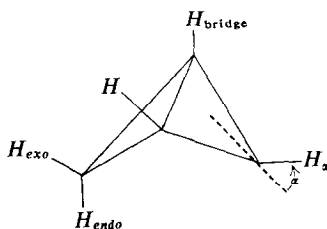


An *Ab Initio* Study of the Bicyclobutyl Radical: An *Anti-W* Long-Range Coupled System

The bicyclobutyl radical is the smallest *rigid* structure for which long-range isotropic hyperfine coupling constants have been reported (1). For this reason, the bicyclobutyl radical is of particular theoretical interest in regard to elucidating the nature of long-range coupling. The bicyclobutyl radical is interesting for a second important reason; it may well be one of the few significant counterexamples to the *W*-plan arrangement formulated by Russell and co-workers (2–4).

The *W*-plan is an empirical rule which predicts that the largest long-range couplings occur when there is an approximate coplanar zig-zag arrangement of bonds between the $2p_z$ orbital “containing the unpaired electron spin” (or a sizable fraction of it) and the long-range proton of interest. Extension to more distant protons is accommodated by $2.5V$ and $3V$ arrangements of bonds with respect to the $2p_z$ orbital.

The bicyclobutyl radical geometry employed was based essentially on the structural parameters reported by Cox *et al.* (5). We have chosen the angle α to be 15° , in order to make a comparison with the INDO calculations reported by Krusic *et al.* (1). No attempt has been made to optimize the geometry to fit the observed hyperfine couplings, nor have we attempted to optimize the orbital exponents. The size of this radical makes this prohibitive in terms of the required computer time. The calculations have been



carried out using the unrestricted Hartree–Fock (UHF) approach with a Gaussian basis (6, 7). Calculations at both the minimal basis (STO–3 G) and extended basis (4–31 G) have been carried out. The calculations are restrictive in two ways. The effects of spin polarization are not accommodated. Their inclusion would require either the application of perturbation theory on the single-determinant ground-state wavefunction or configuration interaction calculations. The UHF ground state is not an eigenstate of S^2 and the results will be in error because of this. However, it is felt that the results are still likely to provide at least qualitative estimates of the appropriate hyperfine coupling constants.

The bicyclobutyl radical displays a rigid stereochemical environment, which has been emphasized by both experimental studies (1–3) and computational efforts (8–11), as an essential factor for the appearance of long-range coupling. The *ab initio* calculations carried out for the bicyclobutyl radical reflect this situation. The calculated

proton isotropic hyperfine coupling constants are listed in Table 1. The entries in Table 1 are results for the minimal basis set, STO-3 G (min), extended basis set, 4-31 G (ext), and the last column lists the experimental values.

TABLE 1
CALCULATED ISOTROPIC PROTON HYPERFINE COUPLING CONSTANTS FOR THE
BICYCLOBUTYL RADICAL (IN GAUSS)

	$a(\text{min})$	$a(\text{ext})$	$ a (\text{exp})^a$
H_{bridge}	4.23	4.02	4.40
H_{α}	-62.81	-59.42	12.64
H_{exo}	-0.55	1.35	0.81 ^b
H_{endo}	1.69	4.63	7.85 ^b

^a Experimental data (absolute values) from Ref. (1).

^b The assignment of a_{exo} and a_{endo} was made on the basis of INDO calculations.

The important feature of the calculation is that we find the a_{endo} coupling constant to be larger than the a_{exo} coupling, in contradiction to what would be anticipated on the basis of the W-plan prediction. Our calculation supports the results of INDO calculations carried out by Krusic *et al.* (1) for the ordering of a_{endo} greater than a_{exo} . It is of interest to note that the *exo*-proton coupling constant changes sign for the two different basis sets which we have employed. This should serve as a warning that, within the UHF approach, smaller coupling constants may be very sensitive to basis set changes. This effect is well noted for larger coupling constants in detailed *ab initio* calculations on small radicals, for example, the methyl radical (12). The actual values for a_{exo} and a_{endo} are in quite satisfactory agreement with the experimental results. The corresponding INDO results are $a_{\text{endo}} \approx 4.6$ G and $a_{\text{exo}} \approx -0.8$ G. The bridgehead couplings are in very close agreement with the experimental values, which is probably fortuitous. The α -proton coupling constant is excessively large, a feature we have found in other situations in which the UHF procedure is employed. The corresponding INDO results are $a_{\text{bridge}} \approx 7.7$ G and $a_{\alpha} \approx -12.9$ G. Our calculated results could be improved by geometry optimization; however, the usually employed energy optimization criterion does not necessarily lead to coupling constants in closer agreement with experiment. The energy of the conformation of the bicyclobutyl radical we have taken is -152.33663 a.u. at the minimal basis level and -153.97355 a.u. at the extended basis level. There is a need for further experimental work on the bicyclobutyl radical, in order to verify the assignment of a_{endo} and a_{exo} . Information on the signs of these two couplings would be of particular interest.

It has been found in calculations on the propyl fragment that contributions arising from spin polarization and spin delocalization are of opposite sign and approximately the same order of magnitude for the *anti*-W conformation (8, 11). The resultant hyperfine coupling is small. The opposite situation was found for the W-arrangement. The spin polarization and spin delocalization contributions are of the same sign, with a result that the overall coupling is large. Similar effects have been found for the *syn*

and *anti* protons of the bicyclo[2.2.1]heptane semidione radical anion (9, 10). In the absence of a configuration interaction calculation to determine the appropriate spin polarization contributions to the *exo* and *endo* protons, we may speculate that the situation found for the propyl radical and the bicyclo[2.2.1]heptane semidione radical anion must be opposite to the situation which exists for the bicyclobutyl radical, if the results for the INDO and the present *ab initio* UHF calculations are at least qualitatively correct. There is clearly a need for a detailed *ab initio* investigation, at the configuration interaction level, of the general angular and distance dependence of long-range coupling to determine the circumstance under which the W-plan or anti-W plan will apply.

REFERENCES

1. P. J. KRUSIC, J. P. JESSON, AND J. K. KOCHI, *J. Amer. Chem. Soc.* **91**, 4566 (1969).
2. G. A. RUSSELL, in "Radical Ions" (E. T. Kaiser and L. Kevan, Eds.), p. 87, Interscience, New York, 1968.
3. G. A. RUSSELL, in "Determination of Organic Structures by Physical Methods" (F. C. Nachod and J. J. Zuckerman, Eds.), Vol. 3, p. 293, Academic Press, New York, 1971.
4. F. W. KING, *Chem. Rev.*, in press.
5. K. W. COX, M. D. HARMONY, G. NELSON, AND K. B. WILBERG, *J. Chem. Phys.* **50**, 1976 (1969).
6. W. J. HEHRE, R. F. STEWART, AND J. A. POPLER, *J. Chem. Phys.* **51**, 2657 (1969).
7. R. DITCHFIELD, W. J. HEHRE, AND J. A. POPLER, *J. Chem. Phys.* **54**, 724 (1971).
8. Y. ELLINGER, A. RASSAT, R. SUBRA, AND G. BERTHIER, *J. Amer. Chem. Soc.* **95**, 2372 (1973).
9. F. W. KING AND F. C. ADAM, *Mol. Phys.* **29**, 337 (1975).
10. F. W. KING, *J. Magn. Resonance* **17**, 362 (1975).
11. Y. ELLINGER, R. SUBRA, B. LEVY, P. MILLIE, AND G. BERTHIER, *J. Chem. Phys.* **62**, 10 (1975).
12. S. Y. CHANG, E. R. DAVIDSON, AND G. VINCOW, *J. Chem. Phys.* **52**, 1740 (1970).

FREDERICK W. KING*
H. BERNHARD SCHLEGEL†

Department of Chemistry
Queen's University
Kingston, Ontario, Canada K7L 3N6

Received January 8, 1976

* Present address: Physical Chemistry Laboratory, Oxford University, Oxford, England.

† Present address: Department of Chemistry, Princeton University, Princeton, New Jersey 08540.