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## Ab Initio Calculations of Isotropic Hyperfine Coupling Constants in $\beta$ -Ketoenolyl Radicals

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### Abstract

Ab initio unrestricted Hartree–Fock (UHF), unrestricted second-order Møller–Plesset (UMP2) perturbation, unrestricted coupled cluster (UCCD), and unrestricted quadratic configuration interaction (UQCISD) calculations have been performed on the organic radicals  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_2\text{CHCH}_2$ ,  $\text{CH}_3\text{CHCOO}^-$ ,  $\text{HCOCHCOH}$ ,  $\text{CH}_3\text{COCHCOH}$ ,  $\text{CH}_3\text{COCHCOCH}_3$ , and  $\text{CH}_3\text{COC}(\text{CH}_3)\text{COCH}_3$ , using double-zeta and split-valence-plus-polarization basis sets. These radicals are derived from common organic ligands and have been observed in recent experimental work on tris( $\beta$ -ketoenolato)cobalt(III) complexes. Their geometry has been optimized at the UHF level using the two mentioned basis sets. From these calculations, values for the isotropic hyperfine coupling constants at the hydrogen atoms are predicted and compared with the experimental results. The usefulness of semiempirical extrapolations based on limited basis sets and treatment of electron correlation effects is carefully analyzed in the examples considered. © 1994 John Wiley & Sons, Inc.

### 1. Introduction

In a recent paper [1], the possibility of producing *in situ* organic radicals directly attached to a transition-metal atom has been advanced. In particular, tris( $\beta$ -ketoenolato)cobalt(III) chelates have been considered as generating complexes, where the “ $\beta$ -ketoenolato” fragment represents, e.g., formylacetate ion  $\text{H}-\text{CO}-\text{CH}-\text{CO}-\text{CH}_3^-$ , the acetylacetate ion  $\text{CH}_3-\text{CO}-\text{CH}-\text{CO}-\text{CH}_3^-$ , etc. A large variety of such organic ligands has been considered in [1], to which we refer for all details. The radicals so obtained have been characterized through electron spin resonance (ESR) measurements, so that experimental values of the isotropic hyperfine coupling constants (hfcc) are available.

Parallel to the experimental work, an ab initio study of these systems has been initiated in our laboratory: in the present article, results concerning the isolated ligands are presented and compared with calculations on well-characterized analogous organic radicals. These results complement preliminary calculations already appeared in [2], allowing a more stringent check of previously advanced hypotheses. The aim of this article is to explore the capability of ab initio techniques to predict isotropic hfcc in such systems, to assess the relative importance of the various contributions to the final hfcc values, and to check the viability of semiempirical extrapolations on the isolated ligands (i.e., with respect to the approximate treatment of electron correlation effects, the use of limited basis sets, etc.) that can then be utilized for the study of the  $\beta$ -ketoenolato complexes.

## 2. The Approach

In this section, the theoretical problem is presented and the approach on which the present calculations are based is briefly discussed, referring to [3] for an interesting review of the general problem and to [2] for a more detailed discussion of the present approach.

The experimental spectra give the isotropic hfcc for the various hydrogen atoms in the organic ligands. The quantities to be evaluated at the theoretical level are therefore the electron spin densities at the hydrogen atoms, which—through the Fermi contact interaction—determine the isotropic hfcc  $a_H$  (through a proportionality factor):

$$a_H = \frac{8\pi}{3} \frac{g_e}{g_0} g_H \beta_H \rho_s(\mathbf{r}_H), \quad (1)$$

where  $g_e/g_0$  is the ratio of the isotropic  $g$  value for the radical to that of the free electron (and will be taken as unity hereafter), and  $g_H$  and  $\beta_H$  are the nuclear magnetogiric ratio and nuclear magneton, respectively, for the hydrogen atom. The  $\rho_s(\mathbf{r}_H)$  are obtained as expectation values of the spin density operator over the electronic wave function:

$$\rho_s(\mathbf{r}_H) = \mathbf{S}_z^{-1} \langle \psi | \sum_{\nu=1}^N \delta(\mathbf{r}_\nu - \mathbf{r}_H) \hat{S}_z(\nu) | \psi \rangle = \rho^\alpha(\mathbf{r}_H) - \rho^\beta(\mathbf{r}_H), \quad (2)$$

where the index  $\nu$  runs on all electrons and  $S_z$  is the quantum number of the total electron spin (1/2 for radicals).

The theoretical approach here adopted to evaluate these quantities consists of performing an unrestricted Hartree–Fock (UHF) calculation, followed by an unrestricted second-order Møller–Plesset (UMP2) perturbative expansion, an unrestricted coupled cluster with doubles (UCCD) calculation, or an unrestricted quadratic configuration interaction with singles and doubles (UQCISD) calculation [4] and therefore corresponds essentially to that proposed in [5, 6]. Such an approach is based on the assumption that—starting with a UHF wave function—the correct inclusion of single and double excitations is sufficient to describe the spin-polarization phenomenon.

The most serious criticism to this approach would be that the wave function consisting of UHF orbitals does not represent a correct spin state of the molecular system under consideration. In a series of studies, it was, however, found empirically [5, 7] and shown analytically [8] that if the sole contaminant is the state of the next higher spin multiplicity then the UCCD or UQCISD wave function will be an essentially pure spin state (for further justification—with respect to spin contamination problems—of the procedure here adopted, see, e.g., [7]).

In hfcc calculations, the choice of an appropriate basis set is fundamental [3]. In the present article, the standard LANL1DZ [9] and 6-31G\*\* [10] basis sets have been utilized, which are of double-zeta (DZ) and split-valence-plus-polarization quality, respectively. Such limited basis sets are not capable of producing accurate results (unless one heavily relies on compensation effects [11]), so that a semiempirical extrapolation procedure has been adopted to correct the theoretical values and compare them with the experimental ones. Such a procedure corresponds to the simple prescription proposed in [2]: In its essence, it assumes that the effects due to incomplete treatment of correlation energy, limited basis sets, and vibrational (and, possibly, environmental) effects only modify the hfcc through a simple proportionality factor. Finally, most of the calculations here reported were performed with the GAUSSIAN-92 [12] codes.

### 3. The Results

In Tables I and II, the results of the UHF, UMP2, UCCD, and UQCISD calculations employing DZ and 6-31G\*\* basis sets are reported for the radicals  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_2\text{CHCH}_2$ ,  $\text{CH}_3\text{CHCOO}^-$ ,  $\text{HCOCHCOH}$ ,  $\text{CH}_3\text{COCHCOH}$ ,  $\text{CH}_3\text{COCHCOCH}_3$ , and  $\text{CH}_3\text{COC}(\text{CH}_3)\text{COCH}_3$  (for space reasons, in the tables Me and acac stand for  $\text{CH}_3$  and  $\text{CH}_3\text{COC}^-\text{COCH}_3$ , respectively). Signs have been included for the theoretical values and for the experimental values when available. For the three hydrogen atoms of a methyl group, only the *mean* value is given: If the three  $a_H$  do not have the same sign, the arithmetic mean and the mean of the absolute values are reported separated by a  $\div$  symbol. The first four molecules have been chosen as test cases, because they are well characterized from the experimental point of view (the experimental values are taken from [3, 16–18]). The stability of the UHF wave function with respect to complex variations, symmetry breaking, etc., has been checked in each case.

The geometry has been optimized at the UHF level, using the DZ basis set for all radicals (Table I) and the 6-31G\*\* basis set for some of them (Table II): Values of optimized geometrical parameters are reported in Table III. As shown in [19], one usually finds a good agreement of UHF-optimized geometries with CAS-SCF and experimental values for this kind of radicals. This corresponds to choosing the isolated molecule as a model. When comparing the theoretical and experimental results, however, one should take into account the influence of solvent or solid-state perturbing factors: both as an additional field and for their indirect influence on the geometry [20]. It is hard to assess the importance of such effects for the radicals here considered: Pioneering calculations are in progress (note that the experimental values for the  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ , and  $\text{CH}_2\text{CHCH}_2$  radicals refer to the gas phase). Vibrational effects have also been neglected. These effects, however, were assumed to be accounted for by the semiempirical extrapolation.

Let us thus analyze the results of Tables I and II. Small basis sets and an incomplete treatment of electron correlation effects (limited essentially to single and double excitations) are considered in the present article, so one should not expect to get fully quantitative results. However, one can check the validity of a semiempirical extrapolation, i.e., one can see if the *ab initio* hfcc can be related to the experimental values through scaling factors obtained from the simplest possible molecule that contains the kind of atom of interest (i.e.,  $\text{CH}_3$  for  $\alpha$ -hydrogen atoms and  $\text{CH}_3\text{CH}_2$  for  $\beta$ -hydrogen atoms). In Tables I and II, the *ab initio* hfcc values thus scaled are given in parentheses and the scaling factors are given in square brackets.

### 4. Analysis of the Results

The section is organized as follows: First, the values for the  $\alpha$ -hydrogen atoms will be discussed, then the values for the  $\beta$ -hydrogen atoms, distinguished into  $\beta$ -hydrogen atoms of a methyl group and  $\beta$ -hydrogen atoms lying on the symmetry plane, and, finally, the values for the  $\gamma$ -hydrogen atoms.

#### *$\alpha$ -Hydrogen Atoms*

**$\text{CH}_3$ :** The theoretical values converge to the experimental one as the basis set and the description of correlation are improved. Indeed, the UQCISD/6-31G\*\* value is still  $\approx 33\%$  larger,

TABLE I. hfcc values (in Gauss) for the H, CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>2</sub>CHCH<sub>2</sub>, CH<sub>3</sub>CHCOO<sup>-</sup>, HCOCHCOH, CH<sub>3</sub>COCHCOH, CH<sub>3</sub>COCHCOCH<sub>3</sub>, and CH<sub>3</sub>COC(CH<sub>3</sub>)COCH<sub>3</sub> radicals, obtained through UHF, UMP2, UCCD, and UQCISD calculations using the LANL1DZ (DZ) or 6-31G\*\* basis sets, and compared with experimental results; the geometry has been optimized at the UHF/DZ level.<sup>a</sup>

System <sup>b</sup>	UHF			UMP2			UCCD			UQCISD		
	DZ	6-31G**		DZ	6-31G**		DZ	6-31G**		DZ	6-31G**	Exp.
H	+470.	+475.										+507.
CH <sub>3</sub>	H <sub>α</sub> -49.7 [.463]	-46.8 [.491]		-38.6 [.596]	-31.5 [.731]		-34.2 [.672]	-28.9 [.795]		-35.7 [.644]	-30.5 [.753]	-23.0
CH <sub>3</sub> CH <sub>2</sub>	H <sub>α</sub> -50.6(23.5)	-47.6(23.4)		-37.9(22.6)	-30.8(22.6)		-33.8(22.8)	-28.6(22.8)		-35.4(22.8)	-30.3(22.8)	-22.5
	H <sub>β</sub> +25.7 [1.047]	+23.5 [1.145]		+23.8 [1.130]	+20.9 [1.287]		+22.3 [1.206]	+20.0 [1.345]		+23.6 [1.141]	+21.1 [1.273]	+26.9
CH <sub>2</sub> CHCH <sub>2</sub>	H <sub>α</sub> <sup>1</sup> -39.3(18.2)	-36.2(17.8)		-22.6(13.5)	-16.9(12.4)		-20.0(13.4)	-16.5(13.1)		-21.7(14.0)	-18.7(14.1)	-13.9
	H <sub>α</sub> <sup>2</sup> -40.4(18.7)	-37.4(18.4)		-23.6(14.1)	-17.8(13.0)		-20.9(14.0)	-17.3(13.7)		-22.6(14.6)	-19.5(14.7)	-14.8
	H <sub>β</sub> +27.6(28.9)	+24.6(28.2)		+5.6(6.3)	+1.5(1.9)		+4.1(4.9)	+2.5(3.4)		+6.0(6.8)	+5.1(6.5)	+4.2
MeCHCOO <sup>-</sup>	H <sub>α</sub> -47.6(22.0)	-43.6(21.4)		-33.9(20.2)	-26.9(19.7)		-30.6(20.6)	-25.6(20.4)		-31.9(20.6)	-27.1(20.4)	19.2
	H <sub>β</sub> +23.5(24.6)	+21.2(24.3)		+21.1(23.9)	+18.5(23.8)		+19.9(24.0)	+17.8(24.0)		+20.8(23.7)	+18.7(23.8)	25.0

HCOCHCOH	H <sub><math>\alpha</math></sub>	-38.5(17.8)	-34.6(17.0)	-21.9(13.1)	-16.9(12.4)	-20.1(13.5)	-16.9(13.4)	-24.3(15.7)	-20.7(15.6)	<sup>c</sup>
	H <sub><math>\beta</math></sub>	+28.7(30.0)	+23.4(26.8)	+0.7(0.8)	-5.8(7.5)	+2.0(2.4)	-1.7(2.3)	+1.9(2.2)	+1.0(1.3)	<sup>c</sup>
MeCOCHCOH	H <sub><math>\alpha</math></sub>	-39.0(18.1)	-35.2(17.3)	-22.7(13.5)	-17.9(13.1)	-20.9(14.0)	—	-24.8(16.0)	—	<sup>c</sup>
	H <sub><math>\beta</math></sub>	+28.6(29.9)	+23.2(26.6)	+0.2(0.2)	-5.9(7.6)	+1.6(1.9)	—	+2.0(2.3)	—	<sup>c</sup>
	H <sub><math>\gamma</math></sub>	-13.2	-10.9	-1.5 $\div$ 2.0	+0.9	-2.7 $\div$ 3.1	—	-1.9	—	<sup>c</sup>
MeCOCHCOMe	H <sub><math>\alpha</math></sub>	-39.8(18.4)	-35.9(17.6)	-23.6(14.1)	-18.7(13.7)	-21.8(14.6)	—	-25.5(16.4)	—	<sup>c</sup>
	H <sub><math>\gamma</math></sub>	-13.1	-10.9	-1.7 $\div$ 2.1	+0.6	-2.6 $\div$ 3.1	—	-1.9	—	<sup>c</sup>
Me-acac	H <sub><math>\beta</math></sub>	+19.2(20.1)	+17.7(20.3)	+16.6(18.7)	+15.3 $\div$ 16.0 (19.7 $\div$ 20.6)	+15.6(18.8)	—	+17.6(20.1)	—	<sup>c</sup>
	H <sub><math>\gamma</math></sub>	-13.2	-11.0	-1.6 $\div$ 2.1	+0.6	-2.8 $\div$ 3.2	—	-2.0	—	<sup>c</sup>

For other calculations on the first three molecules, see [3, 5, 13–15].

<sup>a</sup>Values obtained through the semiempirical extrapolation are given in parentheses; the values of the semiempirical factors are given in square brackets (see text for details).

<sup>b</sup>H <sub>$\alpha$</sub> , H <sub>$\beta$</sub> , and H <sub>$\gamma$</sub>  represent  $\alpha$ -,  $\beta$ - and  $\gamma$ -hydrogen atoms, respectively.

<sup>c</sup>Experimental values not available.

TABLE II. hfcc values (in Gauss) for the  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_2\text{CHCH}_2$ ,  $\text{CH}_3\text{CHCOO}^-$ ,  $\text{HCOCHCOH}$ , and  $\text{CH}_3\text{COCHCOCH}_3$  radicals, obtained through UHF, UMP2, UCCD, and UQCISD calculations using the LANL1DZ (DZ) or 6-31G\*\* basis sets, and compared with experimental results; the geometry has been optimized at the UHF/6-31G\*\* level.<sup>a</sup>

System <sup>b</sup>	UHF		UMP2		UCCD		UQCISD		Exp.
	DZ	6-31G**	DZ	6-31G**	DZ	6-31G**	DZ	6-31G**	
$\text{CH}_3$	-49.7 [.463]	-46.8 [.491]	-38.6 [.596]	-31.5 [.731]	-34.2 [.672]	-28.9 [.795]	-35.7 [.644]	-30.5 [.753]	-23.0
$\text{CH}_3\text{CH}_2$	$\text{H}_\alpha$ -50.5(23.4)	-47.5(23.3)	-37.8(22.6)	-30.7(22.4)	-33.7(22.7)	-28.6(22.7)	-35.3(22.7)	-30.3(22.8)	-22.5
	$\text{H}_\beta$ +26.6 [1.011]	+23.4 [1.150]	+24.8 [1.085]	+21.8 [1.234]	+23.3 [1.155]	+20.9 [1.287]	+24.5 [1.098]	+22.0 [1.223]	+26.9
$\text{CH}_2\text{CHCH}_2$	$\text{H}_\alpha^1$ -39.0(18.0)	-35.9(17.6)	-22.4(13.4)	-16.7(12.2)	-19.8(13.3)	-16.4(13.0)	-21.7(14.0)	-18.6(14.0)	-13.9
	$\text{H}_\alpha^2$ -40.3(18.7)	-37.1(18.2)	-23.5(14.0)	-17.7(12.9)	-20.8(14.0)	-17.3(13.8)	-22.6(14.6)	-19.5(14.7)	-14.8
	$\text{H}_\beta$ +27.0(27.3)	+24.0(27.6)	+5.2(5.6)	+1.2(1.5)	+3.8(4.4)	+2.3(3.0)	+5.9(6.5)	+5.0(6.1)	+4.2
$\text{MeCHCOO}^-$	$\text{H}_\alpha$ -47.5(22.0)	-43.4(21.3)	-33.7(20.1)	-26.9(19.7)	-30.5(20.5)	-25.5(20.3)	-31.9(20.6)	-27.0(20.4)	19.2
	$\text{H}_\beta$ +24.3(24.6)	+22.0(25.3)	+22.0(23.9)	+19.2(23.7)	+20.8(24.0)	+18.6(23.9)	+21.7(23.8)	+19.5(23.8)	25.0
$\text{HCOCHCOH}$	$\text{H}_\alpha$ -40.2(18.6)	-36.5(18.0)	-25.7(15.3)	-20.7(15.1)	-23.4(15.7)	-20.3(16.1)	-26.5(17.1)	-22.6(17.0)	c
	$\text{H}_\beta$ +23.5(23.8)	+17.3(19.9)	-7.4(8.0)	-13.0(16.0)	-4.0(4.6)	-7.1(9.1)	+0.8(0.9)	+0.4(0.5)	c
$\text{MeCOCHCOMe}$	$\text{H}_\alpha$ -41.9(19.4)	-38.1(18.7)	-28.0(16.7)	-22.7(16.6)	-25.5(17.1)	—	-27.6(17.8)	—	c
	$\text{H}_\gamma$ -9.0	-7.6	+3.3	+5.0	+1.0	—	-1.2	—	c

<sup>a</sup>Values obtained through the semiempirical extrapolation are given in parentheses; the values of the semiempirical factors are given in square brackets (see text for details).

<sup>b</sup> $\text{H}_\alpha$ ,  $\text{H}_\beta$  and  $\text{H}_\gamma$  represent  $\alpha$ -,  $\beta$ - and  $\gamma$ -hydrogen atoms, respectively.

<sup>c</sup>Experimental values not available.

TABLE III. UHF/DZ-optimized geometrical parameters for the given organic radicals (UHF/6-31G\*\* parameters are given in parentheses when available).

$CH_3/D_{3h}$   
 $dC_\alpha H_\alpha = 1.074 (1.073)$

$CH_3CH_2/C_s$   
 $dC_\alpha H_\alpha = 1.076 (1.075)$      $dC_\beta H_\beta = 1.085 (1.086)$      $dC_\alpha C_\beta = 1.52 (1.50)$   
 $\angle H_\alpha C_\alpha C_\beta = 121.06 (121.09)$      $\angle H_\beta C_\beta C_\alpha = 109.59 (109.67)$

$CH_2CHCH_2/C_{2v}$   
 $dC_\alpha H_\alpha^1 = 1.075 (1.076)$      $dC_\alpha H_\alpha^2 = 1.074 (1.074)$      $dC_\beta H_\beta = 1.076 (1.079)$   
 $dC_\alpha C_\beta = 1.40 (1.39)$   
 $\angle H_\alpha^1 C_\alpha C_\beta = 121.28 (121.14)$      $\angle H_\alpha^2 C_\alpha C_\beta = 121.27 (121.34)$   
 $\angle H_\beta C_\beta C_\alpha = 117.70 (117.73)$

$CH_3CHCOO^-/C_s$   
 $dC_\alpha H_\alpha = 1.077 (1.079)$      $dC_\beta H_\beta = 1.087 (1.088)$      $dC_\alpha C_\beta = 1.51 (1.50)$   
 $dC_\alpha C(O_2) = 1.51 (1.52)$      $dC(O_2)O = 1.27 (1.24)$   
 $\angle H_\alpha C_\alpha C_\beta = 120. (120.)$      $\angle C_\beta C_\alpha C(O_2) = 120. (120.)$   
 $\angle O_1 C(O_2) C_\alpha = 116.76 (115.81)$      $\angle O_1 C(O_2) O_2 = 127.74 (129.14)$

$HCOCHCOH/C_{2v}$   
 $dC_\alpha H_\alpha = 1.074 (1.077)$      $dC_\beta H_\beta = 1.079 (1.089)$      $dC_\alpha C_\beta = 1.43 (1.44)$   
 $dC_\beta O = 1.28 (1.22)$   
 $\angle H_\alpha C_\alpha C_\beta = 115.83 (116.62)$      $\angle H_\beta C_\beta C_\alpha = 117.05 (115.70)$   
 $\angle C_\alpha C_\beta O = 124.85 (124.66)$

$CH_3COCHCOH/C_s$   
 $dC_\alpha H_\alpha = 1.075$      $dC_\alpha C_\beta^2 = 1.44$      $dC_\alpha C_\beta^1 = 1.43$      $dC_\beta^1 O_1 = 1.29$   
 $dC_\beta^2 O_2 = 1.28$      $dC_\beta^1 H_\beta^1 = 1.080$      $dC_\gamma H_\gamma = 1.082$      $dC_\beta^2 C_\gamma = 1.52$   
 $\angle H_\alpha C_\alpha C_\beta^1 = 115.26$      $\angle H_\alpha C_\alpha C_\beta^2 = 115.23$      $\angle C_\alpha C_\beta^1 O_1 = 125.46$   
 $\angle C_\alpha C_\beta^2 O_2 = 121.80$      $\angle C_\alpha C_\beta^2 C_\gamma = 118.36$      $\angle H_\beta^1 C_\beta^1 C_\alpha = 116.73$

$CH_3COCHCOCH_3/C_{2v}$   
 $dC_\alpha H_\alpha = 1.075 (1.078)$      $dC_\gamma H_\gamma = 1.082 (1.084)$      $dC_\alpha C_\beta = 1.44 (1.46)$   
 $dC_\beta C_\gamma = 1.52 (1.52)$      $dC_\beta O = 1.28 (1.22)$   
 $\angle H_\alpha C_\alpha C_\beta = 115.61 (109.92)$      $\angle C_\alpha C_\beta C_\gamma = 118.09 (116.41)$   
 $\angle C_\alpha C_\beta O = 122.40 (122.51)$

$CH_3COC(CH_3)COCH_3/C_{2v}$   
 $dC_\alpha C_\beta^2 = 1.53$      $dC_\alpha C_\beta^1 = 1.46$      $dC_\beta^2 H_\beta = 1.080$      $dC_\gamma H_\gamma = 1.082$   
 $dC_\beta^1 C_\gamma = 1.52$      $dC_\beta^1 O = 1.28$   
 $\angle C_\beta^2 C_\alpha C_\beta^1 = 118.40$      $\angle C_\alpha C_\beta^1 C_\gamma = 120.62$      $\angle C_\alpha C_\beta^1 O = 122.05$

For each molecule, the *chemical formula/point symmetry group* is given. The bond distances ( $dAB$ ) are given in Å, and the bond angles ( $\angle ABC$ ), in degrees. Note that the  $\pi$ -skeleton is always planar and that, unless otherwise specified, the three hydrogen atoms of the methyl groups have been imposed to be symmetrically disposed with respect to the fourth carbon bond and at the tetrahedral angle (109.4712°). The nomenclature for  $\alpha$  and  $\beta$  carbon and hydrogen atoms is the same as in the text.

but this is only due to basis set effects (see, e.g., [5, 21]). The  $a_H$  are not affected by errors in the optimization of geometrical parameters, because separate calculations employing all the methods here considered (UHF, UMP2, UCCD, and UQCISD) with DZ and 6-31G\*\* basis sets give an optimized planar geometry with a carbon–hydrogen distance ranging from 1.073



to 1.090 Å. Planarity is an essential requirement for the semiempirical extrapolation to work: As shown, e.g., in [21], the hfcc are strongly affected by pyramidalization both in the UHF value and in the relative weight of the correlation correction. On the other hand, the optimized geometries of all molecules always give *planar*  $\pi$ -radicals in our calculations. Note that the experimental value for CH<sub>3</sub> before vibrational averaging is 25 Gauss [3]: In the present approach, vibrational corrections are supposed to be included in the semiempirical extrapolation procedure.

**CH<sub>3</sub>CH<sub>2</sub>:** One has the same behavior as for the CH<sub>3</sub> case, with both DZ- and 6-31G\*\*-optimized geometries (the same happens with the 6-31G basis set). The extrapolated theoretical values practically coincide for UMP2, UCCD, and UQCISD methods, giving a value slightly smaller than that for CH<sub>3</sub>. The residual difference with the experimental value is probably due to differences in the vibrational averaging in CH<sub>3</sub>CH<sub>2</sub> and CH<sub>3</sub> molecules. Note—in contrast—that the UHF method predicts an  $a_H$  larger than that for CH<sub>3</sub>: This suggests the importance of correlation effects even in this simplest case (the same problem is found within the Chipman's SECI approach [13]).

**CH<sub>2</sub>CHCH<sub>2</sub>:** The extrapolated values are poor at the UHF level, but are improved by the introduction of correlation effects, especially at the UQCISD level, which gives quantitative results with both DZ and 6-31G\*\* basis sets and at both DZ- and 6-31G\*\*-optimized geometries. In this case, as in all conjugated systems, correlation effects are extremely important and can only be approximately described at the UMP2 level (in a curious way better for the DZ than for the 6-31G\*\* basis set). Even the UCCD results are not completely satisfactory, suggesting the importance of the single excitation operator in the UQCISD method in improving the starting orbitals (erroneous polarization at the UHF level). In this respect, it would be interesting to see if the UMP2 or UCCD results could be improved by optimizing the energy with respect to the choice of the starting orbitals.

**CH<sub>3</sub>CHCOO<sup>-</sup>:** Results analogous to those for the allyl radical, with the only difference that the conjugation is here less effective and, correspondingly, the importance of correlation effects. Since the situation is not completely clear at the experimental level, calculations have been performed also on the neutral molecule: CH<sub>3</sub>CHCOOH, obtaining however, a worse agreement with the experimental hfcc values.

**HCOCHCOH:** Again, the results closely parallel those for the allyl radical. The main difference is the strong dependence of the hfcc upon *geometry*: The extrapolated value is 15.6 Gauss with the DZ- and 17.0 Gauss with the 6-31G\*\*-optimized geometries. Note, however, that the radical is still planar and the carbon–hydrogen distance close to the standard one: The difference is only due to coupling with spin-polarization of the other bonds. This implies an appreciable dependence of hfcc on vibrational averaging for this molecule (and, therefore, a different result in the Co-complex, where the molecule is not freely vibrating: It will therefore be of importance in future calculations to optimize the ligands' geometry within the full complex).

**CH<sub>3</sub>COCHCOH and CH<sub>3</sub>COCHCOCH<sub>3</sub>:** Results analogous to the HCOCHCOH case.

*$\beta$ -Hydrogen Atoms Within Methyl Groups*

**CH<sub>3</sub>CH<sub>2</sub>**: The theoretical values do not converge to the experimental one as the basis set and the description of correlation are improved, but to a value that is *smaller*. In other words, single and double excitations are not sufficient to describe the hfcc of  $\beta$ -hydrogen atoms (this is a well-known problem of ab initio-correlated treatment of hfcc, see, e.g., [13, 14]). Note also a more pronounced dependence of hfcc upon geometry: The UQCISD/6-31G\*\* value is  $\approx 21$  Gauss with the DZ- and  $\approx 22$  Gauss with the 6-31G\*\*-optimized geometries. As usual, the mean hfcc value is practically unaffected by rotation of the methyl group: This has been verified also for more complex radicals and remains true as long as the hfcc of the three hydrogen atoms have the same sign.

**CH<sub>3</sub>CHCOO<sup>-</sup>**: Despite the fact that the theoretical methods do not give correct results in the basis-set limit, the semiempirical prescription still furnishes reasonable values, especially at the correlated level. The predicted hfcc, however, is somewhat less accurate than for  $\alpha$ -hydrogen atoms:  $\approx 24$  Gauss instead of 25.0 Gauss at the experimental level. By imposing the dihedral angle of the methyl group at the experimental solid-state value ( $\approx 18^\circ$ ), the experimental ratios between the three hydrogen atoms of the methyl group are fairly well reproduced at the UCCD or UQCISD level, but not at the UHF level (slightly better at the UMP2 level). This is no longer true if one utilizes the “experimental” geometry proposed in [17], derived under rather dubious assumptions.

**CH<sub>3</sub>COC(CH<sub>3</sub>)COCH<sub>3</sub>**: The only difference with respect to CH<sub>3</sub>CHCOO<sup>-</sup> is that the UMP2 calculation with the 6-31G\*\* basis set is probably not reliable: It gives a negative value on one of the three  $\beta$ -hydrogen atoms.

 *$\beta$ -Hydrogen Atoms Lying on the Symmetry Plane*

**CH<sub>2</sub>CHCH<sub>2</sub>**: As for all  $\beta$ -hydrogen atoms of conjugated systems, correlation (and basis set) effects are extremely important here: The UHF/DZ value is reduced by a factor  $\approx 7$  by these effects. Correspondingly, the semiempirical prescription is not so reliable in this case: Even the extrapolated UQCISD values present differences larger than usual between DZ and 6-31G\*\* basis sets (even though the numbers are more stable than in all other approaches).

**HCOCHCOH and CH<sub>3</sub>COCHCOCH<sub>3</sub>**: The same can be said for these radicals, with the further complication of a strong dependence of hfcc upon geometry: Even the UCCD values are wildly alternating and only the UQCISD method gives apparently reasonable results.

 *$\gamma$ -Hydrogen Atoms*

This type of hydrogen atom has not been experimentally observed on these radicals [1], and the corresponding  $a_H$  have been assumed to be negligible ( $\leq 1$  Gauss). Nevertheless, we report theoretical values for these atoms, to check the performance of the unrestricted methods also in this case.

**CH<sub>3</sub>COCHCOH, CH<sub>3</sub>COCHCOCH<sub>3</sub> and CH<sub>3</sub>COC(CH<sub>3</sub>)COCH<sub>3</sub>:** The behavior is similar to that obtained for the  $\beta$ -hydrogen atoms lying on the symmetry plane: The theoretical values are largely overestimated at the UHF level, while oscillating around zero at the correlated level. Again, the UQCISD values are the least sensitive to geometry modifications. Note the curious pattern of  $a_H$  as functions of the method and basis set for the DZ-optimized geometries: nearly coincident for the three radicals, even though the corresponding geometrical parameters vary much from a radical to another.

## 5. Conclusions

From the analysis of the results reported in Table I, the following conclusions can be drawn:

The theoretical predictions—before the semiempirical correction—usually improve as the basis set is enlarged and correlation effects are included at a more refined level, but do not furnish quantitative answers. This is because of two main problems: (a) the basis set and (b) the method of calculation.

(a) Chipman introduced specifically devised basis sets [11] for studying hfcc, suggesting, in particular, a [631,41] basis set of contracted Gaussian functions as a good compromise between reliability and computation times. It has been shown [22], however, that much larger basis sets are needed to reproduce the accuracy of numerical calculations. A detailed analysis of the results reported in [11], furthermore, shows that even the [631,41] basis set is based on compensation effects: It works fine for the CH radical but not equally well for the NH and OH radicals. It is not unreasonable, therefore, to try a procedure in which small basis-set results are simply extrapolated to the experimental values. The results of Tables I and II show that—if the theoretical method is correct—such a procedure always works fine. In this respect, note that spin densities have been evaluated at the *hydrogen* atoms only, which greatly simplifies the theoretical problem: The results would probably have been different if spin densities at heavier atoms had to be considered. At a hydrogen atom, in fact, *cusp* problems are not so important (the cusp is underestimated by only  $\approx 7\%$  by DZ and 6-31G\*\* basis sets) and, furthermore, in a localized picture, one has to describe the spin-polarization of just *one* orbital (even though coupled to those of the other bonds).

(b) One of the basic hypotheses of [2] was that—starting with a UHF wave function—the dominant contributions to hfcc were due to single and double excitations. The results of Tables I and II show that this is certainly true for  $\alpha$ -hydrogen atoms. One can thus expect that a series of other methods should give reasonable values for these atoms, such as density functional calculations (see, e.g., [23]), UMP2 or UCCD calculations with optimization of orbitals to take into account relaxation due to correlation (see above), or even semiempirical methods [24], but at the correlated level (CNDO–CI, etc.) and after a previous reparametrization of these methods to make them produce not only reasonable values of energies, but also good values of charge distributions.

This hypothesis, however, does not seem to work well for  $\beta$ -hydrogen atoms. In particular, those of methyl groups can still be reasonably predicted using the semiempirical extrapolation procedure (at the UQCISD level), but those lying on the plane of  $\pi$ -symmetry are extremely difficult to predict. It seems, therefore, that a thorough understanding of the dominant effects on the hfcc of  $\beta$ -hydrogen atoms is still lacking. The same can be said about  $\gamma$ -hydrogen atoms.

Other points worth mentioning are the following:

1. For  $\alpha$ -hydrogen atoms, electron correlation effects are slightly more important when the unpaired orbital is part of a conjugated systems; for  $\beta$ -hydrogen atoms, correlation effects are less important than for  $\alpha$ -hydrogen atoms when considering nonconjugated systems (hydrogen atoms within a methyl group), but are of dramatic importance when there is no zeroth-order effect and the spin polarization is transmitted *through* the conjugated system (see, e.g., the allyl radical). The same seems to be true for the  $\gamma$ -hydrogen atoms of the acetylacetonyl radical: In general,  $\pi$ -conjugation amplifies correlation effects.
2. The semiempirical extrapolation does not give very good results at the UHF level. This is especially true for those  $\alpha$ - and  $\beta$ -hydrogen atoms for which correlation strongly affects hfcc values.
3. The extrapolation is very much improved at the correlated level, especially within the UQCISD approach, which gives quantitative results nearly independently of the basis set utilized. The proposed extrapolation thus represents a *simple and efficient prescription* to make theoretical predictions of reasonable accuracy. The worst case is still represented by the  $\beta$ -hydrogen atoms lying on the symmetry plane.
4. The correlated calculations have also been performed without including excitations from the 1s core orbital of the carbon atoms, obtaining practically indistinguishable results: The hfcc at the hydrogen atoms are not appreciably affected by correlating and spin-polarizing the core.
5. For hydrogen atoms, it is also expected that a localized-orbital approach should work fine: Calculations based on such ideas are in progress.

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