

## AN AB INITIO CALCULATION OF THE CYCLOPROPYLCARBINYL RADICAL

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### ABSTRACT

Ab initio calculations at minimal (STO-3G) and extended (4-31G) basis levels have been carried out for the cyclopropylcarbinyl radical using the unrestricted Hartree–Fock procedure. It is found that the ordering of the long-range proton isotropic hyperfine coupling constants are opposite to the results obtained from semi-empirical INDO calculations. The coupling constants for the extended basis set are  $a_{exo} = -1.71$  G,  $a_{endo} = -4.25$  G,  $a_{\beta} = 11.41$  G,  $a_{\alpha_1} = -66.01$  G and  $a_{\alpha_2} = -64.73$  G.

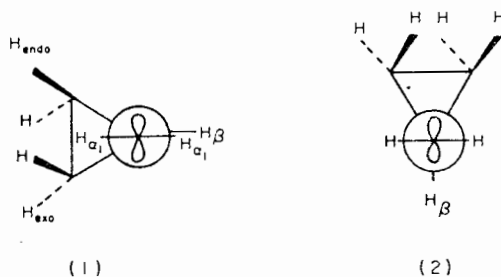
### INTRODUCTION

The cyclopropylcarbinyl radical and its related derivatives have been the subject of active investigation [1–11]. Interest has centered on the stereochemical preferences which these radicals adopt in solution. The stereospecific long-range proton isotropic hyperfine interactions which occur in the cyclopropylcarbinyl radical have received special attention. In this respect, the cyclopropylcarbinyl radical represents an ideal system in which to explore, theoretically, the stereospecific long-range interactions. Although this radical is a fairly small molecular system compared with the majority of other radicals displaying long-range coupling [12], the uncertainty in our knowledge of the geometry complicates the efforts to investigate the long-range interactions. Such interactions are known to be highly sensitive to changes in geometry [12–15].

In the present paper, we report the results of unrestricted Hartree–Fock (UHF) calculations on the cyclopropylcarbinyl radical, with a view to determining both the assignment of the long-range coupling constants  $a_{endo}$  and  $a_{exo}$ , and also their sign. Both of these questions are of considerable importance because the mechanistic arguments, which are put forward to rationalize the long-range coupling constants, are critically dependent on the knowledge of the sign of the coupling constant and on the correctness of the experimental assignment.

## RESULTS AND DISCUSSION

The calculations reported in this paper have been carried out using the Gaussian 70 [16] program system with two different Gaussian basis sets. These are the minimal basis set (STO-3G) [17a] and the extended basis set (4-31G) [17b]. The cyclopropylcarbinyl radical has two possible extreme conformations, the bisected conformation (I) and the perpendicular conformation (II).



Based on the experimental observation that the  $\beta$ -proton coupling constant is very small ( $a_\beta = 2.55$  G) it appears most likely that the effective conformation preferred by the cyclopropylcarbinyl radical under the conditions of the ESR measurements is the bisected conformation. This preference has been supported by the results of semi-empirical INDO calculations [3, 10]. Accordingly, we have restricted ourselves to a consideration of the bisected conformation. The geometry chosen was essentially based on the structural parameters reported by Ford and Beaudet [18]. In this regard, it is difficult to obtain criteria for the reliability for the selected geometry. Krusic et al. [4] have suggested that a distortion takes place which affects the  $\beta$ -carbon and hence, indirectly, the long-range proton coupling constants. The degree to which distortion of the geometry occurs is unknown. In any case, a complete attempt at both geometry and orbital exponent optimization would be prohibitively expensive, in terms of the computer time needed. The energy of the bisected conformation was found to be  $-153.55108$  a.u. at the minimal basis level, and  $-155.18440$  a.u. at the extended basis level.

The calculations have two limitations. Spin polarization corrections are not incorporated. A configuration interaction calculation, or at least a perturbation treatment of the single determinant ground-state wave function would be required to obtain the spin polarization corrections. Also, the UHF wave function is not an eigenstate of  $S^2$ , and this will cause some error.

The calculated results for the proton hyperfine coupling constants of the cyclopropylcarbinyl radical in the bisected conformation are listed in Table 1, along with the INDO calculations of Danen [3] and Stock and Young [10]. The main feature of the calculations is the appearance of the same sign for both the *exo*- and *endo*-proton coupling constants. Both the minimal and the extended basis set calculations yield this result. The calculations indicate that

TABLE 1

Calculated proton isotropic hyperfine coupling constants for the cyclopropylcarbinyl radical (in Gauss)

	$a$ (minimal basis)	$a$ (extended basis)	$a$ (INDO) <sup>a</sup>	$a$ (INDO) <sup>b</sup>	$ a $ (experimental) <sup>c</sup>
H <sub>α<sub>1</sub></sub>	-66.69	-66.01	-19.31	-20.67	20.74
H <sub>α<sub>2</sub></sub>	-58.87	-64.73	-19.45	-21.54	
H <sub>β</sub>	11.53	11.41	1.70	1.34	2.55
H <sub>exo</sub>	-3.23	-1.71	2.86	1.72	2.98 <sup>d</sup>
H <sub>endo</sub>	-3.89	-4.25	-1.78	-1.41	2.01 <sup>d</sup>

<sup>a</sup>Results from Danen [3]. <sup>b</sup>Results from Stock and Young [10]. <sup>c</sup>Only absolute values of the experimental coupling constants are reported. <sup>d</sup>The assignment of the *exo* and *endo* proton coupling constants is arbitrary.

the *endo*-proton has the largest absolute value of the long-range coupling constants. The  $\alpha$ -proton coupling constants are about three times the experimental value. There is an excess of spin density at the  $\alpha$ -protons in the UHF procedure, using the basis sets employed in this work. This difficulty has been found in other calculations [19]. The calculated  $\beta$ -proton coupling constant is somewhat larger than the experimental value, which is an anomalously small coupling. Our calculations are in disagreement with the INDO calculations of Stock and Young [10] and Danen [3]. Both these groups found  $|a_{exo}|$  to be greater than  $|a_{endo}|$ , with  $a_{endo}$  negative and  $a_{exo}$  positive. The conclusion that  $a_{endo}$  is negative is supported by the results of our ab initio calculations; however  $a_{exo}$  is also found to be negative, in contradiction to the INDO calculations. It is very difficult to assess whether these differences are due to small changes in geometry. However, we note that the INDO calculations reported by Danen for the perpendicular conformation give  $a_{endo}$  and  $a_{exo}$  as both negative, while the calculations of Stock and Young give  $a_{endo}$  negative and  $a_{exo}$  positive. It therefore appears possible to obtain either sign for some of the small coupling constants, depending on how the appropriate semi-empirical parameters have been chosen.

Unfortunately, no deuterium-labelling experiments have been carried out to determine the assignment of the absolute values of the coupling constants. This would be a useful experiment, as it would serve to clarify the question of whether the ab initio or the INDO procedure assign the correct order. No sign-determination work has been carried out on the cyclopropylcarbinyl radical. However, some interesting results have been obtained by Stock and Wasielewski [11] on the signs of the coupling constants in some cyclopropane derivatives. These authors found that the sign of  $a_{endo}$  is negative and  $a_{exo}$  is positive in the cyclopropyl ring. It is at least speculative to argue that observations on these derivatives may be used to infer the signs in the cyclopropylcarbinyl radical.

Spin polarization corrections, which may be either positive or negative [13, 15], are not included in our ab initio calculations; they are also absent in the semi-empirical INDO scheme. These corrections may account for part of the disagreement with the experimental results, particularly the possible discrepancies in the signs of the long-range coupling constants; these discrepancies can only be clarified by further experiments. If the INDO predictions are qualitatively correct, some caution will be required in future single-determinant ab initio calculations, since it will be necessary to incorporate the spin polarization corrections to the UHF calculations for long-range coupling. This difficulty does not arise within the INDO scheme, since adjustment of available parameters can offset the missing spin polarization contributions.

## REFERENCES

- 1 J. K. Kochi, P. J. Krusic and D. R. Eaton, *J. Am. Chem. Soc.*, 91 (1969) 1877.
- 2 J. K. Kochi, P. J. Krusic and D. R. Eaton, *J. Am. Chem. Soc.*, 91 (1969) 1879.
- 3 W. C. Danen, *J. Am. Chem. Soc.*, 94 (1972) 4835.
- 4 P. J. Krusic, P. Meakin and J. P. Jesson, *J. Phys. Chem.*, 75 (1971) 3438.
- 5 G. A. Russell and H. Malkus, *J. Am. Chem. Soc.*, 89 (1967) 160.
- 6 N. L. Bauld, R. Gordon and J. Zoeller, Jr., *J. Am. Chem. Soc.*, 89 (1967) 3948.
- 7 C. E. Hudson and N. L. Bauld, *J. Am. Chem. Soc.*, 94 (1972) 1158.
- 8 M. P. Doyle, P. W. Reynolds, R. A. Barents, T. R. Bade, W. C. Danen and C. T. West, *J. Am. Chem. Soc.*, 95 (1973) 5988.
- 9 N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon and J. S. Hyde, *J. Am. Chem. Soc.*, 91 (1969) 6666.
- 10 L. M. Stock and P. E. Young, *J. Am. Chem. Soc.*, 94 (1972) 7686.
- 11 L. M. Stock and M. R. Wasielewski, *J. Am. Chem. Soc.*, 94 (1972) 8276.
- 12 F. W. King, *Chem. Rev.*, 76 (1976) 157.
- 13 F. W. King and F. C. Adam, *Mol. Phys.*, 29 (1975) 337.
- 14 F. W. King, *J. Magn. Reson.*, 17 (1975) 362.
- 15 Y. Ellinger, R. Subra, B. Levy, P. Millie and G. Berthier, *J. Chem. Phys.*, 62 (1975) 10.
- 16 W. J. Hehre, W. A. Lathan, R. Ditchfield, M. O. Newton and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., U.S.A.
- 17a W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, 51 (1969) 2657.
- 17b R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 54 (1971) 724.
- 18 R. G. Ford and R. A. Beaudet, *J. Chem. Phys.*, 48 (1968) 4671.
- 19 F. W. King and H. B. Schlegel, *J. Magn. Reson.*, 22 (1976) 389.