

dependence of l and m , i.e., $l \cong (1 - m)/0.7$, and the equivalence of l and $(1 - Q)$ values (see Table I) for such substrates should be noted.

The full paper describing this work will present comprehensive analyses of literature data using eq 1 and 5, as well as more extensive listings of N_{BS} and l constants, and will provide comparisons of various treatments.

Acknowledgment. This work was supported by grants from the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, Hoffmann-La Roche, Inc., Nutley, N. J., as well as a NATO Postdoctoral Fellowship (to T. W. B.), administered by the Science Research Council, England, and a National Institutes of Health Predoctoral Fellowship (to F. L. S.). We thank Professor Paul E. Peterson for exchange of information prior to publication. W. Sliwinski provided assistance in the computer data analysis.

T. W. Bentley, F. L. Schadt, P. v. R. Schleyer*

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received August 21, 1971

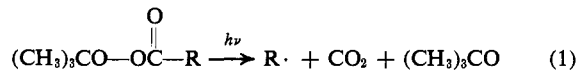
Electron Spin Resonance Spectra and Structure of Bridgehead Adamantyl and Bicyclo[2.2.2]octyl Free Radicals

Sir:

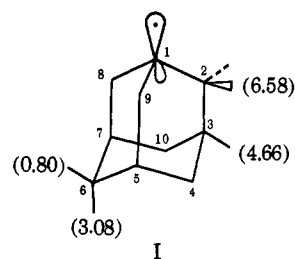
The behavior of organic intermediates can be probed effectively at bridgehead positions of bridged ring systems.¹ Large variations in carbonium ion reactivities are observed.^{1a,c} Reactivity differences in radical reactions are smaller, but are still appreciable.^{1a,1c,2}

The esr spectra of the authentic 1-adamantyl (I) and 1-bicyclo[2.2.2]octyl (II) radicals are reported here for the first time.⁴ These spectra show noteworthy features: anomalously low β hyperfine coupling constants but large δ long-range couplings. In addition, I shows a large γ coupling constant.

The esr spectrum of the 1-adamantyl radical (Figure 1) can be obtained by *in situ* uv photolysis of a dilute solution of *tert*-butyl 1-peroxyadamantanecarboxylate in cyclopropane⁵ (eq 1, R = 1-adamantyl). The com-



plex hyperfine structure can be reconstructed (Figure 1) on the basis of a septet of 6.58 G and three quartets of 4.66, 3.08, and 0.80 G, respectively ($T = -120^\circ$). Comparison with the results of INDO calculations (*vide infra*) suggests the assignment of the quartet hyperfine coupling constants given below (I).⁶



Similarly, photolysis of *tert*-butyl peroxybicyclo[2.2.2]octanecarboxylate yields the spectrum of the 1-bicyclo[2.2.2]octyl radical⁴ which is readily analyzed in terms of two septets of 6.64 and 0.89 G and a doublet of 2.69 G ($T = -74^\circ$). These coupling constants are

Table I. INDO Hyperfine Coupling Constants (G) for Bridgehead Radicals^a

ΔZ , Å ^b	a_{β^H}	a_{γ^H}	a_{δ^H}	$a_{1^3C_1}$	Rel energy ^c
1-Adamantyl (I)					
0.0	5.37	3.47	1.04 ^d	114.5	0.0
0.1	6.45	4.76	1.18 ^d	81.8	-17.07
0.2	7.59	6.57	1.31 ^d	52.9	-24.95
(Exptl)	6.58	4.66	0.80 ^d	3.08 ^e	
1-Bicyclo[2.2.2]octyl (II)					
0.0	5.12	0.72	3.28	114.9	0.0
0.1	6.07	1.05	2.17	81.6	-16.57
0.2	7.01	1.54	0.84	52.3	-24.16
(Exptl)	6.64	0.89	2.69)		

^a For the radicals retaining the structure of the parent hydrocarbons ($\Delta Z = 0$), the calculations assume tetrahedral angles throughout, C-C bond lengths of 1.54 Å, and C-H bond lengths of 1.09 Å. All calculated constants are positive. ^b Inward displacement of the spin-bearing bridgehead carbon along the symmetry axis. ^c Difference between the energy of the tetrahedral radical and the energies of the flattened radicals in kilocalories per mole. ^d Equatorial δ protons. ^e Axial δ protons.

There have been several recent studies of the radicals derived from γ - and X-irradiated adamantane.³ Although production of the 1-adamantyl radical was claimed,^{3a} this interpretation has been shown to be in error.^{3b,c}

(1) Reviews: (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. All-cyclic Chem.*, **1**, 283 (1966); (b) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (c) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

(2) For a review with pertinent references, see C. Rüchardt, *Angew. Chem.*, **82**, 845 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(3) (a) D. R. Gee, L. Fabes, and J. K. S. Wan, *Chem. Phys. Lett.*, **7**, 311 (1970); (b) L. Bonazzola and R. Marx, *ibid.*, **8**, 413 (1971); (c) J. R. Ferrell, G. R. Holdren, Jr., R. V. Lloyd, and D. E. Wood, *ibid.*, **9**, 343 (1971).

nearly independent of temperature: at -102° the values are 6.59, 0.89, and 2.69 G (peak-to-peak line width, -0.12 G). The 2.69-G doublet is obviously caused by the interaction of the unpaired electron with

(4) γ -Irradiation of bicyclo[2.2.2]octane gives the 2 and not the 1 radical (L. Bonazzola and R. Marx, *Mol. Phys.*, **19**, 405 (1970)).

(5) For experimental details see: (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968); (b) *ibid.*, **93**, 846 (1971); (c) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3940 (1969).

(6) The γ bridgehead protons, assigned the largest of the quartet splittings, are in the perfect W arrangements with the half-occupied orbital expected to lead to strong interaction with the unpaired electron (G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 87 ff; G. A. Russell, P. R. Whittle, and R. G. Keske, *J. Amer. Chem. Soc.*, **93**, 1467 (1971)).

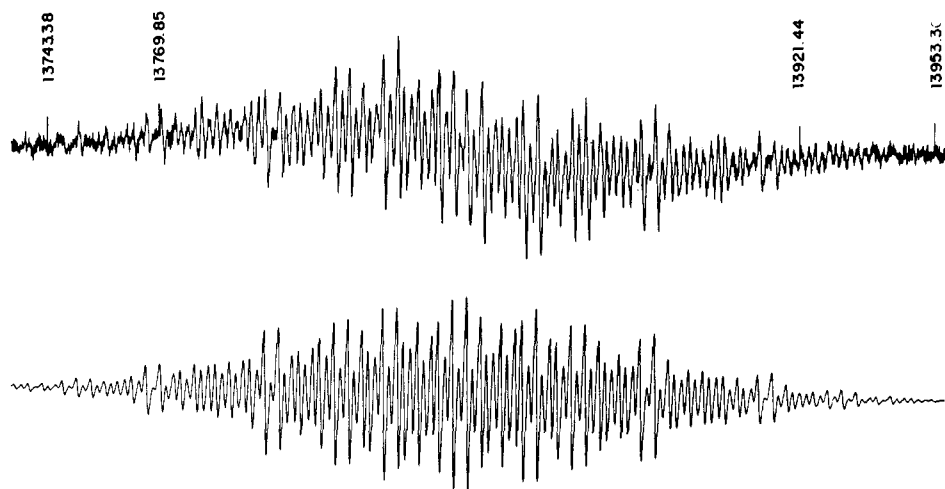


Figure 1. Experimental and calculated esr spectra of the 1-adamantyl radical (I) in cyclopropane solution at -120° . The proton nmr field markers are in kHz.

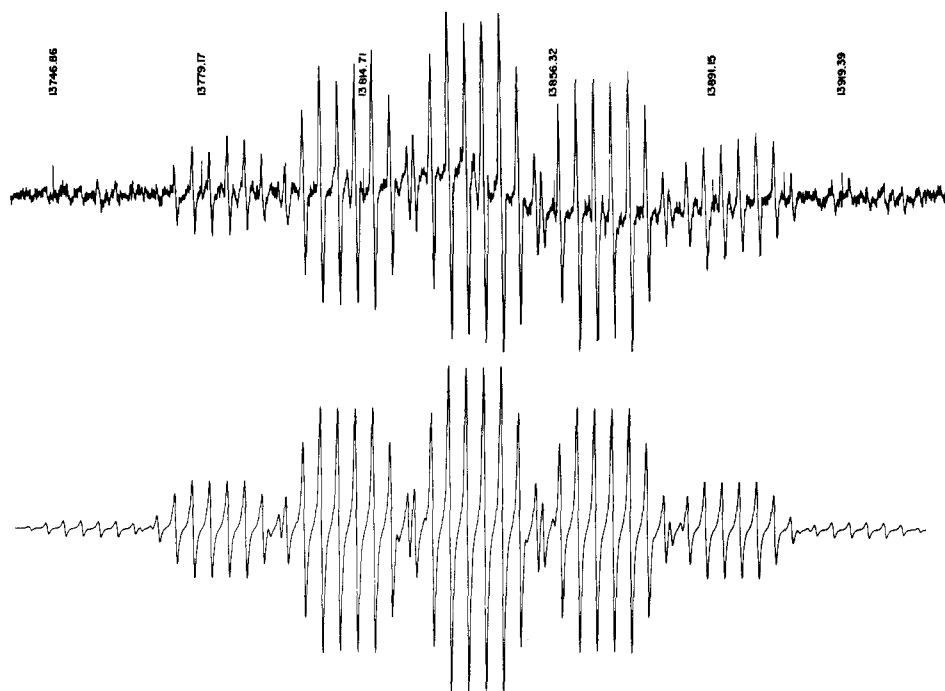


Figure 2. Experimental and calculated esr spectra of the 1-bicyclo[2.2.2]octyl radical (II) in cyclopropane solution at -74° .

the single bridgehead δ proton. This is confirmed by the absence of this splitting in 4-alkyl derivatives; otherwise 4-alkyl groups only produce slight changes. Thus, in the 4-methylbicyclo[2.2.2]octyl radical (-102°) septets with 6.44 and 0.75 G are found (a^{CH_3} is unresolved but the line width is 0.22 G). In the 4-*tert*-butylbicyclo[2.2.2]octyl radical (-125°) the values are 6.63 and 0.73 G, and the *tert*-butyl line width is 0.13 G. By analogy with the 1-adamantyl radical, the larger hyperfine coupling constants in the bicyclooctyl radicals (~ 6.6 G) are assigned to the β -hydrogens; the final assignments shown below are supported by INDO calculations.

The β isotopic hyperfine coupling constants in I and II are of comparable magnitude (6.6 G) and are unusually small.⁷ We attribute these small values to

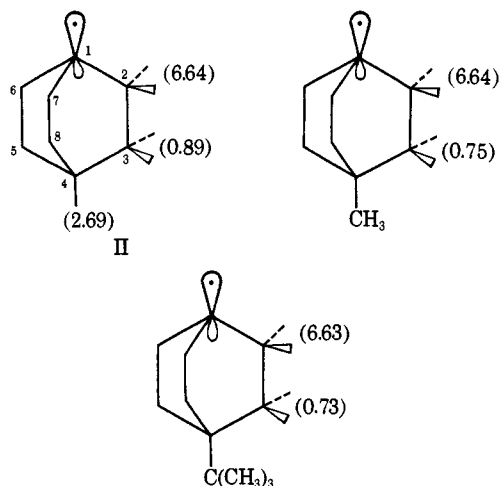
(7) A hypothetical idealized planar bridgehead system with normal bond angles should have $a_\beta \sim 11.4$ G. This estimate is based on the

pyramidal structures at the bridgehead radical sites, an interpretation supported most convincingly by INDO calculations⁸ (Table I). In these calculations the progressive flattening of the radical site from the tetrahedral geometry in the parent hydrocarbon was approximated by simply displacing the spin-bearing carbon inward along the symmetry axis by increments of 0.1 Å.⁹ For both radicals best agreement between the experimental and calculated values of all coupling constants was obtained for slightly flattened ($\Delta Z \cong 0.1$

familiar relationship, $a_\beta = A + B \cos^2 \theta$, by neglecting A as usual, assuming $B/2 = 22.7$ G (from a_β of the *tert*-butyl radical),⁵ and taking $\theta = 60^\circ$. A referee has pointed out that real planar bridgehead systems would have distorted geometries, and the expected hyperfine coupling constants cannot be estimated this simply.

(8) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1968); J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968). Obtained from the Quantum Chemistry Program Exchange, Indiana University.

(9) Coplanarity of C_1 , C_2 , C_8 , and C_9 in I (II is similar) is achieved with $\Delta Z = 0.5$ Å.



Å) but still distinctly pyramidal radicals.^{10,11} A more definite statement concerning the relative geometries of the radical sites, however, must await bridgehead ¹³C-hyperfine coupling data for these radicals (see calculated values in Table I).

The INDO molecular orbital calculations also predict remarkably well the magnitudes of the γ and δ proton hyperfine coupling constants (Table I). The three axial and three equatorial δ protons in the 1-adamantyl radical are strongly differentiated¹² with the largest interaction predicted for the axial protons. Surprisingly, the hyperfine coupling constant of the bicyclooctyl δ proton, situated directly behind the half-filled orbital, not only is smaller in magnitude than the δ -axial hydrogen in I, but also is predicted by the INDO calculations to *decrease* with increased flattening and closer approach of the bridgehead radical center. This casts doubt on the importance of the often involved "backlobe" effect.^{1,12} A "through-bond" mechanism¹³ for spin delocalization would appear to afford a superior explanation for these observations. In I, the δ -axial C-H bonds and the C₂-C₃, C₇-C₈, C₅-C₉ bonds are all aligned in parallel with the half-filled orbital at C. In II a similar parallel alignment is found with C₄-H, C₂-C₃, C₇-C₈, C₅-C₆, and the C₁ half-filled orbital. The predicted (INDO) *positive* signs for these long-range coupling constants are also in accord with such a direct mechanism of direct delocalization of spin density.

Acknowledgments. We thank Drs. J. K. Kochi (Indiana) and A. Rassat (Grenoble) for helpful discussions and Mr. M. Cushing for technical assistance. One of the authors (P. J. K.) would like to thank Professor D. Hadži (Ljubljana) for the hospitality extended to him during the later stages of this work under a program of exchange sponsored by the National Academy of Science and the Council of Yugoslav Academies.

(10) Recent calculations by the extended Hückel MO method also predict a pyramidal structure for the 1-adamantyl radical (H. Fujimoto, Y. Kitagawa, H. Hao, and K. Fukui, *Bull. Chem. Soc. Jap.*, **43**, 52 (1970)).

(11) In view of the rather crude geometrical parameterization, no importance is attached to the fact that the structures best fitting the esr data do not correspond to energy minima (*cf.* Table I).

(12) This differentiation, not seen in the 60-MHz nmr spectrum of the 1-adamantyl cation (P. v. R. Schleyer, R. C. Fort, Jr., W. E. Watts, G. A. Olah, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **86**, 4195 (1964)), is revealed at 100 and 250 MHz (G. Mateescu, Ph.D. Thesis, Case Western Reserve University, 1971). However, the chemical-shift difference between the δ protons is small.

(13) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

Work at Princeton on cage molecules is supported by National Institutes of Health Grant No. AI-07766.

P. J. Krusic, T. A. Rettig
Contribution No. 1774, Central Research Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

P. v. R. Schleyer
Frick Chemical Laboratory, Princeton University
Princeton, New Jersey 08540
Received June 17, 1971

Orbital Hybridization in Small Fused Rings

Sir:

The marked correlation between hybridization and directly bonded ¹³C-H spin-spin coupling constants¹⁻⁴ has provided the basis for using the coupling parameter to estimate the extent of s character in carbon-hydrogen bonds. The empirical relationships between J_{C-H} and s_i , the fractional s character in the C-H bond, is given by eq 1, where K_{C-H} was found to be 500 Hz. The

$$J_{C-H} = K_{C-H}s_i \quad (1)$$

succeeding work of Lynden-Bell and Sheppard⁵ and of Frei and Bernstein⁶ on ¹³C enriched compounds extended these hybridizational arguments to directly bonded ¹³C-¹³C spin-spin coupling constants, and the relationship which characterizes this dependence on the hybridization of the two directly bonded carbons is

$$J_{C-C} = K_{C-C}s_{i(j)}s_{j(i)} \quad (2)$$

where $s_{i(j)}$ and $s_{j(i)}$ are the fractional s characters at each of the two respective bonded carbon atoms i and j . The second subscript in parentheses designates the second atom in the interacting pair. The constant of proportionality, K_{C-C} , was found⁶ to lie in the range 500-575 Hz. While the theoretical work of Pople and Santry⁷ and of Maciel, *et al.*,^{8,9} indicates that other electronic features affect spin-spin coupling constants, these studies do confirm the importance of hybridizational effects especially in molecules of low polarity such as found in simple hydrocarbons. Weigert and Roberts¹⁰ using a $K_{C-C} = 550$ Hz exhibited that the s character in cyclopropyl rings is approximately one-sixth in the C-C bonds indicating that p character dominates the carbon-carbon bonding in such small rings. As eq 2 involves two variables $s_{i(j)}$ and $s_{j(i)}$, an additional condition such as symmetry or other independent data must obtain before eq 2 can be applied. Table I contains the experimental J_{C-C} values obtained on an XL-100-15 Varian spectrometer for a variety of small ring systems. (Note: allene is considered here as a pseudospiro compound for convenience.) The

(1) M. Karplus and D. M. Grant, *Proc. Nat. Acad. Sci. U. S.*, **45**, 1269 (1959).

(2) N. Müller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(3) J. N. Shoolery, *ibid.*, **31**, 1427 (1959).

(4) J. Ranft, *Ann. Phys. (Leipzig)*, **8**, 322 (1961).

(5) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962).

(6) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

(7) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(8) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1, 11, 4151, 4497, 4506 (1970).

(9) P. D. Ellis and G. E. Maciel, *ibid.*, **92**, 5829 (1970).

(10) F. J. Weigert and J. D. Roberts, *ibid.*, **89**, 5962 (1967).