The ¹³C Hyperfine Splittings in ESR Spectra of Prop-2-ynyl and 1-(Trimethylsiloxy)prop-2-ynyl Radicals

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The ¹³C satellite lines were observed in the 9.4 GHz ESR spectra of prop-2-ynyl and 1-trimethylsiloxyprop-2-ynyl radicals generated from precursors containing ¹³C in natural abundance. The ¹³C hfs indicate that prop-2-ynyl radicals adopt the π -delocalized structure, not the σ -allenyl form. The hfs of 1-trimethylsiloxyprop-2-ynyl radicals indicate that there is appreciable delocalization of spin onto the trimethylsiloxy group and that the radical is essentially planar at C(1). A linear correlation of a(C) with a(H) is shown to hold for a number of neutral hydrocarbon π -delocalized radicals. The experimental hfs are compared with spin densities calculated by a variety of semiempirical and ab initio SCF MO methods.

Carbon-13 hyperfine splittings (hfs) in ESR spectra are of particular interest because they indicate more directly than ¹H hfs the distribution of spin density (and hence structure) in free radicals. Rarely, however, can sufficient signal intensity be obtained from transient radicals for the ¹³C satellites to be observed. The two alternative techniques of isotopic enrichment and conversion of the transient radical to a persistent radical by introduction of *t*-butyl substituents, involve lengthy syntheses and in the latter method the basic radical skeleton may be seriously perturbed by the presence of the bulky substituents (*1-3*). Thus rather few ¹³C hfs were known for transient radicals, and no data was available for transient acyclic π -delocalized radicals. Berndt and co-workers (*1*) measured the ¹³C hfs for 1,1,3-tri-*t*-butylprop-2-ynyl radicals 1; the relatively low value of $a(C_1)$ indicating that they have the π -delocalized structure 1 rather than the σ -allenyl structure 2:



Carbon-13 hfs have also been determined for several *t*-butyl-substituted allyl radicals (2, 3) and for cyclopentadienyl (4) and cycloheptatrienyl (5) radicals.

Delocalized radicals have received intensive theoretical (6-9) and experimental (9-12) attention, so it is especially desirable to have ¹³C hfs for comparison and correlation. The best hope of observing satellite spectra with radicals containing only

natural-abundance ¹³C will be for those radicals which can be generated very efficiently in solution and which contain few hydrogens so that the signal intensity is concentrated into the minimum number of resonance lines. Two such radicals are prop-2-ynyl (3) and 1-trimethylsiloxyprop-2-ynyl (4)



and their ¹³C hfs are reported in this paper.

ESR RESULTS

The 1-trimethylsiloxyprop-2-ynyl radical 4 was generated at low temperatures (approximately 135 K) in cyclopropane solution by hydrogen abstraction from 3-trimethylsiloxypropyne by photochemically generated *t*-butoxy radicals. Intense spectra were obtained and the ¹³C satellite lines were clearly visible when conditions of high gain, high time constant, and slow scan were employed. The experimental spectrum and a computer simulation are shown in Fig. 1. The intensity of the satellite lines was $0.54 \pm 0.1\%$ of the main lines, in good agreement with the expected value for ¹³C lines. The ¹³C hfs are reported in Table 1. No ²⁹Si satellite lines were resolvable; thus it is likely that the ²⁹Si hfs is less than the width of the main spectral lines.

Propynyl radicals were generated by hydrogen abstraction from propyne by *t*-butoxy radicals and by bromine abstraction from propynyl bromide by triethylsilyl and trimethyltin radicals. Best signal intensity was obtained with the propynyl bromide-triethylsilane system in cyclopropane solvent. Although lower temperatures and higher signal intensities were achieved with *n*-propane as solvent the spectra were complicated by the lines of the isopropyl radical which made analysis more difficult. Spectra were recorded under conditions of high gain, high time constant, and slow scan and, alternatively, spectra were accumulated with a signal averager. The 13 C satellites were not so well marked as those from radical **4**, but were located with



FIG. 1. 9.4 GHz ESR spectrum of 1-trimethylsiloxyprop-2-ynyl radicals at 135 K showing the ¹³C satellite lines. Upper-trace experimental spectrum, lower-trace computer simulation.

2-ynyl Radicals								
	INDO ^a			UMNDO ^c , p(s)				
Exptl Hfs (G)	hfs $\rho(s)$		$CINPRO^{o}, \\ \rho(s)$					
27.1	28.5	0.0348	0.0117	0.0460				
17.6	-14.3	-0.0174	-0.0058	-0.0345				
21.4	13.9	0.0169	0.0057	0.0308				
18.3	-17.8	-0.0330	-0.0109	-0.0474				
10.7	-8.3	-0.0153	-0.0051	-0.0287				
	3.9	0.0044	0.0015	0.0081				

C₁ C₂ C₃ H₁ H₃ O

Si

<1.0

HFS AND S-ORBITAL	SPIN DENSITIES FOR	1-TRIMETHYLSILOXYPROP
	2-VNVI RADICA	15

TABLE 1

^a INDO calculations for the 1-hydroxypropynyl radical with the optimum MNDO geometry, $\langle S^2 \rangle = 0.7726$.

^b Complete projection of the doublet state at the INDO level of approximation, $\langle S^2 \rangle = 0.7500$, geometry the same as for the INDO calculations.

^c UHF version of the MNDO program package; complete geometry optimization of siloxy-substituted radical 4. $\langle S^2 \rangle = 0.8463$.

reasonable certainty and the hfs are given in Table 2. The intensity of the satellite lines was found to be $0.63 \pm 0.2\%$ of the main lines.

DISCUSSION

The ¹H hfs of propynyl radicals are in agreement with those reported by other workers (13, 14) and the ¹³C hfs are close to, but all slightly greater than those of trit-butylpropynyl radicals ($a(C_1) = 32.2$, $a(C_2) = 17.3$, $a(C_3) = 21.9$ G) reported by Berndt and co-workers (1). The relatively low value of $a(C_1)$ confirms that propynyl, like the tri-t-butyl derivative, adopts the π -delocalized structure 3 rather than the

HFS AND SPIN DENSITIES FOR PROPYNYL RADICALS								
		IN						
	Exptl hfs (G)	hfs	ρ(s)	$\frac{\text{CINPRO}^{b}}{\rho(s)}$	$UMNDO^{c}, \\ \rho(s)$	Ab initio 6-31G ^d $\rho(\pi)$		
C_1	33.9	32.8	0.040	0.0133	0.051	0.851		
C ₂	18.1	-16.8	-0.021	-0.0067	-0.040	-0.451		
C3	22.9	18.9	0.023	0.0078	0.038	0.600		
2H1	18.9	-19.2	-0.036	-0.0116	-0.055			
H ₃	12.7	-11.4	-0.021	-0.0070	-0.035			

TABLE 2

^a INDO with optimized geometry from Hinchliffe (18).

^b Complete projection of doublet state $\langle S^2 \rangle = 0.75$; same geometry as INDO.

^c UHF version of MNDO program. Complete geometry optimization. $\langle S^2 \rangle = 0.8860$.

^d π spin densities calculated by Bernardi *et al.*, (20).

0.0071



FIG. 2. Correlation of a(C) with a(H) for neutral hydrocarbon π radicals. Points: 1, methyl (15); 2, ethyl C α (15); 3, propynyl C(1); 4, benzyl C α (24); 5, propynyl C(3); 6, allyl C(1), endo H (3); 7, allyl C(1) exo H; 8, cyclopentadienyl (4); 9, cycloheptatrienyl (5); 10, allyl C(2) (3). Full line from Eq. [1].

 σ -allenyl form. The ¹³C hfs at C(1) of **3** is considerably greater than $a(^{13}C)$ for C(1) in allyl radicals (approximately 22.3 G (3)), which shows that the triple bond delocalizes spin density less effectively than the double bond. The hfs of trimethylsiloxypropynyl are all lower than the analogous hfs of propynyl as would be expected if spin is delocalized onto the siloxy group. The value of $a(H_1)$ in **4** is only marginally below that of $a(H_1)$ in **3**, but $a(C_1)$ in **4** is nearly 7 G less than $a(C_1)$ in **3**. Thus the ¹³C hfs are far more sensitive to substituent effects than the ¹H hfs. In alkyl radicals with α -oxo-substituents the oxygen-containing group induces bending at the radical center. The increased σ contribution to the orbital containing the unpaired electron results in a larger ¹³C hfs. In hydroxymethyl radicals, for example, $a(^{13}C)$ is 47.5 G as compared with 38.5 G in methyl radicals (15). The higher $a(^{13}C)$ in \cdot CH₂OH indicates a small degree of bending (<5°) at the radical center (15). In trimethylsiloxypropynyl radicals 4 $a(C_1)$ is *less* than in the unsubstituted propynyl radicals 3 and hence bending at C₁ in 4 is unlikely. This is quite reasonable in view of the π -delocalized character of propynyl radicals.

The neutral π -delocalized hydrocarbon radicals, for which data are available, show a surprisingly good linear correlation between the ¹³C hfs a(C) and the hfs of hydrogens attached to carbon, i.e., a(H) (see Fig. 2). The correlation is represented by Eq. [1] the correlation coefficient being 0.994:

$$a(C) = (-2.09 \pm 0.08)a(H) - 7.5 \pm 2.1.$$
 [1]

The correlation does not hold for substituted radicals and, for example, $a(C_1)$ for radical 4 lies well away from the main line. Karplus and Fraenkel showed that spin polarization in carbon 1s and 2s orbitals arises from $\sigma-\pi$ interactions (16). For sp^2

hybridized carbon atoms bonded to three atoms, X_1 , they deduced that $\alpha(C)$ has the form

$$a(\mathbf{C}) = (S^{\mathbf{C}} + \sum_{i=1}^{3} Q_{\mathbf{C}\mathbf{X}_{i}}C)\rho^{\pi} + \sum_{i=1}^{3} Q_{\mathbf{X}_{i}}C\rho_{i}^{\pi}, \qquad [2]$$

where ρ^{π} and ρ_i^{π} are the π -electron densities on atoms C and X_i, respectively. The contribution of the 1s electrons is determined by S^C and that of the 2s electrons by the Q values, where $Q_{BC}A$ is the σ - π parameter for the nucleus of atom A resulting from the interaction between the bond BC and the π -electron density on atom B. Introduction of the well-known McConnell equation, $a(H) = Q_{CH}H\rho^{\pi}$, leads to

$$a(C) = (S^{C} + \sum_{i=1}^{3} Q_{CX_{i}}C)a(H)/Q_{CH}H + \sum_{i=1}^{3} Q_{X_{i}C}C\rho_{i}^{\pi}.$$
 [3]

In general a linear relationship between a(C) and a(H) is obviously not to be expected. However, for carbon atoms of the type $\cdot C(H_2C)$ where the electron density on the neighboring carbon atom is small the second term in Eq. [3] will be small and $\Sigma Q_{CX,C}$ is constant. Most of the carbon atoms in Fig. 2 fall into this category (the α -C atoms of methyl, ethyl, propynyl, allyl, benzyl). The first term in Eq. [3] can be calculated from the parameters given by Karplus and Fraenkel, i.e., $(-12.7 + 2 \times 19.47 + 14.44)a(H)/-23.72 = -1.72 a(H))$, which compares quite well with the "experimental" value of -2.09 from Eq. [1]. The reasons why the correlation holds for the other C atoms (particularly C(2) of allyl) are not clear and linearity may be fortuitous.

SCF MO CALCULATIONS

The propynyl radical geometry has been examined by the INDO (17, 18) and MINDO/3-UHF (19) semiempirical methods and by ab initio calculations (20, 21). Both the INDO (18) and ab initio calculations (20) showed the structure to be 3, i.e., the π -delocalized type. The optimum structure was found to be r[C(1)-C(2)] = 1.401, $r[C(2)-C(3)] = 1.213, r[C(1)-H] = 1.08, r[C(3)-H] = 1.066 \text{ Å}, \angle HC(1)H = 121^{\circ},$ by the Gaussian 70 method with a 4-31G basis set (20). We carried out calculations on propynyl and 1-trimethylsiloxypropynyl radicals using the UHF version of the MNDO program (UMNDO) (22). The optimum geometry for 3 was very similar to that derived from the ab initio work above; the optimum geometry for 4 was r[C(1)-C(2) = 1.401, r[C(2)-C(3)] = 1.207, r[C(1)-O] = 1.321, r[O-Si] = 1.737, r[C(1)-O]H] = 1.095, r[C(3)-H] = 1.050 Å, $\angle HC(1)C(2) = \angle OC(1)C(2) = 120^{\circ}$, $\angle SiOC(1)$ = 129° . A feature of the UMNDO calculations (and the INDO and ab initio work) was the high expectation values of S^2 indicating significant contamination of the wavefunctions by components of higher spin states. Calculations were also carried out for complete projection of the doublet state at the INDO level of approximation using the Harriman method and the CINPRO program package (23). The calculated s-orbital spin densities are reported in Tables 1 and 2. While the INDO and CINPRO spin densities correctly reproduce the order of the experimental hfs, the UMNDO calculations overestimate the amount of negative spin density on C(2) in both radicals. All three methods correctly predict a lower spin density on C(1) of 1-trimethylsiloxypropynyl than on C(1) of 3 but all three methods also underestimate the spin density on C(3) of both radicals. It appears that the semiempirical methods underestimate the extent of delocalization of the unpaired electron onto the triple bond. The ab initio π -spin densities calculated by Bernardi *et al.* (20) give a closer description of the electron delocalization in this respect.

EXPERIMENTAL

Di-*t*-butyl peroxide and triethylsilane were commercial materials purified by passing them down a column of alumina followed by distillation. 3-Bromoprop-2-yne was commercial material purified by trap-to-trap distillation. 3-Trimethylsiloxyprop-2-yne was prepared as follows: trimethylsilyl chloride (9.7 g) was added dropwise to a stirred solution of propynyl alcohol (5 g) and pyridine (7 g) in *n*-pentane (40 ml). After 30 min the solution was filtered several times, the pentane removed by distillation, and the residual oil distilled. This gave 3-trimethylsiloxyprop-2-yne (6.0 g, 52%) bp (760 mm) 90°C, $\delta_{\rm H}$ 0.15 (s, 9H, Me₃Si-), 2.40 (t, J = 2.5 Hz, 1H, \equiv CH), 4.32 (d, J = 2.5 Hz, 2H, $-CH_2C\equiv$); $\delta_{\rm C}$ 0.35 (Me₃Si), 51.20 (C(1)), 73.40 (C(3)), 82.63 (C(2)).

ESR spectra were recorded with a Bruker ER 200D spectrometer; in some experiments a Princeton Applied Research Model 4202 signal averager was employed. Solutions were made up in spectrosil quartz tubes, degassed, and photolyzed with light from a 500 watt Wotan HBO super-pressure Hg arc.

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