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MNDO RHF CI and MINDO/3 RHF CI Calculations of Hyperfine Coupling Constants of π Radicals

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Synopsis. MNDO RHF CI and MINDO/3 RHF CI calculations, in which one type of singly-excited configuration is included, were shown to give hyperfine coupling constants of π radicals which are in better agreement with the experimental values, as compared with the UHF method.

In spite of remarkable progress regarding molecular orbital methods, the simple Hückel and McLachlan methods are frequently used to elucidate the ESR hyperfine coupling (hfc) constants of ring protons in π radicals.[1] More sophisticated UHF SCF methods produces the spin density at the nucleus of the ring proton in the π radical through the spin-polarization mechanism. The magnitude of this spin density is small and the semiempirical UHF method (like

Table 1. Calculated hfc Constants for ^1H

Radical	Atom	MNDO UHF	MNDO UHF-QA	MINDO/3 RHF CI	MNDO RHF CI	Exp[a]
CH_3		−27.6	−9.0	−22.0	−20.6	(−)23.0
NH_2		−17.4	−5.7	−16.8	−14.0	(−)23.9
trans-Butadiene$^-$	CH_2	−16.1	−5.3	−8.7	−8.4	(−) 7.6
	CH	1.9	0.7	−3.4	−3.1	(−) 2.8
Allyl	*trans*	−21.2	−7.0	−11.9	−11.3	(−)13.9
	cis	−21.6	−7.1	−12.7	−11.5	(−)14.8
	CH	14.8	5.0	1.9	2.4	(+) 4.1
Phenoxyl	2	−17.6	−6.2	−6.4	−5.1	(−) 6.6
	3	14.5	5.2	1.0	1.6	(+) 2.0
	4	−19.7	−6.9	−11.4	−13.1	(−)10.4
Nitrobenzene$^-$	2	−14.0	−4.8	−5.0	−4.1	(−) 3.3
	3	12.2	4.3	0.3	0.6	(+) 1.1
	4	−16.7	−5.7	−6.5	−5.6	(−) 4.0
Benzyl	2	−16.4	−6.3	−2.6	−2.1	(−) 5.1
	3	14.6	5.7	0.5	0.7	(+) 1.8
	4	−15.5	−5.9	−2.0	−1.5	(−) 6.1
Benzonitrile$^-$	2	−10.3	−3.5	−3.7	−3.4	(−) 3.6
	3	9.0	3.1	−0.9	−0.2	(−) 0.3
	4	−16.7	−5.6	−7.3	−8.0	(−) 8.4
p-Benzosemiquinone$^-$		−2.8	−0.9	−3.3	−3.0	(−) 2.4
o-Benzosemiquinone$^-$	3	−8.5	−2.8	−4.0	−5.1	(−) 3.7
	4	−0.4	−0.1	−3.5	−3.1	(−) 1.0
Pyridine$^-$	2	−1.7	−0.6	−3.3	−1.3	(−) 3.6
	3	−0.02	0.0	−1.8	−2.1	(−) 0.8
	4	−18.3	−6.0	−11.2	−14.4	(−) 9.7
Pyrimidine$^-$	2	−0.04	−0.01	−2.2	−0.4	(−) 1.3
	3	−15.1	−5.0	−8.4	−8.3	(−) 9.8
	4	10.4	3.5	0.7	1.4	(+) 0.7
Pyrazine$^-$		−1.6	−0.5	−3.1	−2.4	(−) 2.6
Phthalonitrile$^-$	3	5.1	1.7	−0.2	0.5	(+) 0.3
	4	−7.2	−2.4	−3.4	−3.1	(−) 4.2
Isophthalonitrile$^-$	2	1.4	0.5	−0.5	0.4	(+) 0.1
	4	−16.2	−5.4	−8.0	−8.5	(−) 8.3
	5	11.0	3.7	0.7	1.4	(+) 1.4
Terephthalonitrile$^-$		−0.8	−0.3	−2.2	−1.8	(−) 1.6
Napthalene$^-$	1	−9.6	−3.2	−5.1	−5.1	(−) 4.9
	2	0.0	0.0	−1.7	−1.3	(−) 1.8
Anthracene$^+$	1	−5.2	−1.7	−2.4	−2.2	(−) 3.1
	2	0.2	0.1	−1.1	−0.7	(−) 1.4
	9	−11.4	−3.8	−6.5	−6.2	(−) 6.5
Anthracene$^-$	1	−4.7	−1.6	−2.3	−2.1	(−) 2.7
	2	0.3	0.1	−1.1	−0.7	(−) 1.5
	9	−12.8	−4.3	−6.2	−6.6	(−) 5.3
1,4-Napthosemiquinone$^-$	2	−3.1	−1.0	−4.2	−3.6	(−) 3.2

a) Refs. 6 and 8 and references cited therein.

INDO, MINDO/3, MNDO and AM1) cannot well reproduce the experimental values. The anihilation of the qurtet component from the UHF wave function (UHF-QA) is not sufficient to remove the spin contamination. In order to overcome the poor spin density on the 1s orbital, ρ_s, calculated by semiempirical UHF methods, attempts have been reported in which the proportional constant Q_H in $a_H=\rho_s Q_H$ is parametrically adjusted; the Q_H value varies from 400 to 1200 Gauss ($1G=10^{-4}T$), depending on the MO method employed.2) However, the value of Q_H has been determined to be 507 Gauss;3) it seems natural to use this value and to improve the wave function of free radicals. This study shows that the RHF open shell SCF plus configuration interaction (CI) calculation with the MNDO or MINDO/3 approximation gives the spin distribution of π radicals much better than do the UHF methods.

In order to evaluate the efficiency of the methodology, it is necessary to uniquely determine the molecular structure of a radical. In this study, the molecular structure was optimized by the RHF SCF method for the doublet state.4) The spin density on the 1s orbiral, ρ_s, was then evaluated by using the CI wave function. In the CI calculation for the doublet state, only singly-excited configurations were considered. There are four types of such configuration functions.5) Only the fourth type of function, $\Psi_{i\to k}$, mixes directly with the ground configuration, Ψ_g;6) it induces the finite spin density on the ring proton in π radicals. All such functions were included in the CI calculations.7)

$$^2\Psi_g = |\phi_1\bar{\phi}_1\cdots\phi_i\bar{\phi}_i\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| \tag{1}$$

$$^2\Psi_{i\to k} = 1/\sqrt{6}\,\{|\phi_1\bar{\phi}_1\cdots\phi_i\bar{\phi}_k\cdots\phi_m| - |\phi_1\bar{\phi}_1\cdots\phi_k\bar{\phi}_i\cdots\phi_m| + 2|\phi_1\bar{\phi}_1\cdots\phi_i\bar{\phi}_m\cdots\phi_k|\} \tag{2}$$

The calculated RHF CI hfc constants are listed in Table 1. The UHF and UHF-QA values are also listed. As can be seen from Table 1, MNDO RHF CI and MINDO/3 RHF CI calculations give better hfc constants than do the UHF and UHF-QA calculations. The mean deviations of the calculated hfc constants from the experimental values for 44 experimental values of 20 π radicals are 6.0, 2.9, 1.3, and 1.1 Gauss for MNDO UHF, MNDO UHF-QA, MNDO RHF CI, and MINDO/3 RHF CI, respectively.

The effeicency of the INDO RHF CI calculation of hfc constants has been reported,6) where little attention was paid to the molecular structure of radicals. The present results are better than the INDO CI results for π radicals. Since the magnitude of the hfc constants depends largely on the molecular structure of a radical, a simultaneous evaluation of the molecular structure and hfc constants is required in order to elucidate the ESR observation. In that case, an MNDO or MINDO/3 RHF CI calculation can successfully be employed.

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