Evaluation of a new procedure for quantum-chemical estimates of constants of isotropic hyperfine coupling with protons in free radicals

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A new procedure for quantum-chemical estimates of the constants of isotropic hyperfine coupling (IHFC) with protons using the orbital spin populations calculated in the basis set of symmetrically orthogonalized (according to Löwdin) atomic orbitals is tested taking 16 well-studied simplest π-electron and σ-electron radicals as examples. The most probable reasons for and possible ways of correcting large deviations of calculated IHFC constants from experimental values are considered. The efficiency of the semiempirical MNDORU scheme, which makes it possible to consistently estimate the delocalization and spin-polarization contributions to the constants of IHFC with protons in free radicals, is demonstrated.

Key words: ESR spectroscopy, free radicals, constants of isotropic hyperfine coupling with protons, quantum-chemical estimates, symmetrically orthogonalized basis set of atomic orbitals.

Currently, progress in the theory of the structure and reactivity of complex neutral and charged radical systems playing an important role in diverse areas of organic chemistry, catalysis, and biochemistry[1] is to a great extent dependent on how widely are efficient radiospectroscopic methods including simple ESR technique used in these studies. There is no doubt that complex experimental ESR spectra of such systems, which often can hardly be interpreted even semi-intuitively, contain valuable encoded structural-chemical information. Currently, the possibility of reliable and rapid decoding of this information is, typically, associated with the development and application of both versions of density functional theory using adapted basis sets[2] and adequate semiempirical quantum-chemical methods of zero differential overlap (ZDO), which are considered theoretically substantiated[3] in the basis set of atomic orbitals symmetrically orthogonalized according to Löwdin ($\overline{\mathrm{AO}}$).

The problem of elucidating interrelations between the calculated wave functions and experimentally measured radiospectroscopic parameters arises when establishing the "structure—property" correlations in the framework of semiempirical ZDO schemes. For instance, the constant of isotropic hyperfine coupling (IHFC) a^{Z}_{iso}, determined in ESR studies, is, as a rule, related to the spin population ρ^{Z}_{s} of the valence s-AO of a particular atom Z obtained from quantum-chemical calculations using the following expression[3]:

$$a^{Z}_{\mathrm{iso}} = K(\mathrm{Z})\rho^{Z}_{s}. \qquad (1)$$

It has been accepted for a long time that the coefficient of proportionality $K(\mathrm{Z})$ in this expression depends on the type of atom Z irrespective of its chemical environment.

Next, it was suggested to calculate the constants of IHFC with protons by semiempirical ZDO methods using strongly differing values of the coefficient of proportionality $K(\mathrm{H})$.[4,5] On this basis a belief has been stated[6] that it is admissible to describe two fundamentally different mechanisms of the spin density distribution, *viz.*, the polarization and delocalization mechanisms, using two quantities, $K_{\alpha}(\mathrm{H})$ and $K_{\beta}(\mathrm{H})$, whose numerical values are appreciably different. Despite a reasonably logical qualitative explanation[6] for the necessity of using two coefficients of proportionality, $K_{\alpha}(\mathrm{H})$ and $K_{\beta}(\mathrm{H})$, which to some extent smoothes over the contradiction between the recommendations of different authors,[4,5] it was necessary to give a theoretical definition of each of them using adequate mathematical expressions, which take into account the peculiarities of both the mechanisms of the spin distribution and conventional quantum-chemical approximations.

Recently,[7] a scheme of consistent quantum-chemical calculations of constants of IHFC with protons ($a^{\mathrm{H}}_{\mathrm{iso}}$) in free radicals using spin populations ρ^{H}_{s} defined in the basis set of $\overline{\mathrm{AO}}$ was considered[7] taking model σ- and π-electron hydrocarbon fragments as examples. Taking into account that the IHFC with proton

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in a purely π-electron radical is completely determined by the exchange spin polarization, the following relationship was obtained in the framework of valence bonds (VB) scheme with inclusion of σ—π-configuration interaction

$$K_\alpha(\mathrm{H}) = \delta(\mathrm{H})\cdot 2(1 + S^2_{\mathrm{hs}})/3, \tag{2}$$

where δ(H) is the Hartree—Fock value of the coefficient of proportionality (508 Oe) and S_{hs} is the overlap integral between the hybrid h-AO of a heavy atom (C) and the 1s-AO of H atom. From Eq. (2) it follows that at $S_{\mathrm{hs}} \approx 0.75$ (a typical case) the $K_\alpha(\mathrm{H})$ and δ(H) values are virtually equal. It was also established[7] that, in the framework of the MO LCAO theory, the expression for the IHFC constant $a^{\mathrm{H}}_{\mathrm{iso}}$ for π-electron radicals remains unchanged on going from overlapped AO to symmetrically orthogonalized ones.

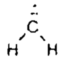
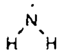
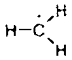
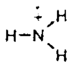
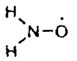
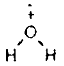
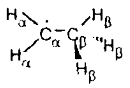
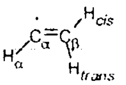
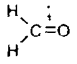
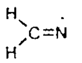
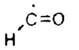
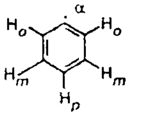
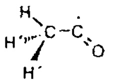
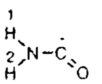
At the same time, it was shown[7] that the constants of IHFC with protons in typical σ-electron radicals, mostly due to the spin delocalization, should be calculated using the coefficient of proportionality $K_\beta(\mathrm{H})$, whose value is larger than the Hartree—Fock one since it is calculated using an essentially modified expression even in the case of simplified consideration of only one-electron contribution $^{\circ}\rho^{\mathrm{H}}_{\mathrm{s}}$ to the spin population of the 1s-AO of H atom in the basis set of $\overline{\mathrm{AO}}$, *viz.*:

$$K_\beta(\mathrm{H}) = \delta(\mathrm{H})\cdot\left[\frac{1}{2}\left(\frac{1}{\sqrt{1-S_{\mathrm{hs}}}} + \frac{1}{\sqrt{1+S_{\mathrm{hs}}}}\right)\right]^2. \tag{3}$$

At $S_{\mathrm{hs}} \approx 0.75$, we get $K_\beta(\mathrm{H}) \approx 950$ Oe, which is approximately equal to the value used[5] for σ-electron radicals.

This work is dedicated to the evaluation of this new procedure for estimating the constants of IHFC with protons taking the simplest experimentally and theoretically well-studied π- and σ-electron radicals as examples. This procedure, which is reduced to the use of relationships (1)—(3) in the framework of the semi-

Table 1. Bond lengths (*d*) and bond angles (φ) in free radicals

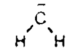
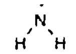
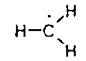
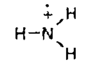
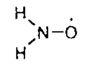
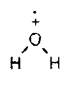
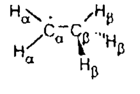
Radical	Type of radical	Bond	*d*/Å	Angle	φ/deg
 **(1)**	π	CH	1.121	HCH	104.4
 **(2)**	π	NH	1.024	HNH	103.0
 **(3)**	π	CH	1.079	HCH	120.0
 **(4)**	π	NH	1.020	HNH	120.0
 **(5)**	π	ON NH	1.300 0.988	ONH	118.9
 **(6)**	π	OH	0.999	HOH	112.6
 **(7)**	π/σ	CH_α CH_β CC	1.093 1.104 1.512	CCH_α CCH_β	121.5 111.0
 **(8)**	σ	CH_α CH_{cis} CH_{trans} CC	1.083 1.085 1.083 1.357	CCH_α CCH_{cis} CCH_{trans}	130.8 122.3 121.4
 **(9)**	σ	HC CO	1.117 1.198	OCH	118.5
 **(10)**	σ	HC CN	1.140 1.250	HCN	118.5
 **(11)**	σ	CH CO	1.125 [a] 1.150 [b] 1.175 [a] 1.180 [b]	OCH	125.0 [a] 123.0 [b]
$\dot{C}{\equiv}C{-}H$ **(12)**	σ	CC CH	1.294 1.054	CCH	180.0
 **(13)**	σ	$C_\alpha C_o$ $C_o C_m$ $C_m C_p$ $C_o H_o$ $C_m H_m$ $C_p H_p$	1.377 1.392 1.389 1.078 1.079 1.078	$C_\alpha C_o C_m$ $C_o C_m C_p$ $C_o C_\alpha C_o$ $C_m C_p C_m$	117.4 120.2 124.2 120.5
$H{-}\dot{C}{=}N$ **(14)**	σ	HC CN	1.175 1.243	HCN	115.8
 **(15)**	σ	CO CC CH CH′	1.190 1.501 1.078 1.084	OCC CCH CCH	130.1 111.0 109.4
 **(16)**	σ	CO CN NH(1) NH(2)	1.200 1.336 0.989 0.996	OCN CNH(1) CNH(2)	131.4 120.3 121.3

Note. Geometric parameters of radicals **1—4**, **7**, and **9—11** were determined experimentally (see Refs. 3, 6); "reliable" geometric parameters of radicals **5**, **6**, and **12—16** were calculated by the *ab initio* UHF/6-31G** method, and those of radical **8** were obtained from UHF/STO-3G calculations.

[a] Variant I.[6]

[b] Variant II.[3]

Table 2. Coefficients of proportionality (K_α(H)/Oe) and constants of IHFC with protons (a^{H}_{iso}/Oe) in free π-electron radicals

Radical	Nucleus	ω [a]	S_{hs} [a]	K_α(H) [b]	a^{H}_{iso}	
					MNDO /UHF	Experiment
	H	2.01	0.590	508 457	−18.7 −16.8	 −16.0
	H	2.11	0.644	508 479	−18.2 −17.1	 −23.9
	H	1.41	0.640	508 477	−27.7 −26.0	 −23.0
	H	1.41	0.547	508 440	−22.7 −19.7	 −25.9
	H	1.44	0.698	508 503	9.0 8.9	 11.9
	H	1.61	0.683	508 496	−15.9 −15.5	 −26.1
	H$_\alpha$	1.38	0.632	508 474	−27.7 −25.8	 −22.4

[a] See Eq. (6).
[b] See Eq. (2).

empirical MNDO method[8] in variants of the restricted and unrestricted Hartree—Fock approximations[3] (RHF and UHF, respectively), was tested with 16 free radicals (Tables 1—3).

Results and Discussion

As is known,[3,6,9,10] the absence of reliable information on the geometry of free-radical systems leads to large errors in calculations of their magnetic resonance parameters by quantum-chemical methods. Unfortunately, experimental data on the geometry of free radicals are either unavailable or often ambiguous (in particular, even for the HCO$^{\cdot}$ radical).[11—13] In this connection noteworthy is that the calculated magnetic resonance characteristics are highly sensitive to changes in the structural parameters and that usually radiospectroscopic data can be reproduced to a reasonable accuracy using NDO methods if the assumed structures of free radicals are close to real structures. Because of this, in the framework of the above-mentioned methods it is possible to predict the electronic structure and geometry of free-radical systems with a greater accuracy than using conventional energy minimization.[3,6,14,15]

Judging from the published data, reliable establishment of the geometry of free radicals in the gas phase using the procedure of energy variation is possible only by *ab initio* calculations with extended basis sets that are at least as good as the 6-31G* basis set.[8,14,15] For this reason, we performed full UHF/6-31G** optimization of structural parameters of those π- and σ-electron radicals for which no experimental data are available; the results obtained using such a procedure were taken as reliable. The experimental lengths of chemical bonds and bond angles (for radicals **1—4**, **7**, **9—11**) and those obtained from *ab initio* calculations (for the remaining radicals), used in estimating the constants of IHFC with protons using relationships (1)—(3) in the MNDO approximation, are listed in Table 1.

The overlap integral S_{hs} between the hybrid h-AO of the heavy atom Y and the 1s-AO of the H atom (Fig. 1) appears in expressions (2) and (3) for the coefficients of proportionality K_α(H) and K_β(H). The following approximate procedure was used to estimate the value of this integral in each particular case. As is known, the hybrid h_i-AO composed of the valence s- and p_i-AO of the heavy atom and directed along the i axis (see Fig. 1) can be represented in the form

$$h_i = (s + \omega_i p_i)/\sqrt{1 + \omega_i^2}\,. \qquad (4)$$

If the hybrid h_i- and h_j-AO are equivalent ($\omega_i = \omega_j$), the following condition is met:

$$1 + \omega^2 \cos\theta = 0, \qquad (5)$$

where θ is the angle between the axes i and j (see Fig. 1). Using relationship (5) and the values of the bond angles and interatomic distances listed in Table 1, as well as corresponding overlap integrals (S_{ss} and S_{sp}) between the Slater valence s- and p-AO, for each Y—H bond we calculated the overlap integral between the hybrid h-AO of atom Y assumed in the free radical and the 1s-AO of the H atom:

$$S_{hs} = (S_{ss} + \omega S_{sp})/\sqrt{1 + \omega^2}\,. \qquad (6)$$

The results of calculations for π-electron radicals are presented in Table 2 in which the experimental constants of IHFC with protons a^{H}_{iso} and their values estimated in the MNDO/UHF approximation are also listed in addition to ω, S_{hs}, and K_α(H) values. The estimates of the constants made by formula (1) were obtained using two values of the coefficients of proportionality corresponding to simplified MO LCAO (K_α(H) = 508 Oe) and VB schemes (Eq. (2)).[7] Despite

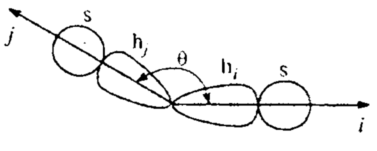
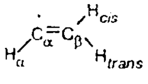
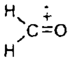
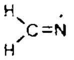
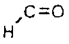
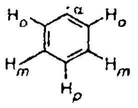
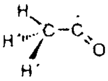
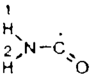
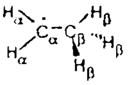


Fig. 1. Hybrid h-AO of the central atom Y and 1s-AO of H atoms involved in σ-bonds Y—H.

Table 3. Coefficients of proportionality (K_β(H)/Oe), delocalization ($^{o}a^{H}_{iso}$/Oe) and polarization ($^{p}a^{H}_{iso}$/Oe) components, and the constants of IHFC with protons (a^{H}_{iso}/Oe) in free σ-electron radicals

Radical	Nucleus	ω^a	$S_{hs}{}^a$	$K_\beta(H)^a$	$^{o}a^{H}_{iso}$	$^{p}a^{H}_{iso}$	a^{H}_{iso}	a^{H}_{iso},
					MNDORU			experiment
	H_α	1.24	0.644	766	45.0	−40.2	4.8	13.4
	H_{cis}	1.37	0.638	758	30.9	2.5	33.4	37.0
	H_{trans}	1.39	0.639	760	59.6	3.6	63.2	65.0
	H	1.45	0.614	729	116.1	−8.3	107.8	132.8
	H	1.45	0.599	713	81.6	−1.4	80.2	92.1
	H	1.32 ^{b} 1.35 ^{c}	0.613 ^{b} 0.596 ^{c}	729 ^{b} 710 ^{c}	142.1 ^{b} 150.1 ^{c}	−3.8 ^{b} −6.3 ^{c}	138.3 ^{b} 143.8 ^{c}	135.4
$\dot{C}\equiv C-H$	H	1.00	0.668	800	0.0	−22.1	−22.1	16.1
	H_o	1.41	0.640	761	5.4	13.9	19.3	17.9
	H_m	1.41	0.640	761	4.1	−15.4	−11.3	5.9
	H_p	1.41	0.640	761	2.3	13.3	15.6	1.9
$H-C\overset{\cdot}{\equiv}N$	H	1.52	0.574	689	147.3	22.5	169.8	137.5
	H	1.67	0.631	749	10.2	−3.3	6.9	
	H′	1.74	0.624	741	10.7	−1.0	9.7	5.1
	H(1)	1.41	0.699	852	1.1	−4.5	−3.4	|1.3|
	H(2)	1.39	0.696	846	61.1	−10.9	50.2	|30.4|
	H_β	1.67	0.610	725	15.3	9.2	24.5	26.9

[a] See Eqs. (3) and (6).

[b] Variant I (see Table 1).

[c] Variant II (see Table 1).

the fact that it is logical to use a coefficient of proportionality equal to the Hartree—Fock coefficient (δ(H) = 508 Oe) in the MNDO/UHF calculations of π-electron radicals, for comparison we also listed the values of the constants of IHFC with protons a^{H}_{iso} obtained from calculations using an alternative procedure for their estimate by relationship (2).

From the data listed in Table 2 it follows that in all cases the coefficient of proportionality K_α(H) determined using Eq. (2) is somewhat smaller than 508 Oe. At the same time, both procedures for estimating the constants of IHFC with protons in π-electron radicals are characterized by approximately equal absolute deviations from the experimental values. Since in practice it is more convenient to perform routine calculations of constants a^{H}_{iso} using a constant value of the coefficient of proportionality (K'_α(H) = 508 Oe), it is this procedure for assessing their values that seems to be more preferential for π-electron radical systems.

It is noteworthy that for isoelectronic π-radicals $CH_2^{-\cdot}$ and $NH_2^{\cdot}$ (as well as for $CH_3^{\cdot}$ and $NH_3^{+\cdot}$) the deviations of calculated IHFC constants from experimental ones are opposite in sign, though relatively small. Analogously, the calculated constant of IHFC with the α-proton for the $C_\alpha H_2C_\beta H_3^{\cdot}$ radical of the "intermediate" π/σ-type with the unpaired electron localized mainly on the C_α atom is somewhat larger, while for the π-radical $H_2NO^{\cdot}$ with the heteroatomic radical center it is somewhat smaller in absolute value than the experimental value. On the whole, the data in Table 2 indicate a fairly good agreement between theory and experiment.

At the same time, noteworthy is an appreciable deviation of the estimated constant of IHFC with protons in the $H_2O^{+\cdot}$ radical from the experimental value. In order to attain better agreement, we varied the value of the H—O—H angle; however, the calculated IHFC constant appeared to be only slightly sensitive to this parameter. Most likely, in the case of π-radical $H_2O^{+\bullet}$ the drawbacks of the semiempirical MNDO approximation are not effectively compensated by the parametrization obtained in the "fitting" procedure.

The results of analogous calculations for several σ-electron radicals are listed in Table 3. Here the values of the coefficient of proportionality $K_\beta(H)$ were determined using expression (3), which implies predominance of the delocalization (one-electron) contribution $^{\circ}\rho^{H}_{s}$ to the spin population of the 1s-AO of the H atom, *i.e.*, the neglect of the spin-polarization[3] correction $^{p}\rho^{H}_{s}$. Therefore, the use of these $K_\beta(H)$ values is justified only in the framework of the RHF approach. For the free-radical systems considered, we calculated the values of the delocalization components ($^{\circ}a^{H}_{iso}$) of IHFC constants a^{H}_{iso} by the MNDO/RHF method using the structural parameters taken from Table 1. They are listed in Table 3.

Particularly large (over 15—20 Oe) differences between the values of the delocalization contributions $^{\circ}a^{H}_{iso}$ obtained and the experimental constants a^{H}_{iso} (see Table 3) are observed for the σ-electron radicals $H_2C{=}CH^{\bullet}$, $HC{\equiv}C^{\bullet}$, and $H_2NCO^{\bullet}$. Let us consider the most plausible reasons for these discrepancies and possible ways of eliminating them in detail, taking the vinyl radical $H_2C{=}CH^{\bullet}$ as an example.

As can be seen from the data in Table 3, the values of constants of IHFC with *cis*- and *trans*-protons distant from the radical center in $H_2C{=}CH^{\bullet}$ are fairly well reproduced by the MNDO/RHF method, whereas for the H_α atom the calculated value differs substantially from the experimental one. First of all it is logical to try to eliminate this discrepancy by varying the value of the $C_\beta{-}C_\alpha{-}H_\alpha \equiv \theta_\alpha$ bond angle taking into account a rather strong angular dependence[3,6] of the calculated constant of IHFC with the α-proton in the vinyl radical. Other (more "rigid") structural parameters can be assumed to be fixed in the course of such a variation (see compound **8** in Table 1).

The dependence of the heat of formation (ΔH_f) of the vinyl radical on the angle θ_α, calculated by the MNDO/RHF method, is shown in Fig. 2. As can be seen, from the computational point of view the ΔH_f value can be thought of as a constant over a rather wide range of θ_α values. For this reason, it is logical to choose the degree of agreement between the theoretically determined and experimental values of the magnetic resonance parameters as a criterion for reliability of the geometric parameters used in calculations for the vinyl radical.

Based on this criterion, in the framework of the MNDO scheme we calculated the dependence of the coefficient of proportionality $K_\beta(H)$ on the angle θ_α using formula (3). The plot of the curve obtained is shown in Fig. 2. As should be expected, the coefficient of proportionality $K_\beta(H)$ monotonically increases as the angle θ_α increases and reaches its limiting value at θ_α = 180°.

Using the plot shown in Fig. 2 and the MNDO/RHF method, we found the angular dependence of the delocalization contribution $^{\circ}a^{H}_{iso}(\alpha)$ to the constant of IHFC with the α-proton in the vinyl radical (Fig. 3, curve *1*). This dependence shows that the $^{\circ}a^{H}_{iso}(\alpha)$ component monotonically decreases as the angle increases and becomes zero at θ_α = 180°. In this case, agreement with the experiment (a^{H}_{iso} = 13.4 Oe) is reached at $\theta_\alpha \approx 170°$ (see Fig. 2, curve *1*). However, this value of the $C_\beta{-}C_\alpha{-}H_\alpha$ bond angle is much larger than that obtained from *ab initio* calculations (see Table 1) or even roughly estimated ($\theta_\alpha \approx 150°$).[16] Therefore, in the framework of the RHF scheme it is impossible to attain reasonable agreement with the totality of ESR data only by varying the geometric parameters of the vinyl radical.

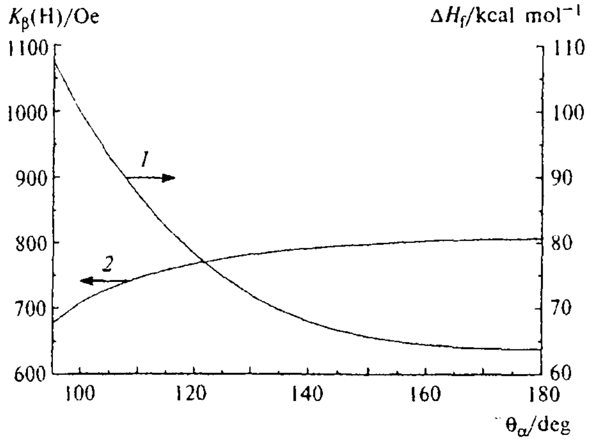


Fig. 2. Angular dependences of the heat of formation ΔH_f (*1*) and the coefficient of proportionality $K_\beta(H)$ (*2*) for the vinyl radical.

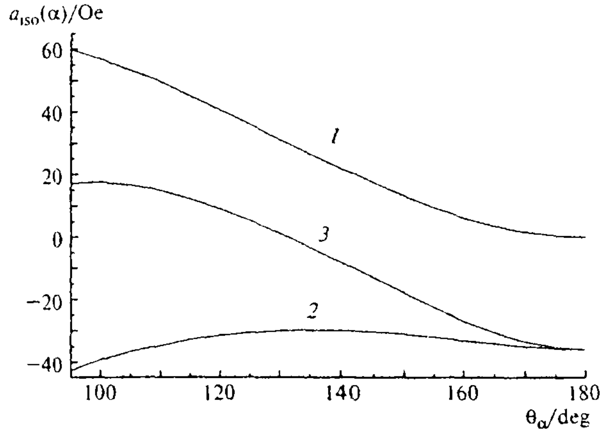


Fig. 3. Dependences of the delocalization (*1*) and spin-polarization (*2*) contributions and the total constant of IHFC with α-proton (*3*) in the σ-electron radical $H_2C{=}CH_\alpha^{\bullet}$ on the angle θ_α.

Yet another apparent procedure for eliminating the discrepancies between the assessed (using quantum-chemical methods) constants of IHFC with protons and those found experimentally is beyond the framework of the RHF approach, according to which the calculated one-electron spin densities ${}^{0}\rho^{\mathrm{RHF}}(\boldsymbol{r})$ at any point $\boldsymbol{r}$ are always nonnegative, whereas negative total spin densities $\rho(\boldsymbol{r})$ are also observed in the experiments. The polarization contribution ${}^{\mathrm{p}}\rho(\boldsymbol{r})$, which is complementary to the one-electron contribution and is mainly due to the exchange electron correlation, is responsible for negative $\rho(\boldsymbol{r})$ values. Because of inclusion of this correlation, electrons with oppositely directed spins become differently delocalized in space.

In practice, quantum-chemical calculations of magnetic resonance parameters of free radicals with inclusion of electron correlation effects are most often performed using the UHF method, in which the delocalization and polarization contributions to the spin density are not separated.[3] One should keep in mind that in some instances the polarization component ${}^{\mathrm{p}}\rho(\boldsymbol{r})$ obtained from such calculations is somewhat overestimated because of incorrect symmetry properties of the wave function in the UHF approximation. In the most consistent UHF schemes, the polarization correction should be defined as the difference

$$ {}^{\mathrm{p}}\rho^{\mathrm{UHF}}(\boldsymbol{r}) = \rho^{\mathrm{UHF}}(\boldsymbol{r}) - {}^{0}\rho^{\mathrm{RHF}}(\boldsymbol{r}). \qquad (7)$$

In the case of the RHF approach (*e.g*,, its CNDO/SP version[3]) this correction is, as a rule, estimated using perturbation theory.

For convenience and unification, in this work we used relationship (7); however, it was taken into account that the polarization component ${}^{\mathrm{p}}\rho(\boldsymbol{r})$ of the spin density can be represented as the sum of contributions of the spin (${}^{\mathrm{sp}}\rho(\boldsymbol{r})$) and exchange (${}^{\mathrm{ep}}\rho(\boldsymbol{r})$) polarizations.[3] In π-radicals, the ${}^{\mathrm{ep}}\rho(\boldsymbol{r})$ component is the only component, while in σ-radicals it is much larger than the ${}^{\mathrm{sp}}\rho(\boldsymbol{r})$ component. Considering the ${}^{\mathrm{sp}}\rho^{\mathrm{H}}{}_{\mathrm{s}}$ corrections in σ-radicals to be negligible and without coming into conflict with the results of the model theoretical study,[7] one should multiply the polarization spin populations ${}^{\mathrm{p}}\rho^{\mathrm{H}}{}_{\mathrm{s}}$ obtained according to expression (7) by the Hartree—Fock coefficient of proportionality $K_{\alpha}(\mathrm{H})$ = 508 Oe when assessing the spin-polarization components ${}^{\mathrm{p}}a^{\mathrm{H}}{}_{\mathrm{iso}}$ using relationship (1). It is this procedure (the MNDORU method) that was used to determine the spin-polarization contributions ${}^{\mathrm{p}}a^{\mathrm{H}}{}_{\mathrm{iso}}$ whose values are listed in Table 3.

The angular dependences of the spin-polarization component ${}^{\mathrm{p}}a^{\mathrm{H}}{}_{\mathrm{iso}}(\alpha)$ and total IHFC constant ($a^{\mathrm{H}}{}_{\mathrm{iso}}(\alpha) = {}^{0}a^{\mathrm{H}}{}_{\mathrm{iso}}(\alpha) + {}^{\mathrm{p}}a^{\mathrm{H}}{}_{\mathrm{iso}}(\alpha)$) calculated for the vinyl σ-radical are shown in Fig. 3 (curves *2* and *3*, respectively). As can be seen in Fig. 3, curve *3* monotonically decreases as the varied angle increases and agreement with the experiment is achieved at $\theta_{\alpha} \approx 125°$ rather than at $\theta_{\alpha} \approx 131°$ (see Table 1), which is quite acceptable from the viewpoint of both the energetics (see Fig. 2) and calculation errors of *ab initio* methods.[17] Thus, because of the inclusion of the spin polarization in the MNDO/UHF approximation, we succeeded in reproducing the experimental value of the IHFC constant $a^{\mathrm{H}}{}_{\mathrm{iso}}(\alpha)$ using geometric parameters of the vinyl radical that are virtually the same as those optimized by the UHF/STO-3G method and taken to be reliable (see Table 1).

Let us discuss now the IHFC constants of other σ-electron radicals in detail. As can be seen in Table 3, in all cases the coefficients of proportionality $K_{\beta}(\mathrm{H})$ are much larger than the Hartree—Fock coefficient of proportionality (508 Oe) and are in good agreement with the best value (743 Oe) fitted[18] using experimental data. Noteworthy is that in many cases the spin-polarization corrections ${}^{\mathrm{p}}a^{\mathrm{H}}{}_{\mathrm{iso}}(\alpha)$ are not so large as in the case of the α-proton in $\mathrm{H_2C{=}CH^{\cdot}}$, *i.e.*, the contribution of spin delocalization every so often appears to be predominant.

Since σ-radicals $\mathrm{H_2CO^{+\cdot}}$ and $\mathrm{H_2CN^{\cdot}}$ are isoelectronic and have the same symmetry, the regularities of the electron and spin density distribution for these radicals should be similar. As can be seen from the data in Table 3, in both cases the delocalization components ${}^{0}a^{\mathrm{H}}{}_{\mathrm{iso}}$ estimated by the MNDO/RHF method are somewhat smaller than the experimental IHFC constants $a^{\mathrm{H}}{}_{\mathrm{iso}}$. The spin-polarization corrections ${}^{\mathrm{p}}a^{\mathrm{H}}{}_{\mathrm{iso}}$ for these radicals are by about an order of magnitude smaller in absolute value than the delocalization contributions ${}^{0}a^{\mathrm{H}}{}_{\mathrm{iso}}$, which indicates that the simplified RHF scheme with the only value of the coefficient of proportionality is acceptable in this case.

Two slightly different sets of experimental structural parameters (see Table 1) are known for the formyl σ-radical ($\mathrm{HCO^{\cdot}}$). It is logical to decide between them on the basis of quantum-chemical estimates of the IHFC constants followed by their comparison with experimental data. As for any σ-radical, for the $\mathrm{HCO^{\cdot}}$ radical not only the spin population of the 1s-AO of the H atom, but also the coefficient of proportionality K_{β} is dependent on its geometry.

The values of the $a^{\mathrm{H}}{}_{\mathrm{iso}}$ constant calculated for the $\mathrm{HCO^{\cdot}}$ radical by the MNDORU method using two sets of geometric parameters (see Table 1) are listed in Table 3. Comparison of these values with the experimental value of $a^{\mathrm{H}}{}_{\mathrm{iso}}$ shows that reasonably good agreement with experimental data was achieved in both cases; however, set 1 of structural parameters seems to be somewhat more appealing. Noteworthy is that the assessed constants of IHFC with the $^{13}\mathrm{C}$ nucleus for the above two structures appeared to be virtually equal (~120 Oe).

For the ethynyl σ-radical with the linear configuration optimized using *ab initio* calculations (see Table 1), our MNDO calculations have led to incorrect spatial symmetry of the MO of the unpaired electron, which is indicated by the zero delocalization contribution (${}^{0}a^{\mathrm{H}}{}_{\mathrm{iso}} = 0$) to the constant of IHFC with proton. Most likely, the reason is that in fact the triple C≡C bond is much shorter than its length obtained from calculations by the UHF/6-31G** method (see Table 1). At a "standard"[19] length of the C≡C bond (1.16 Å), the unpaired electron, as it must be, is delocalized already in the σ-electron system, though the total constant of IHFC with proton calculated by the MNDORU method is strongly overestimated ($a^{H}_{iso} \approx 55$ Oe). It should be noted that in the framework of semiempirical INDO and CNDO/SP^3 approaches the ethynyl radical also belongs to the σ-type and that the constant is positive, though strongly overestimated ($a^{H}_{iso} \approx 45$ Oe).

According to the data of calculations in the MNDO/RHF approximation, the phenyl radical ($C_6H_5^{\cdot}$) belongs to the σ-type. The delocalization contribution $^{o}a^{H}_{iso}$ assessed in this approximation is comparable with the corresponding experimental IHFC constant in value for the proton in *meta-* or *para-*position and is by about a factor of 3 underestimated for the *ortho-*position. Unfortunately, inversion of the highest energy levels with a_1 and a_2 symmetry occurred in the framework of the MNDO/UHF scheme, which artificially imparted π-electron type to the free radical $C_6H_5^{\cdot}$. The energy interval between the above levels is narrow (~0.7 eV) and therefore it is possible to restore the desired order of levels by changing the radical geometry by an appropriate (relatively small) extent.

Radicals $HCN^{-\cdot}$ and $HCO^{\cdot}$ are isoelectronic. From Table 3 it can be seen that the experimental constants a^{H}_{iso} for these radicals are close, while the theoretical values are substantially different. It is logical to explain such a discrepancy by incorrect calculations of structural parameters of the σ-radical $HCN^{-\cdot}$ (see Table 1). In this connection it is noteworthy that calculations with a different basis set (3-21G, 3-21G**, 6-31G, and 6-31G**) have led to virtually the same geometric characteristics of the system.

It is apparent that reliable establishment of the geometry of σ-radical $HCN^{-\cdot}$ using a quantum-chemical procedure for energy minimization involves some difficulties due to peculiarities of its electronic structure, *viz.*, comparability of the contributions of two resonance structures, $H-C^{\cdot}=N^-$ and $H-C^-=N^{\cdot}$, to the ground state. In both these structures the chemical bond between the C and N atoms is a double bond and can be compared with the "standard"[19] length of 1.32 Å, whereas the value calculated by the UHF/6-31G** method (see Table 1) is much smaller. Therefore, in order to reach a better agreement between the experimental constant of IHFC with proton in the σ-radical $HCN^{-\cdot}$ and taking into account structural data for $HCO^{\cdot}$ (see Table 1), we fixed the C—H bond length (1.15 Å) and the value of the H—C—N angle (120°), whereas the interatomic distance *d*(C—N) was varied from 1.2 to 1.4 Å in the MNDO approximation.

As can be seen in Fig. 4 (curve *1*), the calculated heat of formation of the σ-radical $HCN^{-\cdot}$ changes slightly over a rather wide range of *d*(CN) values. At the same time, the a^{H}_{iso} constant (see Fig. 4, curve *2*) monotonically decreases as *d*(CN) increases and agreement with the experimental value is achieved at *d*(CN) = 1.325 Å, which is acceptable from the structural-chemical point of view. This confirms the statement[3,6,14,15] that it is comparison of calculated and experimentally measured radiospectroscopic characteristics rather than conventional procedure based on energy minimization that serves as a basis for more effective determination of structural parameters of free-radical systems.

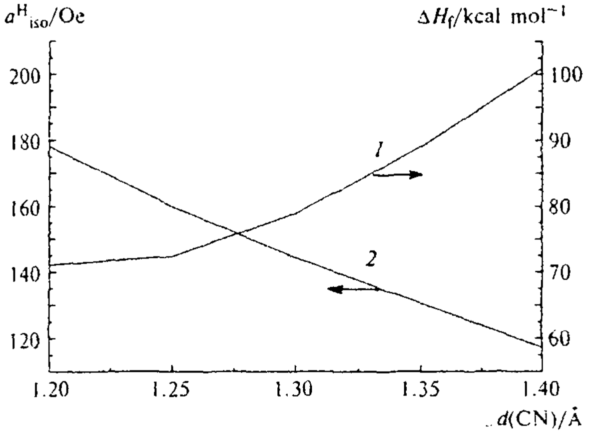


Fig. 4. Dependences of the heat of formation ΔH_f (*1*) and the constant a^{H}_{iso} (*2*) on the interatomic distance *d*(CN) for the σ-electron radical $HCN^{-\cdot}$.

One a^{H}_{iso} constant was experimentally measured[20] for the σ-electron radical $CH_3CO^{\cdot}$, whereas two types of magnetically inequivalent protons and, hence, two different IHFC constants (see Table 3) correspond to the minimum found in the course of energy optimization. This means that experimental data should be described assuming free rotation of the methyl group, *i.e.*, the calculated spin populations of the 1s-AO of three H atoms and corresponding IHFC constants should be averaged. It is easily seen that the averaged IHFC constant ($\bar{a}^{H}_{iso} = 8.8$ Oe) is in reasonable agreement with the experimental value and that the contribution of spin polarization is relatively small.

On the contrary, isotropic splittings for both protons are observed in the experimental ESR spectrum of the σ-electron radical $H_2NCO^{\cdot}$, which means that in this radical rotation about the C—N bond is hindered or, at least, its period is much longer than the characteristic time of the ESR method. In this case the absolute values of IHFC constants a^{H}_{iso} assessed by the MNDORU method are in fairly good agreement with the experimentally determined values.

As was mentioned above, the ethyl radical belongs to a "mixed" π/σ-type, *i.e.*, the constants of IHFC with α-and β-protons in this radical should be determined using the coefficients of proportionality K_{α}(H) and K_{β}(H), respectively (see Eqs. (2) and (3)). When comparing theoretical and experimental data, one should take into account free rotation of the methyl group and average three constants $a^{H}_{iso}(\beta)$. As can be seen in the last line in Table 3, the averaged experimental constant of IHFC with β-protons in the ethyl radical and that assessed by the MNDORU method are close.

Thus, the modified scheme[7] of quantum-chemical calculations of the constants of IHFC with protons in free radicals using orbital spin populations defined in the basis set of AOs symmetrically orthogonalized according to Löwdin naturally eliminates the apparent contradiction associated with the use of two substantially differing coefficients of proportionality in relationship (1) when estimating the above constants by the most widely used semiempirical quantum-chemical methods.[4–6,18] Particular values of these coefficients found from simple correlations and used in the literature are in good agreement with the $K_\alpha(H)$ and $K_\beta(H)$ values listed in Tables 2 and 3. It should be emphasized that the conventional procedure for estimating the IHFC constants a^{H}_{iso} using semiempirical quantum-chemical methods was essentially modified only for free σ-electron radicals, whereas for purely π-electron radicals it remained unchanged.

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