

- (14) J. M. Ziman, "Elements of Advanced Quantum Theory", Cambridge University Press, Cambridge, 1969, p 97.
 (15) M. Dombek, K. R. Sundberg, and K. Ruedenberg, private communication.
 (16) W. England, L. S. Salmon, and K. Ruedenberg, *Fortshr. Chem. Forsch.*, **23**, 31 (1971), and references therein.
 (17) K. D. Jordan, K. M. Griffing, J. Kenney, E. L. Andersen, and J. Simons, *J. Chem. Phys.*, **64**, 4730 (1976).
 (18) B. Liu, K. O.-Ohata, and K. Kirby-Docken, *J. Chem. Phys.*, **67**, 1850 (1977).
 (19) C. F. Melius and W. A. Goddard, III, *J. Chem. Phys.*, **56**, 3348 (1972).
 (20) Deviations from the linear symmetry in this case will give the products $Li(^2S) + H(^2S) + Li(^2S)$ since the in-plane component of $^3\Pi$ mixes with the repulsive $^3\Sigma^+$ surface as $^2A'$ along C_s symmetry paths.

Theoretical Analysis of Long-Range Hyperfine Interactions in Bicyclic Free Radicals. Application Conditions for the W and Anti-W Rules

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Abstract: The ab initio spin-restricted SCF and perturbative configuration interaction methods have been applied to the bicyclobutyl radical. Long-range interactions are found to be critically dependent on the geometry at the radical site. The conditions required for a correct assignment of long-range couplings by means of the W rule are presented. As in aliphatic radicals, strong couplings come from a cumulative effect of the spin-delocalization and spin-polarization contributions.

Long-range interactions have aroused considerable interest because of their high stereospecificity and unusual values, especially in bicyclic radicals.² Assignment of the observed couplings is made in most cases following the so-called "W arrangement".^{2a} However, the conditions required for applying the W rule are still a matter of discussion.

In this respect, we wish to report the main results of an ab initio study of proton hyperfine couplings in the simplest bicyclic radical, i.e., the bicyclobutyl radical observed by Krusic et al. some years ago.³ Our main goal has been to investigate how long-range interactions can be modified by structural deformations occurring at the radical site. The geometrical parameter which has been varied is the torsion angle α between the CH bond and the CCC plane. All other parameters have been kept constant and taken from bicyclobutane.⁴ No geometry optimization has been attempted.⁵

The ground-state wave function is calculated according to the two Hamiltonian spin-restricted SCF formalism developed by Roothaan.⁶ A configuration interaction including all spin-adapted monoexcited configurations with three uncoupled electrons is then carried out using the Epstein-Nesbet formulation of perturbation theory.⁷ The total Fermi contact splitting of any nucleus M is given by

$$a_M = a_d + a_{sp}$$

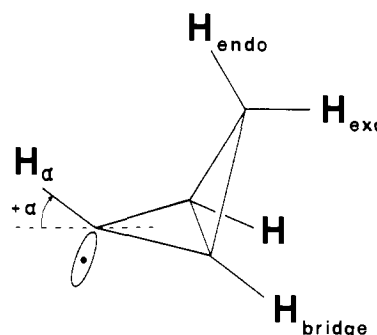
where

$$a_d = \left(\frac{8\pi}{3}\right) \left(\frac{g_e}{g_0}\right) g_M \beta_M |\phi_u(\mathbf{r}_M)|^2$$

$$a_{sp} = \left(\frac{8\pi}{3}\right) \left(\frac{g_e}{g_0}\right) g_M \beta_M \sum_d \sum_{v^*} -2 \frac{\langle \phi_u \phi_d | \phi_u \phi_{v^*} \rangle}{E_0 - E_{d \rightarrow v^*}} \phi_d(\mathbf{r}_M) \phi_{v^*}(\mathbf{r}_M)$$

The ϕ_d are the doubly occupied MOs of the ground state, the ϕ_{v^*} are the virtual MOs, and ϕ_u is the orbital containing the unpaired electron. Under those conditions a_d and a_{sp} correspond to the contributions arising from the delocalization

effects (at the SCF level) and from the spin-polarization effects (at the CI level), respectively.⁸ For coherence with our preceding studies of hydrocarbon radicals,⁹ the same Gaussian basis (9s,5p/4s) has been used and the canonical MOs have been converted into quasi-localized MOs according to the same localization criterion.¹⁰



The variation of proton hyperfine splittings with torsion at the radical site is presented in Figure 1. All couplings are given in gauss. Tables I and II present numerical tabulations of H_{endo} and H_{exo} coupling constants as functions of α .

α and β Coupling Constants. The present calculations confirm the high sensitivity of the α hydrogen coupling with bending at the radical site. The negative coupling found for $\alpha = 0^\circ$ which is almost entirely due to the spin polarization becomes positive for $|\alpha| > 30^\circ$ as a consequence of the rapid increase of the delocalization contribution.

For the β hydrogens (H bridge), the point to be outlined is that the coupling constant decreases when the H_α is moved toward the exo direction ($\alpha < 0$) more rapidly than when it is moved toward the endo direction ($\alpha < 0$). As a consequence, for a given torsion of the radical center, the coupling constant of a β proton trans with respect to the orbital containing the unpaired electron should be lower than the coupling constant of a cis proton.

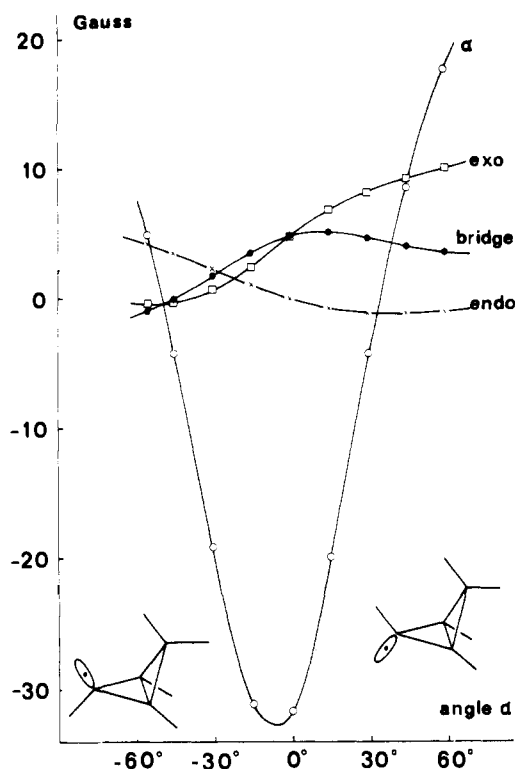
Experimental examples of inequivalent couplings are known for β protons in bicyclic radicals deriving from the bicy-

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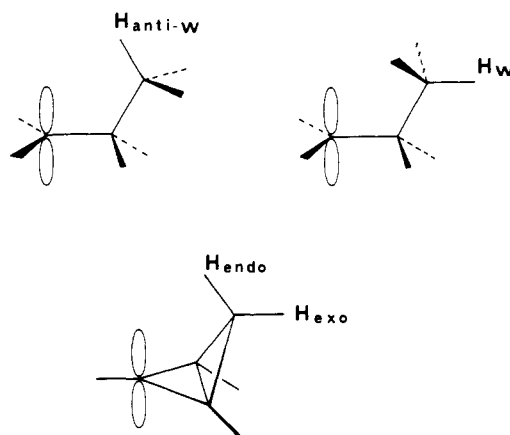
Table I. Calculated γ Splittings for *n*-Propyl and Bicyclobutyl Radicals (G)

	<i>n</i> -propyl ^{7b,c}		bicyclobutyl ($\alpha = 0^\circ$)	
	H_W	H_{anti-W}	H_{exo}	H_{endo}
a_d	2.64	1.11	2.81	0.63
a_{sp}	1.73	-0.91	1.78	-0.76
a	4.37	0.20	4.59	-0.13

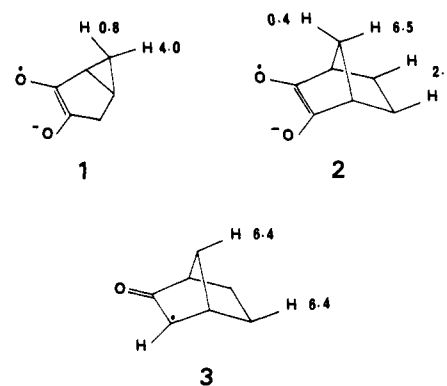
**Figure 1.** Hydrogen hyperfine coupling constants for bicyclobutyl radical.

clo[2.2.1]heptane series. They have been found consistent with a pyramidal geometry around the radical site with a bending of the exocyclic bond toward the endo direction.^{2b,d,g,h} Radicals **5** and **6** are typical examples which corroborate the theoretical calculations. It should be mentioned that similar results have been obtained for cyclopropyl^{9c} and oxiranyl¹¹ radicals in previous ab initio studies. They are also in complete agreement with recent experimental assignments of hyperfine splittings in free radicals deriving from cyclopropane¹² and oxiranyl derivatives.¹³ Once again the validity of the ab initio approach for the calculation of hyperfine coupling properties is confirmed while the INDO method yields to the opposite—erroneous—assignment of the splittings in that case.¹³

γ Coupling Constants for Planar Radical Sites. If the radical center is planar, the “W arrangement” of the bonds is realized between the exo proton and the orbital containing the unpaired electron. In this respect, bicyclobutyl can be compared to the planar *n*-propyl radical in the following conformations.



The different contributions to the γ splittings in both compounds are given in Table I. In the two cases, the contributions of delocalization and of spin-polarization effects (which are both positive) add in the W conformations (H_W and H_{exo}). They are opposite in sign and balance each other in the anti-W conformations to give small values (H_{anti} and H_{endo}). No crucial difference appears at this level of the theoretical approach between the aliphatic and bicyclic radicals. An illustration of this result can be found in the semidione series where monocyclic and bicyclic radicals present hyperfine couplings of the same magnitude for protons in the same stereochemical arrangement.¹⁴ If one considers now bicyclic compounds **1**,^{14,15} **2**,^{1a} and **3**,^{1b} where the radical centers are taken as planar, γ



protons corresponding to the “W arrangement” (H_{anti} and H_{exo}) exhibit large hyperfine splittings. By contrast the splittings due to protons in the anti-W arrangement (H_{syn} and H_{endo}) are weak or unobserved.

γ Coupling Constants for Bent Radical Sites. Evolution of γ couplings reported in Figure 1 can be analyzed in two ways.

Case 1. If the CH bond is bent toward the endo position ($\alpha > 0$), the W rule is still applying to H_{exo} and one observes an enhancement of the positive coupling. The endo coupling remains weak and negative.

Case 2. If the CH bond is bent toward the exo position ($\alpha < 0$), there are drastic changes in the couplings. No W arrangement can be found and the rule no longer applies. One

Table II. Variation of γ Splittings with the Torsion Angle of the Radical Center (G)

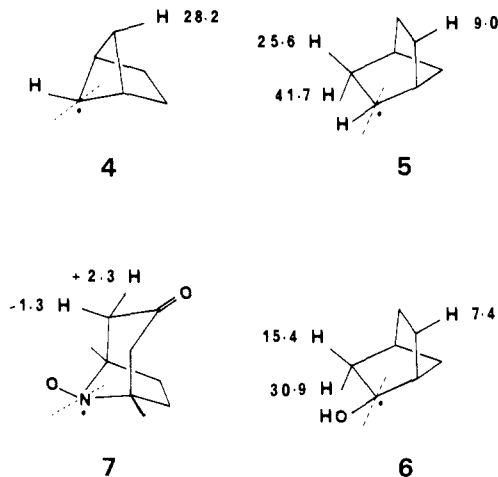
α	-45°	-30°	-15°	0°	15°	30°	45°
a_d	0.17	0.64	1.57	2.81	3.00	4.38	4.76
$H_{exo} a_{sp}$	-0.41	-0.06	0.68	1.78	2.86	3.66	4.27
a	-0.24	0.58	2.25	4.59	6.66	8.04	9.03
a_d	2.18	1.65	1.13	0.63	0.26	0.07	0.00
$H_{endo} a_{sp}$	1.21	0.57	-0.13	-0.76	-1.15	-1.30	-1.30
a	3.39	2.22	1.00	-0.13	-0.89	-1.23	-1.30

observes a complete reverse of the couplings. The endo coupling becomes the strongest one and positive. The exo coupling becomes negative. For intermediate torsions of $\alpha \approx -20^\circ$, both γ couplings are of the same magnitude and small so that they might be masked under low-resolution conditions.

These results throw a new light on a number of experimental studies of bicyclic compounds. Among the various examples which have been observed² let us consider **4**,¹ⁱ **5**,^{1h} and **6**^{1b} where the radical centers are taken as pyramidal with a bending of the exocyclic bond toward the direction indicated on the drawings.

The γ protons corresponding to the "W arrangement" (H_{endo} in **4**, H_{exo} in **5**, **6**) exhibit large hyperfine splittings. By contrast, the splittings due to the associated anti W protons (H_{exo} in **4**, H_{endo} in **5**, **6**) are weak or unobserved. This situation corresponds to case 1.

The remaining γ protons cannot be described by any W arrangement (H_{anti} , H_{syn} in **4**, **5**, **6**). The related splittings are



weak or unobserved. This situation corresponds to intermediate torsions in case 2.

Nitroxide **7**^{1e} provides a remarkable illustration, although its radical center is not totally localized on an atom included in the bicyclic skeleton. The x-ray structure of this compound has been determined¹⁶ and an out-of-plane torsion angle of 24° has been found, the N-O bond being tilted toward the axial direction. Furthermore, all couplings are known and can be attributed by comparison with substituted radicals.^{1e} The couplings reported by Rassat and Ronzaud corroborate the conclusions which can be obtained from the theoretical studies. The couplings corresponding to the "W arrangement" (H_{axial}) are stronger than those corresponding to the "anti-W arrangement" ($H_{\text{equatorial}}$). Moreover, their relative sign is coherent with the theoretical calculations on the simplest bicyclic radical. Other examples of geminal γ protons with coupling

opposite in sign and very different in magnitude are known in the nitroxide series.^{2d,1e,17} On the other hand, the couplings corresponding to protons which cannot be described by a "W or anti-W arrangement" (H_{exo} , H_{endo}) are very weak.

Table II, which gives the variation of the two theoretical contributions to the γ protons hyperfine splittings in the bicyclobutyl radical, is self-explanatory.

As in aliphatic radicals,^{8,9b} the γ couplings are determined by the interplay of the delocalization and spin-polarization terms (Table II), strong couplings coming from the cumulative effect of both contributions.

Our ab initio results unambiguously demonstrate the high sensitivity of long-range interactions to the geometry at the radical site and show the correct guide for better information on the geometry at the radical site—planar or pyramidal—and indicate the direction of the torsion starting from the values of the observed or nonobserved long-range coupling constants.

References and Notes

- (1) (a) Laboratoire de Chimie Organique Physique; (b) Laboratoire de Chimie Quantique.
- (2) (a) G. A. Russell, and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965). (b) J. Gloux, M. Guglielmi, and H. Lemaire, *Mol. Phys.*, **19**, 833 (1970). (c) R. Marx and L. Bonazzola, *ibid.*, **19**, 899 (1970). (d) T. Kawamura, T. Koyama, and T. Yonezawa, *J. Am. Chem. Soc.*, **92**, 7222 (1970). (e) A. Rassat and J. Ronzaud, *ibid.*, **93**, 5041 (1971). (f) A. Rassat and P. Rey, *Tetrahedron*, **29**, 2845 (1973). (g) T. Kawamura, T. Koyama, and T. Yonezawa, *J. Am. Chem. Soc.*, **95**, 3220 (1973). (h) T. Kawamura, Y. Sugiyama, and T. Yonezawa, *Mol. Phys.*, **33**, 1499 (1977). (i) T. Kawamura, S. Hayashida, and T. Yonezawa, *Chem. Lett.*, 267 (1977). (j) For a general discussion on the topic, we refer to the review by F. W. King, *Chem. Rev.*, **76**, 157 (1976).
- (3) P. J. Krusic, J. P. Jesson, and J. K. Kochi, *J. Am. Chem. Soc.*, **91**, 4566 (1969).
- (4) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).
- (5) The potential energy curve presents a double-well form with two minima close in energy ($\alpha = -45^\circ$, $E_{\text{SCF}} = -154.1283$ au; $\alpha = +38^\circ$, $E_{\text{SCF}} = -154.1253$ au). Although the couplings corresponding to the second minimum seem to be rather consistent with the ESR data ($H_2 = +4.40$, other couplings at 12.64, 7.85, and 0.81 G), a definitive assignment cannot, however, be made on the basis of the theoretical and experimental information available at present.
- (6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
- (7) (a) P. S. Epstein, *Phys. Rev.*, **28**, 695 (1926); (b) R. K. Nesbet, *Proc. R. Soc. London, Ser. A*, **230**, 312 (1955); (c) P. Millié, B. Levy, and G. Berthier, *Int. J. Quantum Chem.*, **6**, 155 (1973).
- (8) For further methodological details, we refer to the reader to Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, *J. Chem. Phys.*, **62**, 1 (1975).
- (9) (a) Y. Ellinger, A. Rassat, G. Berthier, and P. Millié, *Chem. Phys. Lett.*, **11**, 362 (1972); (b) Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, *J. Am. Chem. Soc.*, **95**, 2372 (1973); (c) Y. Ellinger, R. Subra, B. Levy, P. Millié, and G. Berthier, *J. Chem. Phys.*, **62**, 10 (1975).
- (10) S. F. Boys in "Quantum Theory of Atoms, Molecule and the Solid State", P. O. Lowdin, Ed., Academic Press, New York, N.Y., 1966, p. 253.
- (11) J. McKelvey and G. Berthier, to be published.
- (12) T. Kawamura, M. Tsumura, and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 373 (1977).
- (13) H. Itzel and H. Fischer, *Helv. Chim. Acta*, **59**, 880 (1976).
- (14) G. A. Russell and R. G. Keske, *J. Am. Chem. Soc.*, **92**, 4458 (1970).
- (15) G. A. Russell in "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N.Y., 1968, p. 87.
- (16) A. Capiomont, *Acta Crystallogr., Sect. B* **29**, 1720 (1973).
- (17) R. M. Dupuyre and A. Capiomont, *J. Mol. Struct.*, in press.