elements sum to zero.

Using the equations for B_y and B_z we can obtain expressions for R_H and R_p:

$$R_H = \left(\frac{K\rho}{B_y}\right)^{1/3}\left(\frac{B_y - B_z}{3B_y}\right)^{1/2}, \tag{6}$$

$$R_p = \left(\frac{-K\rho}{B_y}\right)^{1/3}\left(\frac{2B_y + B_z}{3B_y}\right)^{1/2}. \tag{7}$$

Given an $^\alpha A$ tensor and the spin density ρ one can use Eqs. (6) and (7) to calculate R_H and R_p. It is necessary, however, to find a means of determining ρ that is independent of Eqs. (6) and (7). Either the isotropic or anistropic components of $^\alpha A$ can be used to estimate ρ. The three dipolar elements are directly proportional to ρ and B_x, B_y, or B_z can be used as a measure of ρ. The best choice would be the element that is least affected by changes in free radical geometry. A look at Fig. 2 (left panel) shows that B_z varies only slightly with changes in bond length (R_H). Anticipating that R_H will have the greatest degree of variability, we have selected B_z as a measure of ρ. Thus ρ is determined by Eq. (8). The proportionality

$$B_z = Q_z^{dip}\rho, \tag{8}$$

constant Q_z^{dip} is chosen empirically. We use $Q_z^{dip} = 38.7$ MHz since this value was found by Gordy[10] to reproduce dipolar elements of a range of alkyl radicals when employing Eqs. (3)–(5). Evaluation of Q_z^{dip} is returned to below. It should be noted that a consequence of calculating ρ by Eq. (8) is that R_p is constrained to a narrower range of values than would otherwise be obtained.

Bending of the radical has only a weak influence on B_x, B_y, and, particularly B_z. This can be seen from Fig. 2 (right panel) where we have moved the $^\alpha H$–C bond through the angle θ shown in Fig. 1. This calculation did not include the changes in R_p as the effective centers shift due to sp hybridi-
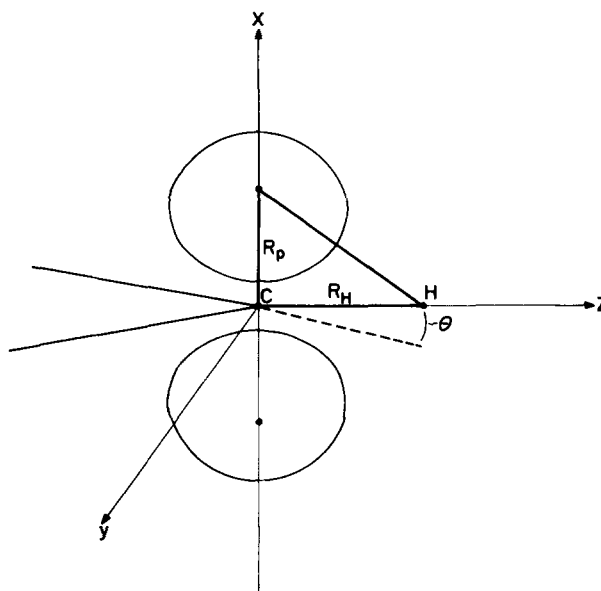

FIG. 1. Diagram of a planar π radical, defining the variables in Eqs. (6) and (7). R_p is the distance from the carbon nucleus to the effective center of the $2p$ orbital lobe, above or below the nodal plane. R_H is the $^\alpha H$–C bond distance. θ is the angle between the $^\alpha H$–C bond and the yz plane as it is rotated in the zx plane. The yz plane is the nodal plane of the $2p$ orbital.

zation. The shift in R_p's will in fact serve to make B_x, B_y, and B_z more constant than shown in Fig. 2 for θ near zero. Most certainly B_z as a measure of ρ is less affected by bending than is $^\alpha a$.

The most severe problem in applying Eqs. (6)–(8) stems from the effect of nonadjacent spin density. To obtain a quantitative estimate and some feeling for this problem we have constructed Fig. 3 and Table I. In Fig. 3 various nonadjacent centers of unpaired spin are shown. These are at different distances R from $^\alpha H$ and the vector connecting each site to $^\alpha H$ makes different angles ψ, with the $^\alpha H$–C bond. In Table I the contribution from each of these sites is estimated for $\rho = 1.0$ at that site. Two estimates are given. One assumes a two-center configuration and employs Eqs. (3) and (5) with $R_H = R$ and $R_p = 0.735$ Å. The other assumes one center, i.e., $R_p = 0.0$. B_z is the strength of coupling that a particular site contributes when H_0 is parallel to the $^\alpha H$–C bond for $\rho = 1.0$ at that site. For example, in a $\dot{C}H_2$–O–R radical one might anticipate a spin density of $\rho \simeq 0.16$ on the oxygen in a $2p$ orbital parallel to the carbon LEO. Using Fig. 3 this corresponds to site 2 and from the $R_p = 0.735$ Å column of Table I the contribution to B_z from site 2 is estimated to be $\rho B_z' = (0.16)(4.5 \text{ MHz}) = 0.7$ MHz. Similarly, the contribution to B_y would be $\rho B_y' = (0.16)(-0.2 \text{ MHz}) \simeq 0.0$.

In any $^\alpha H$ radical, spin polarization will carry spin into the adjacent σ bonds. This source of additional dipolar coupling is important because of its close proximity to $^\alpha H$ and because it will be present in all radicals. Unfortunately, the degree of spin polarization in C–C, C–N, and C–O bonds has not been determined experimentally. If the spin polarization in an $^\alpha H$–C bond is taken as an upper limit, then at site 1–2 in Fig. 3 we would expect $\rho < 64.5$ MHz/1420 MHz $= 0.045$. Using the $R_p = 0.0$ column of Table I the contribution to B_z from site 1–2 is, therefore, estimated to be less than (0.045)
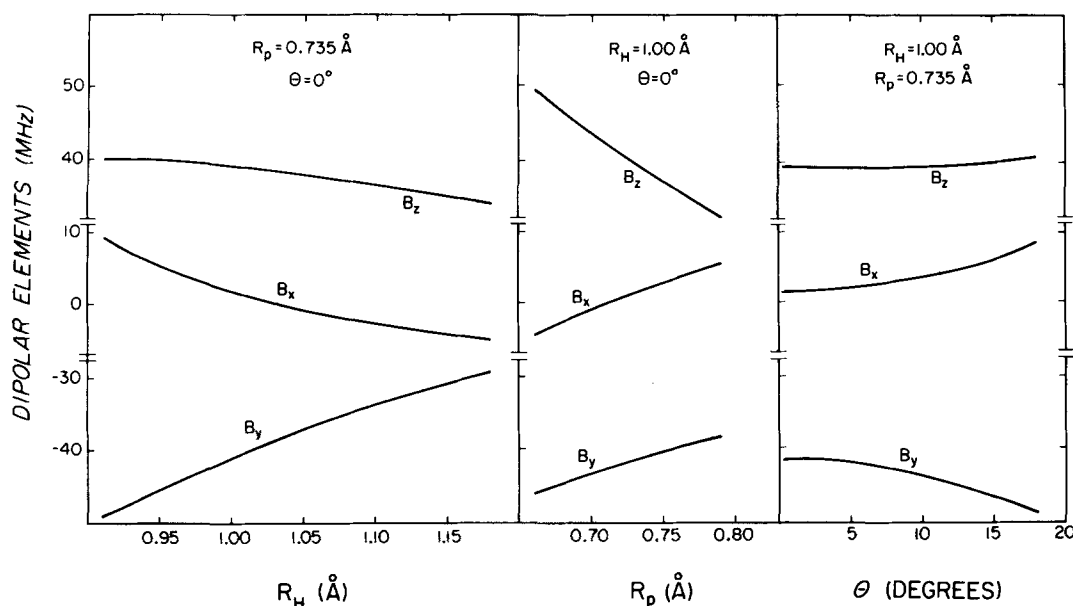
FIG. 2. Variation of the dipolar elements according to Eqs. (6) and (7) with $\rho = 1.0$ and $K = 78.8$ MHz. In the left panel R_p is held constant, in the middle panel R_H is held constant, and in the right panel the angle θ as defined in Fig. 1 is varied with R_H and R_p held constant.

(34.1 MHz) $= 1.5$ MHz. This means that the two σ bonds in a typical $^\alpha$H radical could contribute as much as 3.0 MHz to the observed B_z.

The effect of unpaired spin in the σ bonds is to make the measured value of B_z larger than would be calculated from the two-center dipole approximation. In turn this leads to a larger value of ρ and a longer R_H than would be calculated if no spin density resided in the σ bonds. Fortuitously, this artificial lengthening of R_H partially compensates for the error due to placing the unpaired spin density at just two points. If a more accurate distribution of a $2p$ orbital is used, then the occupied space close to the alpha hydrogen contributes more heavily to B_z than does the space more distant from the alpha hydrogen (due to the R^3 dependence of the

dipole–dipole interaction). Therefore, the effect of placing all of the unpaired spin on the LEO axis is to shrink R_H in order to reproduce the observed values of B_z. It happens, therefore that two of the major sources of error in the two-center dipole approximation tend to cancel one another.

Clearly the choice of Q_z^{dip} in Eq. (8) is important to obtaining physically significant values of R_H and R_p. We have used an empirical approach, choosing Q_z^{dip} to be consistent with expected spin densities while assuming that the two major omissions in this approximation (effects of spin density in the adjacent σ bonds versus the inherent shortening of R_H) cancel one another. There seems to be no way to avoid this circular argument. Thus, looking at Table II we examine succinic acid as one of the alkyl radicals where the effects of spin delocalization and vibrations about the radical center appear minimized. An estimate of Q_z^{dip} is obtained by assuming that the CH_2–$COOH$ substituent will not withdraw more than 0.10 in spin density (CH_3 withdraws ~ 0.08 in liquids).[4] This gives $Q_z^{dip} = 38.8$ MHz. Therefore, Gordy's value of 38.7 MHz appears to be a good choice. Because R_H and R_p depends on ρ to the 1/3 power, the choice of Q_z^{dip} is less critical than one might anticipate. A decrease in Q_z^{dip} from 38.7 to 35.0 MHz decreases R_H by only 0.03 Å, and in view of the observed values of B_z it would be difficult to reconcile a Q_z^{dip} of less than 35.0 MHz.
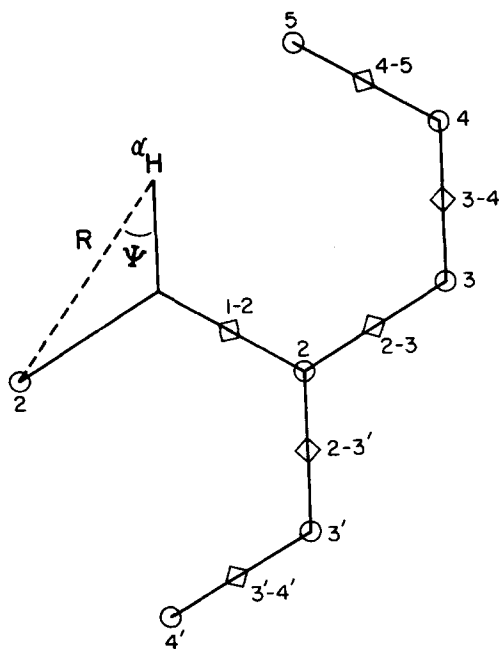
FIG. 3. A model free radical skeleton, based on interbond angles of 120°, showing the relative distance R and angle ψ between an α hydrogen and potential sites of spin density.

RESULTS AND DISCUSSION

Alkyl Radicals

Application of the two-center dipole approximation to the 26 alkyl radicals shown in Table II results in surprisingly uniform values of R_H and R_p. The averages are $R_H = 1.00 \pm 0.01$ Å and $R_p = 0.737 \pm 0.003$ Å. The R_H values indicate that alkyl radicals tend to have shorter $^\alpha$H–C bonds than in the parent compound. Paraffinic H–C bonds range from 1.070 to 1.101 Å.[34] The average R_H would therefore entail a bond shortening of 0.07 to 0.10 Å. Even if one selects

TABLE I. Contribution to the dipolar elements B_z and B_y for the interaction of an $^\alpha$H with unpaired electron spin ($\rho = 1.0$) at various sites as shown in Fig. 3. B'_z and B'_y were calculated from two effective centers separated by $2R_p$ and from a single effective center. R and θ are defined in Fig. 3.

Site	R (Å)	ψ θ (deg)	$R_p = 0.735$ Å		$R_p = 0.0$	
			B'_y (MHz)	B'_z (MHz)	B'_y (MHz)	B'_z (MHz)
1–2	1.5	25	− 3.5	16.6	− 10.9	34.1
2	2.2	37	− 0.2	4.5	− 0.8	6.7
2–3′	2.8	28	− 1.3	3.8	− 1.2	4.8
3′	3.5	22	− 1.0	2.5	− 1.1	2.9
3′–4′	3.8	10	− 1.2	2.4	− 1.3	2.7
4′	4.0	0	− 1.2	2.2	− 1.2	2.4
2–3	2.4	55	4.2	− 2.5	5.7	− 0.1
3	2.8	69	4.7	− 2.1	5.8	− 2.2
3–4	2.6	85	7.0	− 3.9	8.9	− 4.4
4	2.7	80	6.1	− 3.3	8.5	− 4.1
4–5	2.1	66	8.8	− 4.0	13.8	− 4.3
5	1.8	47	4.0	2.1	8.1	5.3

a smaller value of Q_z (35.0 MHz), thereby increasing the calculated R_H's by 0.03 Å there is still a shortening of 0.04 to 0.07 Å.

A look at Table II gives some feeling for the limitation of the two-center dipole equations. Vibrations involving the $^\alpha$H–C bond will tend to decrease the values of B_y and B_z. Though small out-of-plane deformations should have little effect (as judged from Fig. 2), rotations that carry one $^\alpha$H into another, such as that observed in chloropropionamide[14] (Table II, entry 4) lead to large distortions in R_H, R_p, and ρ. Since any type of motion will decrease B_z, Eq. (8) will in general give a lower limit for the true spin density in the LEO. The main exception to this will occur when a significant positive spin density is at sites 3 or 4 or negative spin density is at sites 2 or 5 in Fig. 3. In these cases Eq. (8) will result in an overestimate of ρ.

The degree to which spin density at other sites of the free radical affects the calculation of R_H and ρ can be judged, in part, by comparing the values of B_y, and B_z obtained for the two $^\alpha$H's in the $H_2\dot{C}R$ class of radicals. The differences between the two $^\alpha$H's on the same radical must arise from different $^\alpha$H–C bond lengths and an asymmetry in the distribution of the nonadjacent spin density. Different bond lengths alone will not account for the differences in B_y and B_z observed for the $H_2\dot{C}R$ radicals in Table II. Bond length changes alone would result in one $^\alpha$H, that with the shorter bond, having larger absolute magnitudes of both B_y and B_z. This is not observed. Nonadjacent spin density must contribute 1–2 MHz to the dipolar elements. The shifts in B_z within a given $H_2\dot{C}R$ radical are on the order of ± 3%, thus the values of ρ, in the absence of vibration and large values of spin density at other sites, should be accurate to about ± 3%.

Two entries in Table II illustrate two other points. The L-cyteic[26] radical (entry 19) yields ρ(dip) = 0.95. This overestimate is explainable if negative spin density occurs on the oxygen and/or S–O bonds. In DL-serine (entry 26) the value of ρ(dip) = 0.83 is in accord with expectations but

ρ(iso) = 0.59 appears to be far too low. If this free radical is indeed cyclic, as proposed,[33] it provides an example of a distortion from planarity causing $^\alpha a$ to become less negative, thereby causing an anomalous decrease in ρ(iso).

If one accepts that ρ(dip) generally provides a more accurate measure of the true spin density, then ρ(dip) can be used to calibrate Q^H_{CH} values. For the broad range of alkyl radicals in Table II the average Q^H_{CH} equals 70 ± 6 MHz. Including the aromatic radicals from Tables III and IV changes this value very little. For the total of 52 radicals the average is 70 ± 7 MHz. The variability in Q^H_{CH} provides a measure of the variability that will be obtained in using Eq. (1) to calculate ρ from a fixed value of Q^H_{CH}. The accuracy in measuring spin density, is, therefore, ± 10% using Eq. (1) with a fixed Q^H_{CH} as compared to ± 3% using Eq. (8) with a fixed Q^{dip}_z.

Aromatic radicals

In applying Eqs. (6)–(8) to aromatic radicals, the accuracy of R_H and ρ(dip) decrease due to the reduction in LEO spin density relative to other nearby sites of spin density. Even so the values of R_H and R_p show consistent trends. For the electron gain radicals, entries 1–8, in Table III, R_H = 0.96 ± 0.03 Å, slightly shorter than the alkyl radicals. In contrast, the electron loss radicals, entries 1–5 in Table IV, give R_H = 1.12 ± 0.05 Å, not only longer than R_H of the alkyl radicals but also longer than normal aromatic H–C bonds.[34] Also, R_p for the electron gain radicals is 0.740 ± 0.002 Å and for electron loss radicals is 0.705 ± 0.021 Å, fitting the expectation that electron gain π radicals will contain the unpaired electron at a distance further from the nodal plane of the radical than would an electron loss π radical. It appears, therefore, that the R_H and R_p values can be employed to distinguish electron gain from electron loss π radicals.

The radicals formed by hydrogen addition to carbon (Table III entries 12–15) give R_H and R_p values that are

TABLE II. Alkyl radical bond lengths, effective spin centers, and spin densities calculated from dipolar elements of $^\alpha H$ hfc tensors.

Entry	Crystal	Radical assignment	Temp[a] (K)	B_y (MHz)	B_z (MHz)	R_H (Å)	R_p (Å)	$^\alpha a$ (MHz)	ρ (iso)[b]	ρ (dip)[c]	Q^H_{CH} (MHz)[d]	Ref.
1	succinic acid	$\dot{C}H_2-CH_2-COOH$	4	−36.7	35.2	1.01	0.736	−59.6	0.85	0.91	66	11
				−37.0	34.7	1.00	0.738	−60.1	0.85	0.90	67	
2	β-alanine	$\dot{C}H_2-CH_2-NH_3^+$	4	−35.2	34.2	1.02	0.734	−57.4	0.82	0.88	65	12
				−35.9	33.1	0.99	0.738	−56.7	0.81	0.86	66	
3	succinamic acid	$\dot{C}H_2-CH_2-CO-NH_2$	4	−31.2	31.1	1.03	0.732	−65.8	0.94	0.80	82	13
				−35.3	31.8	0.98	0.740	−64.7	0.92	0.82	79	
4	chloropropionamide	$\dot{C}H_2-CH_2-CO-NH_2$	4	−19.5	15.8	0.92	0.743	−63.0	0.90	...	...	14
5	glycine · HCl	$\dot{C}H_2-COOH$	4	−32.4	30.6	1.00	0.737	−60.6	0.87	0.79	77	15
				−32.5	33.1	1.04	0.729	−59.3	0.85	0.85	69	
6	glycine	$\dot{C}H_2-COOH$	77	−33.9	32.2	1.00	0.737	−58.6	0.84	0.83	70	16
				−34.0	33.5	1.03	0.733	−59.5	0.85	0.87	69	
7	malonic acid	$HOOC-\dot{C}H-COOH$	296	−29.6	28.3	1.01	0.736	−57.4	0.82	0.73	78	17
8	succinic acid	$HOOC-\dot{C}H-CH_2-COOH$	4	−32.4	31.0	1.01	0.736	−59.3	0.85	0.80	74	11
9	succinic acid	$HOOC-CH_2-\dot{C}H-COOH$	4	−33.0	31.5	1.01	0.736	−60.7	0.87	0.81	74	11
10	hydroxyproline · HCl	$HOOC-\dot{C}H-CH_2-CH(OH)-CH_2-NH_3^+$	4	−32.1	30.9	1.01	0.736	−55.2	0.79	0.80	69	18
11	hydroxyproline	$HOOC-\dot{C}H-CH_2-CH(OH)-CH_2-NH_2$	77	−32.4	30.6	1.00	0.737	−57.2	0.82	0.79	72	19
			125	−32.4	31.1	1.01	0.735	−56.5	0.81	0.80	70	
12	citric acid	$HOOC-\dot{C}H-CH(COOH)-CH_2-COOH$	4	−31.8	29.5	0.99	0.738	−60.5	0.86	0.76	79	20
13	β-alanine	$HOOC-\dot{C}H-CH_2-NH_3^+$	90	−32.7	30.6	1.00	0.738	−60.0	0.86	0.79	76	21
14	L-asparagine · H_2O	$H_2N-\dot{C}O-CH-CH(NH_3^+)-COO^-$	100	−32.7	30.9	1.00	0.737	−60.8	0.87	0.80	76	22
15	inositol	$-CH(OH)-\dot{C}H-CH(OH)-$	4	−35.9	32.8	0.98	0.739	−60.8	0.87	0.87	72	23
16	DL-serine	$HN_3^+-\dot{C}H-CH_2OH$	4	−36.3	33.7	0.99	0.739	−58.7	0.84	0.87	67	24
17	histidine · HCl	$NH_3^+-\dot{C}H-CH_2-imidazole$	4	−37.1	34.4	0.99	0.739	−57.1	0.82	0.89	64	10
18	cysteine · HCl	$NH_3^+-\dot{C}H-CH_2SH$	4	−37.0	34.7	1.00	0.738	−67.8	0.97	0.90	76	25
19	L-cyteic acid	$NH_3^+-\dot{C}H-CH_2-SO_3^-$	4	−37.8	36.6	1.02	0.735	−66.2	0.95	0.95	70	26
20	acetylglycine	$\dot{C}H_2-NH-CO-CH_3$	4	−30.1	27.5	0.98	0.740	−50.1	0.72	0.71	71	27
				−31.9	29.3	0.99	0.739	−40.5	0.58	0.76	54	
21	glycylglycine · HCl	$\dot{C}H_2-NH-CO-CH_2-NH_3^+$	4	−30.5	27.7	0.98	0.740	−50.4	0.72	0.72	70	28
				−31.1	27.1	0.96	0.742	−49.0	0.67	0.70	67	
22	β-Me-D-galactopyranoside	$\dot{C}H_2-O-CH(OR)-CH(OH)-$	6	−34.2	32.8	1.01	0.736	−53.1	0.76	0.85	63	29
				−35.3	31.5	0.97	0.741	−51.8	0.74	0.81	64	
23	α-D-glucose	$\dot{C}H(OH)-CH(OR)-CH(OH)-$	77	−34.4	31.8	0.99	0.739	−58.2	0.83	0.82	71	30
24	α-Me-D-glucopyranoside	$\dot{C}H(O^-)-CH(OR)-CH(OH)-$	77	−28.8	31.8	1.10	0.716	−61.2	0.87	0.82	61	31
25	α-Me-D-glucopyranoside	$CH(OH)-R$	77	−33.9	33.1	1.02	0.734	−49.4	0.71	0.85	58	32
26	DL-serine	$O-\dot{C}H-CH(NH_3^+)-CO$	300	−35.4	31.9	0.98	0.740	−41.3	0.59	0.83	50	33
	Average excluding entries 4 and 26					1.00 ± 0.01	0.737 ± 0.003				70 ± 6	

[a] Measurement temperature.
[b] Calculated using Eq. (1) with C^H_{CH} = 70 MHz.
[c] Calculated using Eq. (8) with Q^{dip}_z = 38.7 MHz.
[d] Calculated from $^\alpha a \div \rho(dip)$.

TABLE III. Aromatic radicals due to electron or hydrogen addition: bond lengths, effective spin centers, and spin densities calculated from elements of $^\alpha$H hfc tensors.

Entry	Crystal	Radical assignment	Alpha hydrogen	Temp[a] (K)	B_y (MHz)	B_z (MHz)	R_H (Å)	R_p (Å)	$^\alpha a$ (MHz)	ρ (iso)[b]	ρ (dip)[c]	Q_{CH}^H (MHz)[d]	Ref.
1	thymidine	$^+e^-$	H6	4	−22.7	19.8	0.96	0.742	−32.8	0.47	0.51	64	35
2	5'UMP	$^+e^-$	H6	4	−23.0	19.8	0.95	0.742	−36.1	0.52	0.51	70	36
3	3'CMP	$^+e^-$	H6	4	−23.3	21.3	0.98	0.740	−36.0	0.51	0.55	65	36
4	cytosine HCl	$^+e^-$	H6	4	−28.1	25.7	0.98	0.739	−45.9	0.66	0.66	69	37
5	5'd CMP	$^+e^-$	H6	6	−24.3	18.5	0.89	0.740	−39.0	0.56	0.48	82	38
6	5-Br-Uridine	$^+e^-$	H6	4	−24.4	22.3	0.98	0.740	−37.0	0.53	0.58	64	37
7	adenine HCl	$^+e^-$	H8	4	−16.1	13.8	0.95	0.743	−24.5	0.35	0.36	69	39
8	adenosine:5BR-Uracil	$^+e^-$ on adenine	H8	6	−6.7	5.9	0.96	0.742	−12.3	0.18	0.15	81	40
			H2		−16.5	16.0	1.01	0.735	−29.7	0.42	0.41	72	
9	cytosine · H_2O	$^+e^- + H^+$ on 02	H6	77	−13.3	15.3	1.12	0.707	−26.7	0.38	0.39	68	41
10	5-F-uracil	$^+e^- + H^+$ on 04	H6	80	−11.7	14.4	1.17	0.687	−27.0	0.39	0.37	73	42
11	5-Cl-uracil	$^+e^- + H^+$ on 04	H6	80	−15.7	16.7	1.07	0.723	−32.5	0.46	0.43	75	43
12	1-Me-uracil	C5 + H	H6	4	−31.9	29.6	0.99	0.739	−54.3	0.78	0.76	71	44
13	1-Me-cytosine	C5 + H	H6	4	−32.3	29.6	0.98	0.740	−48.8	0.70	0.76	49	45
14	1-Me-cytosine	C6 + H	H5	4	−30.0	27.0	0.97	0.741	−49.9	0.71	0.71	50	45
15	tryptamine · HCl	C7 + H	H6	295	−15.8	15.1	1.01	0.736	−28.1	0.40	0.39	72	46
			H4		−20.6	18.6	0.98	0.740	−36.8	0.53	0.48	77	
			H5		−3.9	3.9	1.03	0.732	−7.8	0.11	0.10	77	
16	histidine · HCl	C2 + H	H4	4	−11.0	12.7	1.13	0.706	−20.2	0.29	0.33	62	10
	average overall entries						1.00 ± 0.07	0.732 ± 0.015				69 ± 9	
	average of entries 1–8						0.96 ± 0.03	0.740 ± 0.002				71 ± 7	
	average of entries 9–11						1.12 ± 0.05	0.706 ± 0.018				72 ± 4	
	average of entries 12–15						0.99 ± 0.02	0.736 ± 0.007				66 ± 13	

[a] As in Table II.
[b] As in Table II.
[c] As in Table II.
[d] As in Table II.

TABLE IV. Aromatic radicals due to electron loss and alkyl radicals: bond lengths, effective spin centers, and spin densities calculated from dipolar elements of $^\alpha$H hfc tensors.

Entry	Crystal	Radical assignment	Alpha hydrogen	Temp[a] (K)	B_y (MHz)	B_z (MHz)	R_H (Å)	R_p (Å)	$^\alpha a$ (MHz)	ρ (iso)[b]	ρ (dip)[c]	Q^H_{CH} (MHz)[d]	Ref.
1	imidazole:barbital	$-e^-$(imidazole)	H5	6	-16.0	17.9	1.11	0.712	-30.0	0.43	0.46	65	47
			H4		-17.1	19.0	1.10	0.713	-30.5	0.44	0.47	62	
			H2		-16.5	18.8	1.12	0.709	-37.0	0.53	0.48	76	
2	5'd CMP	$-e^-$(cytosine)	H5	6	-20.9	23.6	1.11	0.711	-41.9	0.60	0.61	69	38
3	5-nitro-6-Me-uracil	electron loss π radical	H5	4	-25.1	26.6	1.07	0.723	-48.4	0.69	0.69	69	48
4	histidine (HCl)	$-e^-$	H4	4	-14.1	17.7	1.18	0.681	-29.7	0.42	0.46	65	10
			H2		-15.4	15.5	1.04	0.731	-33.9	0.48	0.40	85	
5	tyrosine	$-e^-$	H3	4	-7.7	10.2	1.22	0.662	-17.3	0.25	0.26	66	49
			H5		-8.6	10.2	1.14	0.702	-17.4	0.25	0.26	67	
6	barbituric acid	$-$H5	H5	80	-28.6	29.1	1.05	0.729	-55.0	0.79	0.75	73	50
7	1-Me-uracil	$-$H1	both H1's	77	-32.1	29.2	0.98	0.740	-55.3	0.79	0.76	73	51
8	thymidine	$-$H5	H5(1)	300	-22.6	22.2	1.02	0.733	-43.2	0.62	0.57	75	52
			H5(2)		-23.2	21.8	1.00	0.737	-43.8	0.63	0.56	78	
			H6		-13.5	14.4	1.08	0.721	-28.7	0.41	0.37	77	
9	dimethylglyoxime	CH_2–C(R) = N–OH	H1	77	-24.2	23.8	1.02	0.733	-43.1	0.62	0.61	70	53
			H2		-20.9	20.4	1.02	0.734	-42.8	0.61	0.52	81	
10	cytidine	CH_2–C(R) = CH–R'	H	300	-22.8	22.8	1.04	0.731	-43.5	0.62	0.59	74	54
			H'		-24.7	23.9	1.01	0.735	-44.2	0.63	0.62	72	
			H"		-11.2	12.3	1.09	0.717	-25.9	0.37	0.32	81	
11	3'CMP	CH_2–C(R) = CH–R'	H	77	-21.7	24.0	1.10	0.715	-37.2	0.53	0.62	60	55
			H'		-21.6	21.5	1.03	0.732	-39.7	0.57	0.56	71	
			H"		-14.4	18.3	1.19	0.676	-25.2	0.36	0.47	53	
12	5'd CMP	CH_2–C(R) = CH–R'	H	77	-26.9	25.5	1.00	0.737	-44.3	0.63	0.66	67	56
			H'		-23.7	24.4	1.05	0.727	-43.5	0.62	0.63	69	
			H"		-10.8	12.4	1.12	0.706	-24.1	0.34	0.32	75	
	average of all entries						1.07 ± 0.06	0.717 ± 0.020				71 ± 7	
	average of entries 1–5						1.12 ± 0.05	0.705 ± 0.021				69 ± 7	
	average of entries 8–12						1.05 ± 0.05	0.724 ± 0.017				72 ± 8	

[a] As in Table II.
[b] As in Table II.
[c] As in Table II.
[d] As in Table II.

William A. Bernhard: Unpaired spin density and free radical geometry

between those of aromatic electron gain radicals and alkyl radicals. On the other hand the π radicals formed by protonation of an exocyclic oxygen after electron gain (Table III, entries 9–11) give R_H and R_p values similar to the electron loss π radicals (Table IV, entries 1–5). This suggests that formation of the enol group (at O_2 in cytosine and O_4 in uracil) renders the cyclic core more positive, i.e., similar to an electron loss π radical. If this proves true, the values of R_H and R_p may provide a means of determining whether or not electron gain π radicals are protonated at exocyclic oxygens. More ENDOR studies are necessary in order to test this possibility.

Entries 8–12 in Table IV are for alkyl-like radicals. In each case the $^\alpha H$ that has the smaller hfc yields a significantly larger value of R_H, e.g., in thymidine H6 gives $R_H = 1.08$ Å while the two H5's give 1.00 and 1.02 Å. This is an illustration of the influence of nonadjacent spin density increasing as the spin density adjacent to the $^\alpha H$ decreases.

Contribution of β spin density to $^\alpha a$

The imidazole electron loss π radical is particularly informative with respect to examining the factors that affect the isotropic hfc of an alpha hydrogen. The dipolar elements given in entry 1 of Table IV were determined using four different crystallographic planes, insuring high accuracy and no ambiguity as to the principal values of the $^\alpha A$ tensors. From the principal axes it is known that the $^\alpha H$–C bonds in the imidazole electron loss π radical are coplanar to better than $0.5°$. Any variations in $^\alpha a$, therefore, cannot be ascribed to bending. Yet note that $^\alpha a$ for H_2 is 23% greater than H4 or H5 (numbering given below). One might presume that this is due to the spin

IMIDAZOLE π RADICAL
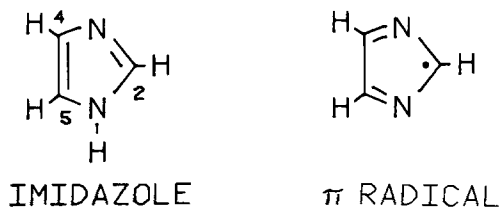
density being 23% greater at C2 than C4 and C5 but ρ(dip) indicates these three sites have nearly equal spin density. [Using the spin distribution $\rho_2 = \rho_4 = \rho_5 = 0.47$ and $\rho_1 = \rho_3 = -0.20$, the error introduced into the ρ(dip) values via nonadjacent spin sites is estimated to be $\pm 3\%$.] The difference in $^\alpha a$ between H2 and H4, H5 must be due to either a change in the degree of spin polarization or due to hfc stemming from density at sites β to the α hydrogen.

It has been proposed by Brunton et al.[57] that oxygen substituents in alkyl radicals cause the values of $^\alpha a$ to become less negative as a result of positive spin delocalized onto the substituent oxygen hyperconjugating with the $^\alpha H$. In other words, it is necessary to apply Eq. (2) to the spin density located on atoms that lie β to the $^\alpha H$ of interest. The imidazole electron loss π radical being planar requires that ϕ in Eq. (2) be equal to zero. If $\rho_1 = \rho_3 = -0.20$ and $B_0 = 14$ MHz, then the hfc stemming from the nitrogen-centered spin density would contribute $2\rho_N B_0 = 2(-0.2)(14 \text{ MHz}) = -6$ MHz to $^\alpha a$ of H2. On the other hand, the contribution to $^\alpha a$

of H4 (or H5) would be $(\rho_{N3} + \rho_{C5})B_0 = (-0.20 + 0.47)(15 \text{ MHz}) = +4$ MHz. Thus back spin polarization alone would yield an $^\alpha a$ for H2 that is 10 MHz more negative than for H4 or H5. A B_0 of 10 MHz is sufficient to account for the observed difference of 7 MHz.

It is quite possible that much of the variability in Q_{CH}^H of Eq. (1) stems from contributions to $^\alpha a$ from β spin density. When ϕ of Eq. (2) is nonzero the B_2 term becomes important. Since B_2 has the values of 128 and 263 MHz for spin centered on C and O, respectively, the positive contribution to $^\alpha a$ would increase dramatically for adjacent spin on an O vs C when a radical is nonplanar. This is in accord with the observation by Dobbs et al.[7,8] that the value of $^\alpha a$ is dramatically reduced in alkyl radicals with more than one oxy substituent. Caution is needed, therefore, when attempting to use isotropic alpha hfs as a measure of the degree of bending at the radical center.

CONCLUSIONS

The two-center dipole approximation, using the maximum dipolar element as a measure of ρ, appears to be a convenient and informative means of characterizing free radical structure. The relative changes appear significant.

R_H calculated for electron gain π radicals, alkyl radicals, and electron loss π radicals yields values of 0.96 ± 0.03 Å, 1.00 ± 0.01 Å, and 1.12 ± 0.05 Å, respectively. Considering the boundaries of the approximation, it is predicted that the $^\alpha H$–C bond shrinks by 0.05 to 0.10 Å upon alkyl radical or electron gain π-radical formation and expands by 0.04 to 0.09 Å upon electron loss π-radical formation.

The effective center distance changes from $R_p = 0.705 \pm 0.021$ Å in electron loss π radicals to $R_p = 0.740 \pm 0.002$ Å in electron gain π radicals.

Accuracy of the two-center dipole equations is decreased when vibrational or rotational amplitude of the $^\alpha H$ bond becomes large and when the spin density adjacent to $^\alpha H$ is small compared to other nearby sites of spin density. In general the spin density can be more accurately determined by the maximum dipole components of $^\alpha A$ (about $\pm 3\%$) than by the isotropic component of $^\alpha A$ (about $\pm 10\%$). The problems in using the isotropic components are due to its sensitivity to bending and spin density at positions β to the $^\alpha H$ carbon. It is suggested that spin polarization or hyperconjugation arising from spin density on either side of the $^\alpha H$ carbon is a major factor in causing changes of Q_{CH}^H through variations in substituents. Using the spin densities found from dipolar interactions, a broad average value for Q_{CH}^H of 70 ± 8 MHz was calculated.

ACKNOWLEDGMENTS

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