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Calculation of the Hyperfine Coupling Constants of Some σ Electron Radicals

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The isotropic hyperfine coupling constants of cyclopropyl, vinyl, formaldiminoxy, formyl, and hydrogen cyanide anion radicals are calculated by a method which corresponds to the extension of the McLachlan procedure. These hyperfine coupling constants are then studied, and the contributions from the spin delocalization and spin polarization mechanisms are estimated. The role of one-center exchange integrals in the estimation of these hyperfine coupling constants is also studied; it is shown to be important in the claculation of the hyperfine coupling constants of the nuclei of the radical-center atom and of the atoms bonded to it.

Recently the hyperfine coupling constants of σ-electron radicals have attracted much theoretical interest; many authors have calculated them with the hyperconjugation method,[1] with the extended Hückel method,[2,3] and with the semiempirical or *ab initio* unrestricted SCF methods.[4-7]

In this work, we will calculate the isotropic hyperfine coupling constants of some σ-electron radicals containing hydrogen, carbon, nitrogen, or oxygen atoms by a method[8] which is an extension of the McLachlan procedure.[9] The results of the present calculations will then be compared with the results obtained by other methods, and the effects of the spin polarization will be shown to be important even in the case of σ-electron radicals.

Method and Parameters

The differences between Fock's operators for α and β spin electrons in the unrestricted SCF method can be treated as a perturbation. Taking the first-order approximation with respect to exchange

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[1] W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965).
[2] G. A. Petersson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966).
[3] a) R. S. Drago and H. Petersen, Jr., *J. Amer. Chem. Soc.*, **89**, 3978 (1967); b) R. S. Drato and H. Petersen, Jr., *ibid.*, **89**, 5774 (1967); c) R. E. Cramer and R. S. Drago, *ibid.*, **90**, 4790 (1968).
[4] T. Yonezawa, H. Nakatsuji, T. Kawamura and K. Kato, This Bulletin, **40**, 2211 (1967).
[5] N. M. Atherton and A. Hinchliffe, *Mol. Phys.*, **12**, 349 (1967).
[6] J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).
[7] A. Hinchliffe and D. B. Cook, *Chem. Phys. Lett.*, **1**, 217 (1967).
[8] T. Yonezawa, T. Kawamura and H. Kato, *J. Chem. Phys.*, **50**, 3482 (1969).
[9] A. D. McLchlan, *Mol. Phys.*, **3**, 233 (1960).

interaction, the elements of the spin-density matrix can be written as:8)

$$\rho_{vw} = p^0_{vw} - \frac{1}{4}\sum_r\sum_s(\pi^\alpha_{vw,rs}+\pi^\beta_{vw,rs})\sum_t\sum_u p^0_{tu}(rt|us), \quad (1)$$

where the electron repulsion integral is denoted as:

$$(rt|us) = \iint \chi_r(1)\chi_t(1)(e^2/r_{12})\chi_u(2)\chi_s(2)\,\mathrm{d}v_1\mathrm{d}v_2$$

and where $\pi^\alpha_{vw,rs}$ and $\pi^\beta_{vw,rs}$ are mutual polarizabilities defined as:

$$\pi^\alpha_{vw,rs} = 2\sum_{j<0}\sum_{i\geqq 0}(C_{iv}C_{jw}+C_{jv}C_{iw})C_{ir}C_{js}/(\varepsilon_i-\varepsilon_j)$$

$$\pi^\beta_{vw,rs} = 2\sum_{j\leqq 0}\sum_{i>0}(C_{iv}C_{jw}+C_{jv}C_{iw})C_{ir}C_{js}/(\varepsilon_i-\varepsilon_j). \quad (2)$$

The molecular orbitals (MO), obtained by an extended Hückel MO method, are denoted by *i* and *j*; a positive number represents a doubly-occupied MO, zero is for the singly occupied MO, and vacant MO's are expressed by negative numbers. The coefficient of the *r*th atomic orbital (AO), χ_r, in the *i*th MO and its orbital energy are denoted as C_{ir} and ε_i respectively, while p^0_{tu} represents the "odd-electron" density matrix element, $C_{0t}C_{0u}$.

When multicenter integrals for the Dirac delta function are neglected, the isotropic hyperfine coupling constant of the nucleus Y, a^{Y}, becomes:

$$a^{\mathrm{Y}} = \frac{8\pi}{3}g_{\mathrm{Y}}\beta_{\mathrm{N}}\sum_v^{\text{on Y}}\sum_w \rho_{vw}\langle\chi_v|\delta(r_{\mathrm{Y}})|\chi_w\rangle \text{ gauss}, \quad (3)$$

where $\delta(r_{\mathrm{Y}})$ is the Dirac delta function and where g_{Y} and β_{N} have their usual meanings. As to the AO's χ_v and χ_w in Eq. (3), the valence-shell and inner-shell AO's are taken into consideration, while the effects of outer-shell AO's are neglected. Inner-shell electrons are assumed to be localized in one inner-shell AO in a zero-order approximation to exchange interaction.

Under these approximations, a^{Y} can be divided into three terms according to their mechanisms; the spin-delocalization term, $a^{\mathrm{Y}}_{\mathrm{D}}$: the spin-polarization term due to valence-shell electrons, $a^{\mathrm{Y}}_{\mathrm{PV}}$, and the spin-polarization term concerning inner-shell electrons, $a^{\mathrm{Y}}_{\mathrm{PI}}$, as:

$$a^{\mathrm{Y}} = a^{\mathrm{Y}}_{\mathrm{D}} + a^{\mathrm{Y}}_{\mathrm{PV}} + a^{\mathrm{Y}}_{\mathrm{PI}}. \quad (4)$$

The contribution to a^{Y} from the term due to the spin-delocalization mechanism, $a^{\mathrm{Y}}_{\mathrm{D}}$, can be given from Eq. (3) and the first term of Eq. (1) as:

$$a^{\mathrm{Y}}_{\mathrm{D}} = A^{\mathrm{Y}}_{\mathrm{V}}P^0_{vv} \quad (5)$$

$$A^{\mathrm{Y}}_{\mathrm{V}} = \frac{8}{3}\pi g_{\mathrm{Y}}\beta_{\mathrm{N}}\langle\chi_v|\delta(r_{\mathrm{Y}})|\chi_v\rangle, \quad (6)$$

where χ_v is the valence-shell *s* AO of the atom Y. The values of $A^{\mathrm{Y}}_{\mathrm{V}}$ adopted in this work for ^{1}H, ^{13}C, ^{14}N, and ^{17}O are listed in Table 1.

The valence-electron spin-polarization term, $a^{\mathrm{Y}}_{\mathrm{PV}}$, comes from the second term of Eq. (1) and is given by:

$$a^{\mathrm{Y}}_{\mathrm{PV}} = -\frac{1}{4}A^{\mathrm{Y}}_{\mathrm{V}}\sum_r\sum_s(\pi^\alpha_{vv,rs}+\pi^\beta_{vv,rs})\sum_t\sum_u p^0_{tu}(rt|us), \quad (7)$$

where the suffix *v* denotes the valence-shell *s* AO of the atom Y. In the estimation of the multicenter electron erpulsion integrals, the zero-differential-overlap approximation is adopted. One-center exchange integrals, which are expected to play an important role in the calculation of hyperfine coupling constants, are taken into account. The one-center Coulomb integral, $(rr|rr)$, is estimated by Pariser approxiamtion10) by using the valence-state ionization potentials and electron affinities tabulated by Pritchard and Skinner.11) The one-center exchange integrals are estimated from the table of Hinze and Jaffe.12) To assure rotational invariance, the one-center Coulomb integral between p_π AO and p_σ AO is evaluated as:

$$(\sigma\sigma|\pi\pi) = (\sigma\sigma|\sigma\sigma) - 2(\sigma\pi|\pi\sigma).$$

The other Coulomb integrals are estimated by means of the Ohno approximation.13)

The inner-shell-electron spin-polarzation term, $a^{\mathrm{Y}}_{\mathrm{PI}}$,s come from the second term of Eq. (1):

$$a^{\mathrm{Y}}_{\mathrm{PI}} = -\frac{1}{4}A^{\mathrm{Y}}_{\mathrm{I}}\sum_r\sum_s(\pi^\alpha_{vw,rs}+\pi^\beta_{vw,rs}+\pi^\alpha_{wv,rs}+\pi^\beta_{wv,rs})$$
$$\times\sum_t\sum_u p^0_{tu}(rt|us), \quad (8)$$

Table 1. Values of $A^{\mathrm{Y}}_{\mathrm{V}}$, $A^{\mathrm{Y}}_{\mathrm{I}}$, and one-center electron repulsion integrals including inner-shell AO's

Nucleus Y	$A^{\mathrm{Y}}_{\mathrm{V}}$a) (gauss)	$A^{\mathrm{Y}}_{\mathrm{I}}$a) (gauss)	(1*s*2*p*|2*p*2*s*)a) (eV)	(1*s*2*s*|2*s*2*s*) (eV)	(1*s*2*s*|2*p*2*p*) (eV)
^{1}H	877	—	—	—	—
^{13}C	1210	−5340	0.6373	−0.3167	−0.1689
^{14}N	604	−2580	0.7924	−0.4095	−0.2195
^{17}O	−1810	7540	0.9481	−0.5036	−0.2708

a) Ref. 8.

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10) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

11) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

12) J. Hinze and H. H. Jaffe, *J. Chem. Phys.*, **38**, 1834 (1963).

13) K. Ohno, *Theor. Chem. Acta*, **2**, 219 (1964).

where v and w denote the valence-shell $2s$ and the inner-shell $1s$ AO's respectively, and where A_{I}^{Y} is given by:

$$A_{\text{I}}^{\text{Y}}=\frac{8}{3}\pi g_{\text{Y}}\beta_{\text{N}}\langle\chi_v|\delta(r_{\text{Y}})|\chi_w\rangle, \tag{9}$$

the values of which are listed in Table 1. The multicenter electron repulsion integrals in Eq. (8), including the inner-shell AO's, may be ignored because the differential overaps between the inner-shell AO and the AO's centered on the other atoms are negligible. The energy differences between the inner-shell orbitals and the valence-shell vacant MO's are approximated as the negative values of the inner-shell-electron X-ray term values listed by Slater.[14] Therefore, we obtain:

$$a_{\text{PI}}^{\text{Y}}=\frac{A_{\text{I}}^{\text{Y}}}{2E_w}\Big(\sum_{j<0}+\sum_{j\leqq 0}\Big)\Big[\sum_{r}\sum_{t}\sum_{u}^{\text{VAO's on Y}}C_{jv}C_{jr}p_{tu}^{0}(rt|uw)\Big], \tag{10}$$

where E_w is the X-ray term value of the inner-shell $1s$ AO of the atom Y (χ_w), where r, t, and u denote valence-shell AO's on the atom Y, and where v represents the valence-shell $2s$ AO of the atom Y. For the computation of a one-center electron repulsion integral including both inner-shell $1s$ AO and valence-shell $2s$ AO, $1s$ and $2p$ Slater AO's[15] and the following orthogonalized $2s$ AO function are adopted:

$$\chi_{2s}'=(1-S^2)^{-1/2}(\chi_{2s}-S\chi_{1s}),$$

where S is the overlap integral between Slater AO's χ_{1s}-χ_{2s}. The estimated values of the integrals are listed in Table 1. The evaluated values of $(1s\ 2p|2p\ 2s)$ are reliable when compared with the other estimation,[8] but the estimation of the other electron-repulsion integrals concerning inner-shell $1s$ AO's seems to be less reliable.

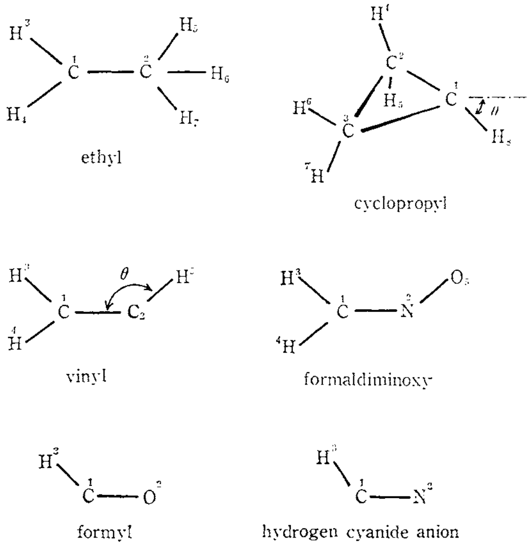
The zero-order MO's are calculated with an exended Hückel MO method by solving a secular equation:

$$|H_{rs}-\delta_{rs}\varepsilon|=0$$

where r and s cover all the valence-shell AO's of the radical. The diagonal element of the Hamiltonian, H_{rr}, is approximated as the negative value of Mulliken's orbital electronegativity, as tabulated by Pritchard and Skinner.[11] The off-diagonal elements of the Hamiltonian are estimated as:

$$H_{rs}=\begin{cases}(K/2)S_{rs}(H_{rr}+H_{ss}) & \text{(for nearest neighbors)}\\ 0 & \text{(for non-nearest neighbors),}\end{cases} \tag{11}$$

where S_{rs} is the χ_r-χ_s overlap integral: the Wolfsberg-Helmholz[16] parameter, K, will be fixed



ethyl cyclopropyl

vinyl formaldiminoxy

formyl hydrogen cyanide anion

Fig. 1. Numbering of atoms of calculated radicals.

TABLE 2. DEPENDENCE OF CALCULATED HYPERFINE COUPLING CONSTANTS OF METHYL AND ETHYL RADICALS ON WOLFSBERG-HELMHOLZ PARAMETER K

Radical	Nucleus Y	a^{Y} (gauss)			
		Value of K			Exp.
		0.6	0.7	0.8	
Methyl	H	−27.09	−24.41	−21.66	(−) 23.04[a]
	C	41.18	35.40	30.58	(+) 38.34[b]
Ethyl	3H, 4H	−25.28	−22.20	−19.74	(−) 22.38[a]
	βH[c]	27.37	26.75	26.27	(+) 26.87[a]
	1C	38.54	33.15	28.65	(+) 39.07[b]
	2C	−5.64	−5.24	−4.84	(−) 13.57[b]

a) Ref. 18.
b) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).
c) The mean value of hyperfine coupling constants of 5H, 6H, and 7H.

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[14] J. C. Slater, "Quantum Theory of Atomic Structure," Vol. I, McGraw-Hill Book Co., New York (1960), p. 206.

[15] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[16] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

to fit selected experimental values of hyperfine coupling constants in the following section. We use Slater $2s$ and $2p$ AO's for first-row elements and the Slater-type $1s$ AO with the orbital exponent of 1.2 for hydrogen.

Results and Discussion

The numberings of the atoms and the conformational parameters of the calculated radicals are shown in Fig. 1.

Wolfsberg-Helmholz Parameter, K, and Calculated Coupling Constants. To obtain the appropriate value of the parameter, K, of Eq. (11), the ^1H and ^{13}C hyperfine coupling constants of methyl and ethyl radicals are calculated by changing the value of K.

The hyperfine coupling constants of the protons of the methyl radical and the α protons (3H and 4H) of the ethyl radical arise mainly through the valence-electron spin-polarization mechanism. The spin densities which appear through valence-and inner-shell-electron spin-polarization determine the ^{13}C coupling constants of the methyl and ethyl radicals. On the other hand, the hyperfine coupling constant of the β protons (5H, 6H, and 7H) of the ethyl radical are determined mainly by the spin delocalization. Therefore, the contributions of the spin delocalization, the valence-shell-electron spin-polarization, and the inner-shell-electron spin-polarization mechanism to the hyperfine coupling constants will be estimated with the set of parameters which gives good calculated values of the hyperfine coupling constants of these radicals.

Table 3. Calculated hyperfine coupling constants of cyclopropyl radical (gauss)

θ	0°	20°	40°	60°	Exp.
a^{4H}	35.6	33.7	26.1	18.1	(+) 23.42[a,b]
a^{4H}_{D}	34.6	33.2	26.3	19.4	
a^{4H}_{PV}	1.0	0.5	−0.2	−1.3	
a^{5H}	35.6	32.6	27.2	17.6	(+) 23.42[a,b]
a^{5H}_{D}	34.6	32.0	27.9	20.1	
a^{5H}_{PV}	1.0	0.6	−0.7	−2.5	
a^{8H}	−22.9	−21.0	−16.7	−12.2	±6.51[a]
a^{8H}_{D}	0.0	0.5	1.6	2.4	
a^{8H}_{PV}	−22.9	−21.5	−18.3	−14.6	
a^{1C}	34.0	43.0	65.2	91.0	——
a^{1C}_{D}	0.0	8.5	30.1	56.0	
a^{1C}_{PV}	41.6	41.7	41.3	39.8	
a^{1C}_{PI}	−7.6	−7.2	−6.2	−4.8	
a^{2C}	−5.3	−4.7	−2.9	−0.35	——
a^{2C}_{D}	0.0	0.1	0.5	0.94	
a^{2C}_{PV}	−5.3	−4.7	−3.0	−0.55	
a^{2C}_{PI}	~0.0	−0.1	−0.4	−0.7	

a) Ref. 18.
b) The average of a^{4H} and a^{5H} was observed.

The calculated values of the hyperfine coupling constants of the methyl and ethyl radicals are listed in Table 2, together with the values of K used. The best results are obtained for $K=0.7$, so we will use this value in the following calculations.

Cyclopropyl Radical. The geometry of this radical is assumed to be the same as that of cyclopropane[17] except for the angle between the 1C–8H bond and the carbon plane. This angle, θ, varies in the calculations. The calculated hyperfine coupling constants are listed in Table 3, together with the contributions from the spin-delocalization, the valence-electron spin-polarization, and the inner-shell-electron spin-polarization mechanisms. These results show that the spin-polarization mechanism is important in the estimation of the hyperfine coupling constants of the nuclei of the radical-center atom and of the atoms bonded to it. Dixon[1] successfully calculated the hyperfine coupling constants of the β protons of this radical with the assumed geometry of $\theta=54.75°$. Drago and Petersen[2b] calculated the hyperfine coupling constants of the protons of this radical by the extended Hückel method. They obtained 7.56, 22.00, and 18.96 gauss for 8H, 5H, and 4H respectively, when $\theta=20°$. These results agree with the experimental values[18]; they predicted that the angle would be approximately 20°. The present results show that the spin-polarization mechanism contributes about −14 gauss to the hyperfine coupling constant of 8H, even when $\theta=60°$. The extended Hückel calculation presents only the spin density due to the spin-delocalization mechanism. When the present results and their extended Hückel calculations are compared, the angle is predicted to be large than 20°. The sign of the hyperfine coupling constant of 8H can not be fixed, because the present estimation of the positive contribution of the spin-delocalization mechanism to the 8H coupling constant (+2.4 gauss, $\theta=60°$) appears too small when compared with the results of other calculations.[2,3] The present calculation predicts that, when θ increases, the constant of 1C will steeply increase, mainly because of the increase in the s-nature of the odd-electron orbital on 1C. As is shown in Table 3, the hyperfine coupling constants of β protons (4H and 5H) arise dominantly from spin-delocalization. Therefore, the hyperfine coupling constants of β protons can be estimated directly by Roothaan's restricted open-shell SCF MO method[19] or by a simple MO

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[17] "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. by L. E. Sutton, Special Publ. Nos. 11 and 18, The Chemical Society, London (1958 and 1965).

[18] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[19] C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

TABLE 4. CALCULATED HYPERFINE COUPLING CONSTANTS OF VINYL RADICAL (GAUSS)

θ	120°	130°	140°	150°	180°	Exp.
a^{1C}	−6.0	−7.0	−7.8	−8.7	−9.9	(−) 8.55[a]
a_{D}^{1C}	1.7	1.3	1.0	0.6	0.0	
a_{PV}^{1C}	−7.7	−8.2	−8.4	−9.2	−9.9	
a_{PI}^{1C}	−0.1	−0.1	−0.1	−0.1	~0.0	
a^{2C}	106.0	87.7	70.3	55.6	38.0	(+) 107.57[a]
a_{D}^{2C}	68.6	50.8	34.2	20.2	0.6	
a_{PV}^{2C}	42.4	42.4	42.1	41.8	40.8	
a_{PI}^{2C}	−5.0	−5.5	−6.0	−6.4	−7.0	
a^{3H}	73.6	75.8	76.6	76.0	64.4	(+) 68[b]
a_{D}^{3H}	73.0	74.5	74.7	73.6	61.8	
a_{PV}^{3H}	0.6	1.3	1.9	2.4	2.6	
a^{4H}	19.3	26.3	33.9	42.0	64.4	(+) 34[b]
a_{D}^{4H}	19.0	25.7	33.0	40.7	61.8	
a_{PV}^{4H}	0.3	0.6	0.9	1.3	2.6	
a^{5H}	−8.3	−11.5	−14.9	−18.1	−23.2	±13.39[c]
a_{D}^{5H}	11.2	8.5	5.9	3.5	0.0	
a_{PV}^{5H}	−19.5	−20.0	−20.8	−21.6	−23.2	

a) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).
b) E. L. Conchlan, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).
c) Ref. 18.

method such as the extended Hückel method.

Vinyl Radical. The geometry of the vinyl radical is assumed to be planar, with a 1.34 Å CC bond, 1.08 A CH bonds, and a 120° H–C–H bond angle. The bond angle of 1C–2C–5H, θ, varies in the calculations. Table 4 shows the calculated hyperfine coupling constants of the vinyl radical and the contributions of the spin-delocalization, the valence-electron spin-polarization, and the inner-shell-electron spin-polarization mechanisms. The comparison between the calculated and the experimental ratios of $|a^{3H}/a^{4H}|$ and $|a^{1C}/a^{2C}|$ shows that the angle θ may be in the $130° < \theta < 150°$ range. The results in Table 4 show that only the hyperfine coupling constants of β protons (3H and 4H) can be directly calculated with a restricted MO method, because the spin-polarization mechanism makes a minor contribution to them. The present calculation predicts that the 1C and 5H hyperfine coupling constants will be negative; the prediction for the former coincides with that of the unrestricted SCF calculation done with the INDO approximation of Pople, Beveridge and Dobosh.[6] The sign of the calculated 5H coupling constant agrees with our semiempirical unrestricted SCF calculation.[4] The present calculation shows that the odd-electron density on 2C attracts, through exchange interaction, electrons with the same spin as the odd electron, resulting in negative spin densities at the nuclei of 1C and 5H.

Formaldiminoxy Radical. Although the electron-spin-resonance spectrum of the formaldiminoxy radical has, so far as we know, not been reported, the hyperfine coupling constants of this radical have been calculated and compared with those of the aldiminoxy radicals. The geometry of this radical is assumed to be planar, with bond lenghts of r(CH)=1.08Å, r(CN)=1.28Å, and r(NO)=1.24Å, and with bond angles of ∠HCH=120° and ∠CNO=125°. The calculated values are summarized in Table 5. The calculated hyperfine coupling constant of ^{14}N agrees with the experimental values of the acetaldiminoxy and benzaldiminoxy radicals. The proton *trans* to the odd-electron orbital on the nitrogen has a larger coupling constant than that of the *cis* proton, as in the case of the vinyl radical. The ^{17}O coupling constant

TABLE 5. CALCULATED HYPERFINE COUPLING CONSTANTS OF FORMALDIMINOXY RADICAL (IN UNIT OF GAUSS)

Nucleus Y	a_{D}^{Y}	a_{PV}^{Y}	a_{PI}^{Y}	a^{Y}	Exp.[a]
^{14}N	22.9	16.3	−1.7	37.5	(+) 30—33
^{13}C	2.41	−6.43	−0.23	−4.30	—
^{17}O	−0.02	−8.71	0.78	−7.95	—
3H	62.8	−1.7	—	61.6	(+) 27.0
4H	11.0	−0.8	—	10.2	(+) 5.2, 6.5

a) Data for *syn*-acetoaldiminoxy and *syn*- and *anti*-benzaldiminoxy radicals. J. R. Thomas, *J. Amer. Chem. Soc.*, **86**, 1446 (1964); B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.*, *B*, **1966**, 727. The identification of Tohomas for *syn*- and *anti*-isomers are not proper.

TABLE 6. CALCULATED HYPERFINE COUPLING CONSTANTS OF FORMYL AND HYDROGN CYANIDE ANION RADICALS (GAUSS)

Radical	Nucleus Y	a_D^Y	a_{PV}^Y	a_{PI}^Y	a^Y	Exp.
HCO	^1H	57.5	−13.3	——	44.2	(+) 137[a]
	^{13}C	119	33.3	−3.4	149	(+) 134.7[b]
	^{17}O	−0.12	−5.13	0.77	−4.48	——
HCN^-	^1H	48.8	−10.1	——	38.7	(+) 137[c]
	^{13}C	81.2	25.5	−2.9	103.8	(+) 74 [c]
	^{14}N	0.40	4.82	−0.65	4.57	(+) 6.5[c]

a) Ref. 21. b) Ref. 22. c) Ref. 23.

of the iminoxy radical can be predicted to be about −8 gauss.

Formyl and Hydrogen Cyanide Anion Radicals. The formyl and hydrogen cyanide anion (HCN^-) radicals are isoelectronic, and both radicals are predicted to have essentially the same conformation and electronic configuration from Walsh's scheme for the molecular orbitals of HAB molecules.[20] The formyl radical has been prepared by Adrian *et al.*;[21] the isotropic proton hyperfine coupling has the extremely large value of 137 gauss, and the ^{13}C coupling is 134.7 gauss.[22] The electron-spin-resonance spectrum of the HCN^- radical was studied by Symons and his co-workers,[23] who reported that the hyperfine coupling constants of ^1H, ^{13}C, and ^{14}N are 137, 74, and 6.5 gauss respectively. The isotropic hyperfine coupling constants of the formyl radical have been calculated by the extended Hückel method,[2] the unrestricted SCF method with CNDO/2 approximations,[5] and the *ab initio* unrestricted SCF MO method.[7]

The geometry of the formyl radical used in the present calculation has a 1.09Å CH bond, a 1.198Å CO bond, and a bond angle of 119.5°. The structure of the hydrogen cyanide anion radical is assumed to have $r(CH)=1.09$Å, $r(CN)=1.26$Å, and $\angle HCN=120°$. The calculated hyperfine coupling constants of these radicals are listed in Table 6. The calculated proton coupling constants for HCO and HCN^- are too small when compared with the experimental values, as when calculated with the extended Hückel method.[2] The results for the ^{13}C constants are passable. Inner-shell electrons make minor contributions to these ^{13}C coupling constants. It is interesting to point out that the spin-polarization of valence-electrons gives about 1/4 of the coupling constant of the nucleus of the radical-center atom of these σ electron radicals.

The present calculation predicts that the ^{17}O coupling constant will be small and negative; this prediction coincides with the calculation by the *ab initio* unrestricted SCF MO method.[7] The calculated value of the ^{14}N coupling constant of HCN^- agrees fairly well with the experimental value. The present calculation show that a positive spin density arises at the position of the oxygen or the nitrogen nucleus of the HCO or HCN^- radical.

TABLE 7. CONTRIBUTIONS TO a_{PV}^Y FROM ONE-CENTER EXCHANGE INTEGRALS BETWEEN ATOMIC ORBITALS CENTERED ON THE RADICAL-CENTER ATOM (IN UNIT OF GAUSS)

Radical	Nucleus Y[a]	a^Y [b]	a_{PV}^Y[b]	Condtribution[c]
Cyclopropyl	1C	65.2	41.3	42.7
$\theta=40°$	2C	−2.9	−3.0	−0.81
	8H	−16.7	−18.3	−14.4
Vinyl	2C	87.7	42.4	43.8
$\theta=130°$	1C	−7.0	−8.2	−3.3
	5H	−11.5	−20.0	−20.0
Formald-iminoxy	N	37.6	16.3	18.1
	C	−4.3	−6.4	−1.83
	O	−8.0	−8.7	−0.97
HCO	C	149	33.3	42.1
	O	4.48	−5.13	3.10
	H	44.2	−13.3	−13.3
HCN^-	C	103.8	25.5	32.0
	N	4.57	4.82	−0.65
	H	38.7	−10.1	−8.78

a) Numbering of atoms are shown in Fig. 1.

b) Calculated value listed in Tables 3—6.

c) The contribution to the hyperfine coupling constant of nucleus Y from one-center exchange integrals between AO's centered on the radical-center atom. Estimated as $-(1/4)A_V^Y\sum'_{r,s,t,u},$ $(\pi_{vv,rs}^{\alpha}+\pi_{vv,rs}^{\beta})p_{tu}^0(rt|us)$, where $\sum'$ denote the summation over one-center exchange integrals between AO's on the radical center atom and v expresses the valence shell s AO atom Y.

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The mechanism of these spin densities is as follows: the spin density on the 2*s* AO of the oxygen or the nitrogen atom arises from the valence-electron spin-polarization contribution, $a^{\rm O}_{\rm PV}$ or $a^{\rm N}_{\rm PV}$. The main part (about 120%) of $a^{\rm O}_{\rm PV}$ or $a^{\rm N}_{\rm PV}$ comes from terms containing odd-electron density matrix elements, p^{o}_{tu}, between the AO's of the oxygen atom or of the nitrogen atom. That is, the odd electron in the in-plane orbital on the radical-center carbon atom delocalizes into the in-plane lone-pair orbital on the oxygen or the nitrogen atom, which in turn induces a positive spin density on the 2*s* AO of the oxygen or the nitrogen atom of the HCO or HCN^- radical through the exchange interaction, as in the case of π-electron radicals. This situation is also observed in the case of the ^{17}O coupling constant of the formaldiminoxy radical.

Role of One-center Exchange Integrals. For the calculation of the hyperfine coupling constants of σ electron radicals with a semiempirical unrestricted SCF MO method, Atherton and Hincliffe[5] adopted CNDO/2 approximations, whereas Pople, Beveridge and Dobosh[6] used INDO approximations. In the former method, one-center exchange integrals are neglected, while in the latter they are included. Although it is well established that one-center exchange integrals are essential in the calculation of the hyperfine coupling constants of π electron radicals,[24,25] the role of these integrals in the calculation of the hyperfine coupling constants of the σ electron radicals has not yet been sufficiently studied. The present method can give the contribution from each electron repulsion integral to the hyperfine coupling constants.

Table 7 shows the contributions through one-center exchange integrals between valence-shell AO's centered on the radical-center atom to the hyperfine coupling constants of the calculated σ electron radicals. Except for the ^{17}O coupling constants of HCO and the formaldiminoxy radical, and the ^{14}N coupling constant of HCN^-, the one-center exchange integral contributions listed in Table 7 approximately determine the value of $a^{\rm Y}_{\rm PV}$, the hyperfine coupling which arises through the valence-electron spin-polarization, of the nuclei of the radical-center atoms and of the atoms bonded to them. As has been mentioned in the preceding section, the hyperfine coupling constants of the ^{17}O of HCO and H_2CNO or of the ^{14}N of HCN^- arise through the odd-electron density delocalized into the in-plane lone-pair orbital on the oxygen atom or on the nitrogen atom, and the contribution listed in Table 7 is not important.

The results listed in Tables 3—7 show that, in the case of σ-electron radicals, spin-polarization make contributions to the hyperfine coupling constants of the nuclei of radical-center atoms and the atoms bonded to them that cannot be neglected, and that, in estimating these contributions, one-center exchange integrals should be included in the calculations.

The calculations were carried out on the HITAC 5020E electronic computer of the University of Tokyo and on the FACOM 230 computer of Kyoto University. The authors wish to acknowledge the help of the staff of each computer.

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