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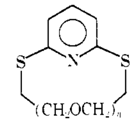

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An Electron Spin Resonance Study of the 1-Norbornyl Radical

Sir:

The 1-norbornyl radical offers an opportunity to study the vicinal and long-range proton hyperfine interactions in a radical with a pyramidal radical center and of unusually rigid structure. In this communication we report an ESR study of this radical.

Figure 1A shows the ESR spectrum of the 1-norbornyl radical observed during photolysis[1] of a cyclopropane solution[2] of bis(norbornane-1-carbonyl) peroxide[3] at -121°. To improve the signal-to-noise ratio of the spectrum, the low field wing of the spectrum (underlined part a of Figure 1A) was computer averaged using signals from eight samples.[6] The improved low field wing of the spectrum is shown in Figure 1B. The absorptions are analyzed as five sets of 1:2:1 triplets (9.81, 2.35, 1.23, 0.49, and 0.36 G) further split into a 1:1 doublet of 2.45 G. Figure 1C shows the low field wing of the simulated spectrum with the parameters given above. The assignment of the 2.45 G doublet to H_4 is straightforward.

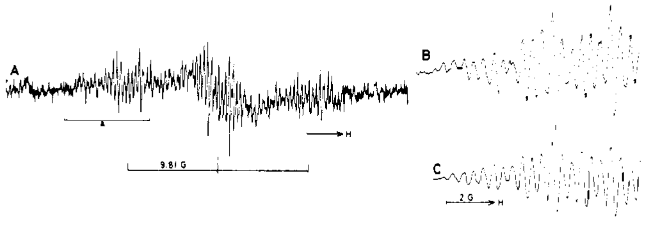


Figure 1, (A) ESR spectrum of the 1-norbornyl radical in cyclopropane solution at -121°; (B) accumulated spectrum of part a of the spectrum in A; (C) low-field wing of the simulated spectrum.

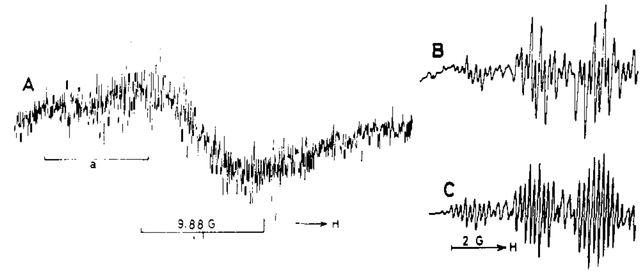
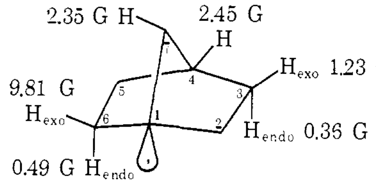


Figure 2, (A) ESR spectrum of the *exo,cis*-2,3-dideuterio-1-norbornyl radical at -122°; (B) computer averaged spectrum of part a of the spectrum in A; (C) low-field wing of the simulated spectrum.

Table I. INDO Hyperfine Coupling Constants (G) for the 1-Norbornyl Radical

Z, Å	H_{2exo}	H_{2endo}	H_{3exo}	H_{3endo}	H_4	H_7
0.0	7.67	0.19	0.31	0.17	2.46	1.23
0.1	9.67	0.30	0.73	0.12	3.64	1.36
0.2	11.91	0.47	1,44	0.10	5.68	1.44
0.3	14.42	0.67	2.64	0.12	8.99	1.43
Obsd	9.81	0.49	1.23	0.36	2.45	2.35

For assignments of the hyperfine splitting constants (hfsc) of the triplets, the *exo,cis*-2,3-dideuterio-1-norbornyl radical[7] was examined at -122°. Figure 2A shows a whole spectrum of the deuterated radical. Figure 2B shows the low field wing of the spectrum (underlined part a of Figure 2A) obtained by computer averaging of signals from 22 samples. The spectra were analyzed as three sets of doublets (9.88, 1.23, and 2.53 G) of three sets of 1:2:1 triplets (2.38, 0.53, and 0.34 G) further slit into two sets of 1:1:1 triplets (1.50 and 0.17 G). A comparison of these parameters with those of the 1-norbornyl radical shows that the hfsc's of 9.81 and 1.23 G belong to H_{2exo} and H_{3exo}, and that the hfsc's of 2.35, 0.49, and 0.36 G are due to H_7, H_{2endo}, and H_{3endo}. An inspection of a stereomodel suggests the assignment of the 9.81 G triplet to H_{2exo} and H_{6exo}. The proton hfsc's of the radical were calculated by an unrestricted Hartree–Fock method with INDO approximations[8] and are listed in Table I. INDO calculations were performed with the structure in which H_1 was simply taken off from the parent molecule[9] and also with structures in which C_1 was displaced Z Å (Z = 0.1, 0.2, and 0.3) inward along the C_1–H_1 bond axis in the parent hydrocarbon. From a comparison between the calculated and observed hfsc's, the experimental hfsc's are assigned as shown below.



In Figure 3 the β-proton hfsc's of the 1-norbornyl radical are plotted against values of $\cos^2 \theta$, where θ are the dihedral angles between the axis of the odd electron orbital on C_1 and the C_β–H_β bonds (approximated by the dihedral angles between the C_1–H_1 bond axis and the corresponding C–H bonds in norbornane[9]). The three experimental values of $a_\beta{}^H$ fit fairly well the line $a(H_\beta) = B\rho \cos^2 \theta$, where B = 16 G and ρ = 0.892 (INDO spin density on C_1 of the radical with Z = 0.1). This suggests that the $\cos^2 \theta$ relation for the β-proton hfsc's holds for the pyramidal 1-norbornyl radical although the coefficient B is about a quarter of the corre-

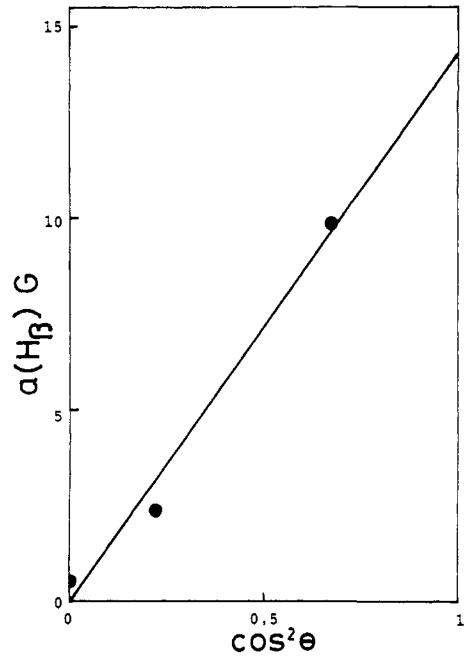


Figure 3. Relationship between the β-proton hfsc's of the 1-norbornyl radical and the dihedral angles θ.

sponding constant for planar radicals. The β-proton hfsc's of 1-adamantyl and bicyclo[2.2.2]oct-1-yl radicals (6.58 and 6.64 G, respectively)[10] are about twice as large as the values predicted from the relationship in Figure 3. Thus the B value seems to have a large dependence on the degree of nonplanarity at the radical site.

The bridgehead proton hfsc in the 1-norbornyl radical (2.45 G) is somewhat smaller than the hfsc of the bridgehead proton in the bicycl[2.2.2]oct-1-yl radical (2.69 G),[10] although the H_4 in the former is closer to the radical site than the bridgehead proton in the latter radical. The calculated value of $a(H_4)$ for the 1-norbornyl radical in Table I increases with increasing flattering of the radical site and with the closer approach of C_4 to C_1. This suggests that the odd electron is delocalized onto the bridgehead hydrogen atom through a "through-space" mechanism (i.e., rear-lobe overlap, homohyperconjugation[11]) in the case of the 1-norbornyl radical, whereas in the bicyclo[2.2.2]oct-1-yl radical a "through-bond" interaction is dominant.[10] When the "through-space" interaction between C_1 and C_4 was artificially turned off in performing INDO calculations, the calculated $a(H_4)$ of the 1-norbornyl radical (Z = 0.0 Å) decreased from 2.46 to 0.56 G. On the other hand $a(H_4)$ of the bicyclo[2.2.2]oct-1-yl radical[12] was calculated to increase from 3.20 to 6.83 by omitting the "through-space" interaction between C_1 and C_4 in the INDO calculation.[13] These results also support conclusions on the odd electron delocalization mechanisms mentioned above. This type of interchange of the dominant interaction accompanying the change of the number of bridging carbon atoms has been predicted in a theoretical study of the interaction between lone pairs in bridgehead diazabicyclic alkanes.[14]

The further experimental confirmation of the assignments of the hfsc's in the 1-norbornyl radical as well as theoretical studies on the effects of "through-space" and "through-bond" interactions on long-range hfsc's are in progress and will be published in the near future.

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Mechanism of the Reaction of Dithiols with Flavins

Sir:

We are extending the work of Gascoigne and Radda[1] on the aqueous reaction of flavins (e.g., 3-carboxymethyllumiflavin (I) which cannot undergo ionization at N(3) (riboflavin p$K_a \sim 10$)[2]) with dithiols (e.g., dithiothreitol (DTT)). We confirm that the reaction is first order in flavin and dithiol. Linear buffer catalysis is observed between pH 7 and 11 and a change in rate determining step occurs below pH 7 and above pH 11. Our results support the mechanism depicted in Scheme I, in which a C(4a) adduct is formed. This scheme may be compared with mechanisms suggested previously by others.[1,3]

Data (open circles) for the solvent reaction are compared in Figure 1 with a theoretical curve (solid line) based on best fit values for the rate constants for attack processes and for breakdown of the covalent intermediate.[4] The correspondence between curves a0, a1, a2, and b in Figure 1 and the rate constants of Scheme I is presented in Table I. Details of the kinetic analysis shall be presented elsewhere.