Correlations between magnetic resonance parameters of ESR and NMR spectra

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Empirically established correlations between magnetic resonance parameters of free radicals (g-factors, isotropic hyperfine coupling constants) and isostructural molecules (chemical shifts, isotropic spin-spin coupling constants) or structurally similar ligands in paramagnetic transition metal complexes (isotropic chemical shifts) are systematized and critically discussed. Quantum-chemical analysis of the suggested spin distribution damping coefficients in model systems and structurally similar chemical compounds is performed. Based on the results obtained, physicochemical interpretation of the observed correlations between the parameters of ESR and NMR spectra is given.

Key words: ESR; NMR; magnetic resonance parameters, correlations; quantum-chemical analysis.

Introduction

Basic theoretical concepts[1] suggest that a close correlation should exist between magnetic resonance parameters, which characterize magnetic interactions in isostructural paramagnetic and diamagnetic molecular systems. The formal analogy between the most significant individual components of spin-Hamiltonians[2] of a free radical ($\hat{\mathbf{H}}_S$) and the corresponding molecule ($\hat{\mathbf{H}}_I$) in the magnetic field ($\mathbf{H}$) expressed through electronic ($\hat{\mathbf{S}}$) and nuclear ($\hat{\mathbf{I}}$) spin variables and so-called magnetic resonance parameters (g_{uv}, A_{uv}, σ_{uv}, J_{uv}), which, in the general case, are tensor values, also indicates that parameters of ESR and NMR spectra can be related:

$$\hat{\mathbf{H}}_S = \hat{\mathbf{S}}_u \cdot g_{uv} \cdot \mathbf{H}_v + \sum_q \hat{\mathbf{S}}_u \cdot A_{uv}^{(q)} \cdot \hat{\mathbf{I}}_v^{(q)} , \qquad (1)$$

$$\hat{\mathbf{H}}_I = \sum_q \hat{\mathbf{I}}_u^{(q)} \cdot \sigma_{uv}^{(q)} \cdot \mathbf{H}_v + \sum_{q \neq p} \hat{\mathbf{I}}_u^{(p)} \cdot J_{uv}^{(p,q)} \cdot \hat{\mathbf{I}}_v^{(q)} . \qquad (2)$$

A similar analogy also can be observed for some other components of spin-Hamiltonians $\hat{\mathbf{H}}_S$ and $\hat{\mathbf{H}}_I$, for example, for those describing spin-rotational interactions.

At the same time, it should be emphasized that although the corresponding terms in Eqs. (1) and (2) are formally similar, they can have different natures. For example, the hyperfine coupling (HFC) constants ($A^{(q)}$) of unpaired electrons with magnetic nuclei q can be determined in the first order of the perturbation theory, while the spin-spin coupling (SSC) constants ($J^{(p,q)}$) of magnetic nuclei p and q are determined in the second order. In addition, in a certain case, we use wave functions of a paramagnetic compound in quantum-chemical calculations and, in another case, wave functions of a diamagnetic particle are used. It also should be taken into account that geometric parameters of a free radical and related molecule usually noticeably differ.[2]

Despite this fact, specific correlations between magnetic resonance parameters of ESR and NMR spectra can be experimentally established for sufficiently wide classes of molecular systems. As will be shown below, these correlations can be theoretically substantiated. The practical interest in correlations between different magnetic resonance parameters is due to the fact that data obtained by ESR and NMR methods can supplement each other. This gives additional possibilities for decoding and interpretation of ESR and NMR spectra and for establishing the structure of chemical compounds. For example, easily accessible data on NMR spectra of molecules can be used for the qualitative prediction of the shape of ESR spectra of unknown free radicals. Deviations from correlations should be taken into account when the geometry of short-lived particles is discussed and when some other structural chemical problems are solved.

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* Dedicated to the memory of Academician V. V. Voevodskii (to the 80th anniversary).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1575—1583, September, 1997.

1066-5285/97/4609-1501 $18.00

Correlation between g-tensors in free radicals and chemical shift tensors in isostructural molecules

Nuclear magnetic shielding σ-tensors and g-tensors are among the most important magnetic resonance parameters in radiospectroscopy and its applications to chemical problems. The comparison of the well-known Ramsy (for σ-tensor) and Stone (for g-tensor) equations showed[3] that for one-electron systems in the nondegenerate state, these equations are closely related. This correlation can be presented as follows:

$$g_{vv} = 2 + \sum_{A} Z^{A} \cdot \sigma^{A}_{vv} , \tag{3}$$

where g_{vv} is the main component of the g-tensor along the main v axis, and σ^{A}_{vv} is the corresponding component of the shielding tensor for the A nucleus with the Z^A charge. It is reasonable to expect that multielectronic systems should be characterized by a correlation between σ- and g-tensors, which is similar to Eq. (3), but is more approximate. However, at the present time, this problem is insufficiently discussed in the literature, although it is doubtless of interest for quantitative analysis and systematization of radiospectroscopic data.

Correlation between isotropic hyperfine coupling constants in free radicals and isotropic spin-spin coupling constants in isostructural molecules

In two independent works,[4,5] the authors observed a certain correspondence (Fig. 1) between the isotropic hyperfine coupling (IHFC) constants ($a^{H'}_{iso}$) in radicals with the free valence of the C atom and the indirect spin-spin coupling (SSC) constants ($J_{HH'}$) in molecules, in which this free valence is saturated with the H atom. The qualitatively established correlation can be explained as follows.

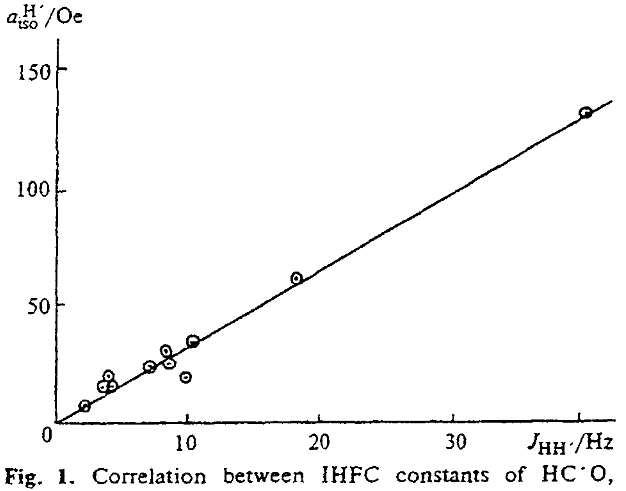


Fig. 1. Correlation between IHFC constants of $HC^{\cdot}O$, $HC^{\cdot}{=}CH_2$, $H_3C^{\cdot}CO$, $H_3CC^{\cdot}H_2$, $HC{\equiv}C^{\cdot}$, and $Ph^{\cdot}$ radicals and SSC constants of isostructural molecules.[5]

In the presence of the magnetic moment of the H proton, any doubly-occupied MO of the molecule (Ψ_d), which has no node on the H nucleus, is split into two spatially different orbitals $\Psi_d{}^\alpha$ and $\Psi_d{}^\beta$, since due to the contact interaction, one electron of the electron pair, for example, β-electron, is somewhat shifted to this proton, and the α-electron is "pushed out" to other nuclei to the same extent. This weak polarization in the molecule results in the noncompensated spin cavities, which should be distributed approximately in the same manner as in the isostructural radical that is formed after the elimination of the H atom.

This follows from the consideration of a hypothetical limiting case[6] when the extraordinarily great nuclear magnetic moment $\mu^H = \infty$ results in such a strong redistribution in the molecule that it converts into some artificially created "virtual" radical. In this hypothetical system, the β-electron with the lowest energy is entirely "captured" by the H proton and completely shields this proton from other electrons with the β-spin. At the same time, all electrons with the α-spin cannot be present in the area contacting with the disturbing H proton, because it has an infinitely great magnetic moment.

When this limiting situation is formally analyzed in terms of a simple quantum-chemical scheme, it can be shown by the theorems of the matrix algebra[6] that when $\mu^H \to \infty$, all $\varepsilon_d{}^\beta$ eigenvalues (orbital energies) of the Hartree—Fock matrix decrease for β-electrons in the molecule, and the lowest of them $\varepsilon_d{}^\beta \to -\infty$, while all others tend to the $\varepsilon_s{}^\beta$ eigenvalue of the corresponding matrix for β-electrons in the isostructural free radical. Naturally, the contribution of the 1s-AO centered on the H proton disappears in all MO except the lowest one, and, in the limit, they become identical to the spatial $\Psi_s{}^\beta$ MO of the radical. Orbitals of α-electrons undergo similar transformations with the only difference that, when $\mu^H \to \infty$, the highest eigenvalue $\varepsilon_d{}^\alpha \to +\infty$, and all other orbital energies increase to the $\varepsilon_s{}^\alpha$ values inherent in the free radical.

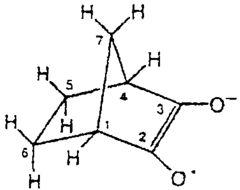
It is noteworthy that previous works[4—6] mainly discussed planar σ-electron radicals ($C_6H_5^{\cdot}$, $HC^{\cdot}O$, $^{\cdot}C{\equiv}CH$, $HC^{\cdot}{=}CH_2$, *etc.*), whose geometric parameters are almost the same as those of the corresponding molecules (C_6H_6, H_2CO, $HC{\equiv}CH$, $H_2C{=}CH_2$). Evidently, hybrid σ-AO of unpaired electrons in these radicals differ slightly in shape from σ-AO participating in the formation of chemical C—H bonds in the isostructural molecules, and hence, the direct comparison of the $a^{H'}_{iso}$ and $J_{HH'}$ constants is valid. When the structural analogy of radicals and molecules is not so complete (see structures **A**—**G** presented below), the following scheme of reasoning can be suggested.[7]

Let χ_μ and φ_μ be hybrid AO of the C atom in the molecule and free radical, respectively. When χ_μ and φ_μ are real, the following expressions hold:

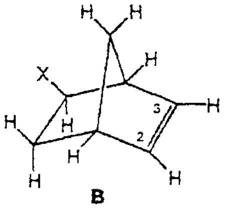
$$\chi_\mu = \sum_{v} a_{\mu v} \varphi_v , \tag{4}$$

$$\rho_\mu \equiv \chi_\mu^2 = \sum_{\nu,\lambda}[a_{\mu\nu}^2\varphi_\nu^2 + a_{\mu\nu}a_{\mu\lambda}\varphi_\nu\varphi_\lambda] . \qquad (5)$$

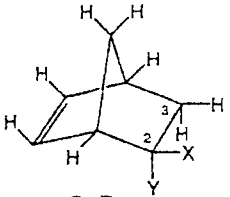
The HFC constants of the radical and molecule cannot be directly compared, because Eq. (5) contains multiplicative terms ($\varphi_\nu\varphi_\lambda$), which disappear only when $\chi_\mu = \varphi_\mu$. The comparison is not difficult when the difference in hybridization of AO of the C atom in the molecule and free radical concerns only two (of the four) AO. This situation can take place when the structure of the molecule (radical) is rigid and, hence, hybridization of the two other AO is fixed. Structures **A—G**,[7] whose fragments containing the C(2) (or C(3)) atom are presented in Fig. 2, are attributed to the case described.



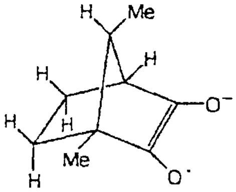
A



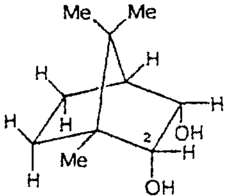
B



C, D



E



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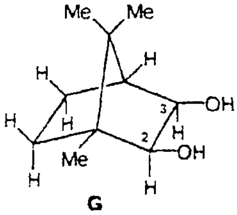

G

B: X = OH, CN
C: X = H; Y = OH, CN, COOMe
D: X = OH, CN, COOMe; Y = H

The geometric parameters of these fragments in the molecules (M^1 and M^2) and in the radical (R) should not noticeably differ. Then the σ_3- and σ_4-AO can be approximately considered to be unchanged, and the structure of the radical center R can be considered to be planar. According to Eq. (4),

$$\pi = (1/\sqrt{2})(\sigma_1 - \sigma_2), \qquad (6)$$

$$\sigma = (1/\sqrt{2})(\sigma_1 + \sigma_2), \qquad (7)$$

from where

$$\sigma_1^2 + \sigma_2^2 = \sigma^2 + \pi^2, \qquad (8)$$

$$\pi^2 = \sigma_1^2 + \sigma_2^2 - \sigma^2. \qquad (9)$$

It follows from Eq. (9) that the spin population of the π-AO of the R radical can be presented as a superposition of the spin populations on the σ_1-, σ_2-, and σ-AO of the corresponding M^1 and M^2 molecules. Therefore, the $a_{\text{iso}}^{\text{H}}$ constants in radicals should be compared to the $J^1 + J^2 - J$ combination of the constants in molecules. This comparison[7] demonstrated that regularities of long-range hyperfine interactions in structurally similar bicyclic compounds (see structures **A—G**) are common.

All the aforesaid makes it possible to show a certain similarity in distributions of noncompensated spin densities in paramagnetic and related diamagnetic molecular systems. Successive theoretical interpretation of experimentally observed correlations should be based unambiguously on detailed analysis of mechanisms of hyperfine interactions of magnetic moments of electrons and nuclei in radicals and molecules.

Taking this into account, one should pay attention to the simplified method for calculation of $J_{\text{HH}'}$ constants, which can be reduced to the isolation of two MO (bonding and antibonding), which are formed of MO of the unpaired electron of the free radical and 1s-AO of the H atom.[8] Although this approach results automatically in the correlation, it is rather formal because it does not consider the mechanism of spin perturbation in molecules. The successive analysis of this mechanism requires one to take into account all MO. In addition, difficulties arise when the method suggested is used for the calculation of $J_{^1\text{H}^{13}\text{C}}$ constants.

Qualitative analogies between electronic and nuclear spin effects suggest that the similarity of "damping" coefficients of hyperfine interactions of magnetic moments of electrons and nuclei in isostructurally free radicals (K^{R}) and molecules (K^{M}) is a reason for the existence of correlations between parameters of ESR

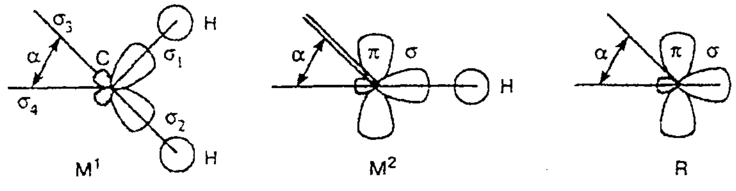

Fig. 2. Fragments of structures **A—G**.

and NMR spectra. The K^R and K^M values calculated for both protons and ^{13}C nuclei in the σ-electron C_6H_5, $HC^{\cdot}{=}CH_2$, $^{\cdot}C{\equiv}CH$, and $HC^{\cdot}O$ radicals and in the corresponding C_6H_6, C_2H_4, C_2H_2, and H_2CO molecules are compared below.

It is known that in terms of the MO LCAO method, the isotropic spin-spin coupling constant (J_{AB}) can be expressed through the fundamental physical constants (g_e, β_e, $\hbar$, γ_B) and atom-atomic polarizability ($\pi_{s_As_B}$):

$$J_{AB} = \kappa_B \cdot \rho^M_{s_B}, \qquad (10)$$

where

$$\kappa_B = (8\pi/3)g_e \cdot \beta_e \cdot \hbar \cdot \gamma_B \cdot |s_B(0)|^2,$$

and the value

$$\rho^M_{s_B} = (1/4) \cdot \kappa_A \cdot \pi_{s_As_B} \qquad (11)$$

should be interpreted as the spin population of the s_B-AO, which is induced in the molecule by the magnetic A nucleus. In the same approximation for IHFC in free radicals

$$a^B_{iso} = \kappa_B \cdot \rho^R_{s_B}, \qquad (12)$$

where $\rho^R_{s_B}$ contains the one-electron and spin-polarization contributions[2] to the spin population of the s_B-AO. It can be seen from Eqs. (10) and (12) that the discussion about the correlation considered is reduced to the analysis of the dependence between ρ^R and ρ^M.

In terms of the RHT method,[2] let us consider the simplest model of two interacting equivalent σ-bonds (Fig. 3, $\bar{F}_{\sigma\sigma'} = \bar{F}_{\lambda\lambda'}$) that are formed of the same orthogonalized atomic orbitals ($\overline{AO}$) and are characterized by the resonance integral $\bar{F}_{\sigma\lambda} = \eta \cdot \bar{F}_{\sigma\sigma'}$ ($\eta < 1$). The elementary calculation of the atom-atomic polarizabilities (π_{AB}) gives the following expression for the damping coefficient:[9]

$$K^M = \frac{\rho^M_{\lambda\lambda'}}{\rho^M_{\sigma\sigma}} = \frac{\pi_{\sigma'\lambda'}}{\pi_{\sigma'\sigma}} = \frac{5\eta^2 + \eta^4}{8 + \eta^2} \cong \frac{5}{8}\eta^2 . \qquad (13)$$

In the case of the model σ-radical formed by the elimination of the σ′-"atom," for the damping coefficient of the one-electron contribution to the spin population of AO, we have

$$K^R_0 = \rho^R_{\lambda\lambda'}/\rho^R_{\sigma\sigma} = \eta^2 . \qquad (14)$$

The ratio of coefficients $K_0{}^R/K^M = 1.6$ is very close to the value of ~1.4 estimated from the empirical correlation.[5] Assuming that the spin-polarization contribution $\Delta\rho^R_{\lambda'\lambda'}$ is caused only by the spin population of the σ-AO, it can be easily obtained from the perturbation theory[9] that

$$K^R_p = \frac{\Delta\rho^R_{\lambda\lambda'}}{\rho^R_{\sigma\sigma}} = \frac{\pi^R_{\sigma\lambda'} \cdot \lambda_p \cdot \rho^R_{\sigma\sigma}}{\rho^R_{\sigma\sigma}} = -\lambda_p \cdot \eta^3 \cdot \frac{(1 - 2\eta^2)}{(1 + \eta^2)^{5/2}} . \qquad (15)$$

It can be seen that $K_p{}^R$ differs from $K_0{}^R$ in sign (at $\eta < 0.7$). This indicates that account for the spin polarization should decrease the $K_0{}^R/K^M$ value. In calculations by the RHT method[2] when dimensionless values are used, it is commonly accepted that $\lambda_p \approx 1$ and $\eta \approx 0.5$.

For the elucidation of the mechanism of appearance of spin populations of atoms, which are more remote from the disturbing center, let us compare hypothetical systems of two and four interacting σ-bonds. These hypothetical systems were modeled by H_2 molecules located at a distance of 1.5 Å with the variable θ angle (Fig. 4). They were calculated by the widely used semiempirical MNDO method.[10]

The ratios of damping coefficients without ($K_0{}^R/K^M$) and with account (K^R/K^M) for the spin-polarization correction at three values of the θ angle are given in Table 1 for the hypothetical structures of three and four H atoms. The data in the last line in Table 1 indicate that the degree of curvature of the model system has almost no effect on the K^R/K^M ratio for the fourth center, and it is not greater than 1.5 for all θ. This agrees with the value estimated above for the simpler model and, in addition, is much closer to the experimentally determined value of ~1.4. The conclusion that this ratio should be somewhat greater when the spin-polarization correction is not taken into account was also confirmed.

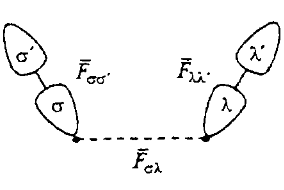

Fig. 3. Model of two interacting equivalent σ-bonds.

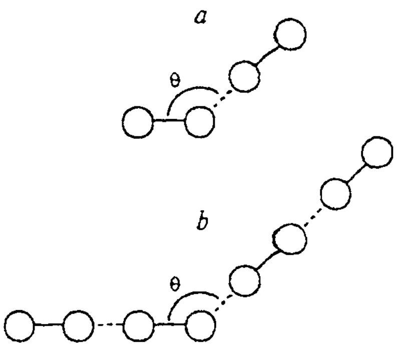

Fig. 4. Model of two (*a*) and four (*b*) interacting σ-bonds.

Table 1. Ratios of damping coefficients of spin distributions (K) in model systems with three and four centers

Center No.	θ = 180°		θ = 135°		θ = 90°	
	K_0^R/K^M	K^R/K^M	K_0^R/K^M	K^R/K^M	K_0^R/K^M	K^R/K^M
2	1.0	1.0	1.0	1.0	1.0	1.0
3	0.07	2.03	0.16	2.83	0.19	3.01
4	1.54	1.46	1.53	1.46	1.53	1.46

It is noteworthy that the regularities of damping of spin distributions for the third center differ strongly from those for the fourth center.

The results of similar calculations for the model system of four interacting σ-bonds (see Fig. 4) are presented in Table 2. It can be seen from comparison of the data in Tables 1 and 2 that when the number of σ-bonds in the hypothetical molecular structure increases, the main regularities of the spin distribution damping in this structure remain unchanged. In fact, the K_0^R/K^M value increases as the single-type AO is removed from the disturbing center, and when the contribution of the spin polarization is taken into account, it somewhat decreases for even AO and sharply increases for odd AO.

It should be specially emphasized that the two strongly different semiempirical approaches resulted in qualitatively similar and quantitatively very close results. This additionally confirms that the calculation RHT scheme, which is simple and clear for chemists, is adequate.[2] In addition, based on the quantum-chemical analysis of model systems (see Figs. 3 and 4), we can prognosticate that no correlation should be expected when IHFC in free radicals is caused by the spin polarization. This prognostication is important for the structural chemistry and radiospectroscopy.

For checking the conclusions obtained by simplified model systems in terms of the RHT method, neglecting the σ—π-exchange interaction, C_6H_6, C_2H_4, C_2H_2, and H_2CO molecules and the corresponding σ-electron radicals were calculated.[9] "Damping" coefficients were determined by analogy to Eqs. (13) and (14) from the ratio of spin populations of the AO of the H (or C) atoms to the spin population of the hybrid σ-AO, which is nonbonding in σ-radicals and forms the localized MO with the AO of the H atom in the molecules. The spin populations of AO in radicals were calculated without and with account for the spin polarization. The correlation dependences between K^R and K^M for the radicals and molecules considered are presented in Figs. 5 and 6. Dark and light circles correspond to the K^R and K^M values determined with and without account for the polarization correction, respectively. As can be seen, they are characterized by an approximate linear dependence.

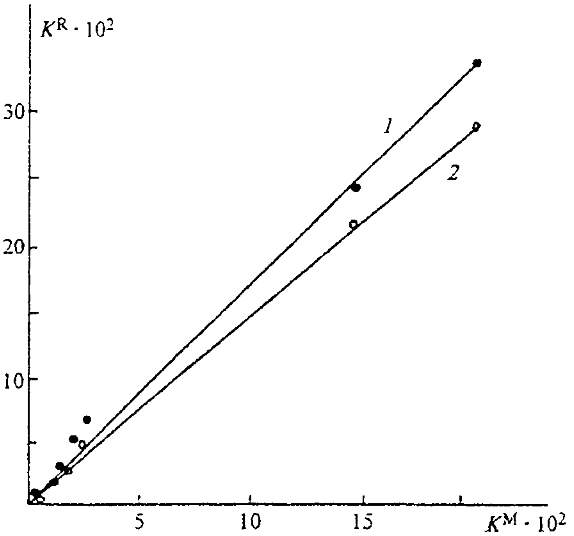

Fig. 5. Correlation between damping coefficients of isotropic HFC with protons in HC˙O, HC˙=CH$_2$, HC≡C˙, and Ph˙ σ-radicals and isostructural molecules determined without (*1*) and with account (*2*) for the polarization correction.[9]

Thus, the results of our calculations agree with those considered above for the simplified model systems and make it possible to draw the following conclusions:

1. When only one-electron spin populations of AO of free radicals are taken into account, the K_0^R/K^M ratio tends to increase as the atoms are removed from the disturbing center.

2. An additional contribution of the spin polarization in radicals results in the fact that relative coeffi-

Table 2. Calculated ratios of damping coefficients of spin distributions (K) in model systems with seven and eight centers

Center No.	θ = 180°				θ = 135°,		θ = 90°,	
	RHT		MNDO		MNDO		MNDO	
	K_0^R/K^M	K^R/K^M	K_0^R/K^M	K^R/K^M	K_0^R/K^M	K^R/K^M	K_0^R/K^M	K^R/K^M
2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
3	0	2.2	0.10	2.41	0.14	2.72	0.17	2.90
4	1.6	1.2	1.64	1.59	1.63	1.59	1.62	1.58
5	0	5.1	0.32	5.91	0.36	6.32	0.38	6.53
6	2.1	1.1	2.20	2.04	2.20	2.04	2.20	2.03
7	0	10.4	0.51	12.70	0.54	12.95	0.57	13.25
8	2.4	1.1	2.52	2.28	2.50	2.27	2.50	2.27

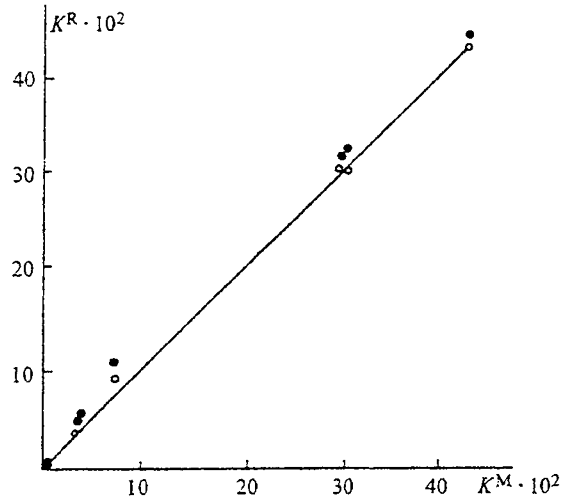

Fig. 6. Correlation between damping coefficients of isotropic HFC with ^{13}C nuclei in $HC^{\cdot}O$, $HC^{\cdot}{=}CH_2$, $HC{\equiv}C^{\cdot}$, and $Ph^{\cdot}$ σ-radicals and isostructural molecules.[9]

cients become closer, *i.e.*, a linear dependence between K^R and K^M appears.

3. A linear correlation, which is the same as that for protons, should exist between IHFC constants with ^{13}C nuclei. (Available experimental data are still insufficient to check this prediction.)

4. The degree of curvature of molecular fragments has almost no effect on the ratio of damping coefficients.

5. The K^R/K^M ratio for both ^1H (*cf.* Fig. 5) and ^{13}C nuclei (*cf.* Fig. 6) is close to unity.

6. Variation of semiempirical parameters or choice of the different calculation scheme affects substantially only absolute values of IHFC constants, and the correlation ratio between K^R and K^M remains almost unchanged.

The resemblance in regularities of HFC in isostructural radicals and molecules stimulated the application of all sufficiently simple and physically clear schemes, which were developed for systems with open electron shells, for analysis of J constants. For example, according to the general RHF/SP approach that was tested for free radicals, IHFC in molecules was supposed[11] to be estimated from the expression

$$J_{AB} = (1/4)\lambda^J{}_{AB} \cdot \kappa_A \cdot \kappa_B \cdot \pi_{s_A s_B}, \qquad (16)$$

in which the calibrating $\lambda^J{}_{AB}$ parameter was inserted additionally as compared to Eq. (10). This parameter is necessary to "correct" the π_{AB} polarizabilities calculated using not energies of singlet-triplet excitations, but normal differences between orbital energies, and, in addition, to take into account the difference of effective nuclei charges in molecules from the corresponding values for free atoms. (The κ_A and κ_B parameters are taken with the Hartree—Fock densities of atomic s-functions on the A and B nuclei.)

Table 3. Experimental and calculated spin-spin coupling constants (J) in the molecules studied

Molecule	Atomic nuclei		J/Hz		
	A	B	experiment	INDO	MNDO
C_6H_6	H_α	H_o	7.5	8.9	8.8
	H_α	H_m	1.4	2.5	1.7
	H_α	H_p	0.7	0.6	0.6
	H_α	C_α	157.5	134.6	140.1
	H_α	C_o	1.0	2.0	1.1
	H_α	C_m	7.4	6.1	7.9
	H_α	C_p	1.1	0.1	0.3
	C_α	C_o		63.9	66.2
	C_α	C_m		0.4	0.3
	C_α	C_p		5.1	5.2
C_2H_4	H	H_α	2.5	10.7	7.0
	H	H_{cis}	11.7	9.8	10.7
	H	H_{trans}	19.1	24.8	23.0
	H	C_α	156.4	154.4	157.6
	H	C_β	2.4	2.0	1.3
	C	C	67.6	68.9	70.7
C_2H_2	H	H	9.5	10.2	7.8
	H	C_α	248.7	249.9	253.3
	H	C_β	49.3	8.9	9.2
	C	C	171.5	182.3	168.6
H_2CO	H	H	40.2	29.9	28.7
	H	C	172.0	180.0	176.1

The isotropic spin-spin coupling constants in the aforediscussed C_6H_6, C_2H_4, C_2H_2, and H_2CO molecules, which were experimentally determined and calculated from Eq. (16) in terms of the INDO and MNDO methods at $\lambda^J{}_{HH} = 7$, $\lambda^J{}_{HC} = 4.5$, $\lambda^J{}_{CC} = 4$ and $\lambda^J{}_{HH} = 4$, $\lambda^J{}_{HC} = 3$, $\lambda^J{}_{CC} = 3$, respectively, are compared in Table 3. As the data in Table 3 show, these approaches reproduce satisfactorily the majority of the qualitative regularities, which are well known for a number of molecules. A correct order of the $J_{HH'}$ and $J_{^1H^{13}C}$ constants was obtained, which characterizes the spin-spin coupling of the ^1H and ^{13}C nuclei in the *ortho-*, *meta-*, and *para*-positions of the benzene ring. Among proton-proton coupling constants, in the C_2H_4 molecule, $J_{HH'}$ related to *trans*-H is most significant. As a whole, the MNDO method reproduces the measured spin-spin coupling constants somewhat better than a simpler semiempirical variant of INDO. Nevertheless, in the case of molecules, both approaches are appropriate for simplified quantum-chemical calculations.

The theoretical interpretation of IHFC in aromatic and planar nonsaturated molecules often raises a question concerning the role of π-electrons in the spin-spin coupling between protons located in the zero plane of the π-AO (φ_A and φ_B) (Fig. 7). When this problem is considered in terms of the perturbation theory with account for one-centered exchange integrals ($æ_{\mu\nu}$), the following formula can be easily derived[12]

$$J^\pi{}_{HH'} = (1/16)(\kappa_H)^2 \cdot æ_{Aa} \cdot æ_{Bb} \cdot \pi_{AB} \cdot \pi_{aH} \cdot \pi_{bH'}, \qquad (17)$$

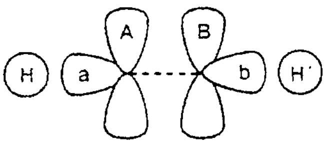

Fig. 7. Fragments of the molecular system with nonsaturated chemical bonds.

which takes the simple form in assumption of localized C—H bonds:

$$J^{\pi}_{\mathrm{HH'}} = (1/4)Q^2_{\mathrm{CH}} \cdot \pi_{\mathrm{AB}}, \tag{18}$$

where Q_{CH} is the spin-polarization constant entering the known McConnel relation.[2] It is noteworthy that the more complicated but less exact formula has been previously obtained[13] instead of Eq. (18). The use of this formula for delocalized π-electron systems meets some basic objections.[14]

Correlation between IHFC constants in radicals and isotropic chemical shifts in structurally similar ligands of paramagnetic transition metal complexes

The problematic work[5] discusses the correspondence between the $a^{\mathrm{H}}_{\mathrm{iso}}$ and $J_{\mathrm{HH'}}$ values considered in the previous section and also a certain similarity between the IHFC constants with protons ($a^{\mathrm{H}}_{\mathrm{iso}}$) in free radicals ($C_6H_5^{\cdot}$, $HC^{\cdot}{=}CH_2$) and isotropic chemical shifts (δH) in structurally related ligands (NC_5H_5, $HN{=}CH_2$) in the coordination sphere of paramagnetic Ni^{II} and Co^{II} ions. To the present time, there are many examples of this similarity and due to this, it became obvious that the problem of analysis and systematization of regularities of IHFC in complicated paramagnetic complexes with multiatomic organic ligands can be reduced to considerably less labor-consuming and more reliable quantum-chemical calculations of structurally related free radicals.

It should be emphasized that a large experimental material[15,16] on the spin density distribution in complex organic ligands of paramagnetic complexes is available. At the same time, problems on theoretical interpretation of experimental data are insufficiently studied. There were rare attempts to estimate relative spin populations of AO of organic ligands on the basis of theoretically determined results for similar radicals. In addition, only few calculations of HFC in simple paramagnetic complexes were performed in terms of simplified semiempirical quantum-chemical methods.[17] This is because sufficiently reliable semiempirical methods for studying the electronic structure of complex compounds are absent, and it is technically difficult to calculate complexes with four or six multiatomic ligands. Therefore, search for approximate schemes, which partially eliminate these difficulties and are appropriate for estimation calculations providing possibilities for quantitative comparison and analysis, is justified.

A linear correlation between IHFC constants in ligands of paramagnetic complexes and the corresponding free radicals is a prerequisite for the formulation of the approximation given below.[5] It is this correlation whose existence justifies the approximations that lie at the basis of the simple calculation scheme, in terms of which the problem on delocalization of spin densities in paramagnetic complexes can be divided into two stages.

In the first stage, a subsystem consisting of a metal ion and hybrid AO of unshared electron pairs of coordinated atoms is distinguished from the complex. (In further discussion, to be specific, let us restrict our consideration to the case of coordinated N atoms.) In the second stage, we consider the distributions of spin densities in ligands that appear due to the resonance and exchange interactions between an unpaired electron localized on the antibonding χ_{A} orbital and electrons of the ligands. The resonance and exchange interactions result in the appearance of the one-electron and polarization contributions, respectively, to spin populations of AO of the ligands. The squares of the resonance integrals or exchange integrals for the χ_{A} orbital and MO of the ligands should be taken proportional to the spin populations of AO of coordinated unshared electron pairs of nitrogen atoms (ρ^0_{N}).

For simplification, let us assume that the central metal ion has only one unpaired electron, although the generalization of the model for the central ion with a greater multiplicity is not difficult. When the AO of the unpaired electron of the central ion is designated as φ_0 and the hybrid AO of the unshared electron pair of the N atom as φ_{N}, for the bonding and antibonding orbitals with the ε_{b} and ε_{a} energies, we obtain

$$\chi_b \equiv N_{\mathrm{b}}(\varphi_{\mathrm{N}} + \omega\varphi_0), \tag{19}$$

$$\chi_a \equiv N_{\mathrm{a}}(\varphi_0 - \omega\varphi_{\mathrm{N}}), \tag{20}$$

where $\omega \ll 1$, and N_{b} and N_{a} are the normalizing coefficients. In the first stage, the spin population of the coordinated atom ($\rho^0_{\mathrm{N}} \sim \omega^2$) can be empirically estimated from IHFC with the magnetic N nucleus.

Let us determine the one-electron contributions to the spin densities of the ligand. Since $\omega \ll 1$, the wave function of the unpaired electron can be determined by the perturbation theory in the second stage. Taking into account the resonance $\beta_{\mathrm{N},i}$ integrals for the φ_{N} AO and the Ψ_i MO of the ligand with the ε_i energies in the basis of orbitals with appropriate (σ or π) symmetry, we obtain the following expressions for the MO of the unpaired electron:

$$\Psi_0(r) = N_0\left[\chi_{\mathrm{a}} - \omega N_{\mathrm{a}} \sum_i{}' \frac{\beta_{\mathrm{N},i}}{\varepsilon_i - \varepsilon_{\mathrm{a}}} \Psi_i(r)\right] \tag{21}$$

Table 4. Spin populations (ρ) and damping coefficients (K) in *ortho*-, *meta*-, and *para*-positions of the σ-electron $C_6H_5^{\cdot}$ radical calculated by the RHT and perturbation theory (PT) methods

ω^2	ρ_H^o		K_H^o,	ρ_H^m		K_H^m,	ρ_H^p		K_H^p,
	RHT	PT	PT	RHT	PT	PT	RHT	PT	PT
1.00	0.042	0.041	≅1	0.010	0.010	≅1	0.006	0.005	≅1
0.49	—	—	0.48	—	—	0.53	—	—	0.48
0.25	—	—	0.24	—	—	0.25	—	—	0.24
0.09	—	—	0.09	—	—	0.09	—	—	0.08

and for the one-electron contributions to the spin densities of the ligand:

$$\rho^0(r) \cong N_0{}^2 \cdot N_a{}^2 \cdot \omega^2 \cdot \left[\sum_i{}' \frac{\beta_{N,i}}{\varepsilon_i - \varepsilon_a} \Psi_i(r)\right]^2 \cong$$
$$\cong N_0{}^2 \cdot N_a{}^2 \cdot \omega^2 \cdot \Phi(r). \qquad (22)$$

(In Eqs. (21) and (22), the summation is performed over $i \neq$ a.) Since $\rho_N^0 = N_0{}^2 \cdot N_a{}^2 \cdot \omega^2$, the relative spin populations of the φ_μ AO of the ligand ($\rho_{\mu\mu}^0/\rho_N^0 = \Phi_{\mu\mu}$) are independent of ω in the first approximation, but fairly sensitive to differences between the ε_a and ε_i orbital energies. Data on HFC with the nucleus of the coordinated atom are necessary for estimations of absolute spin populations.

Unlike the case of free radicals (see Ref. 2), in this case, the contribution of the spin polarization should be written in the form

$$\rho_{\mu\mu}^{sp} = -\lambda_a \cdot \pi_{a\mu} \cdot \rho_{aa}^0 - \lambda_p \sum_{v \neq a} \pi_{\mu v} \cdot \rho_{vv}^0 , \qquad (23)$$

since there are grounds to expect a strong deviation of the λ_a parameter of the ion from the average λ_p value for organic paramagnetic systems.

In σ-complexes with aromatic ligands, for atoms that are sufficiently remote from the coordinating center, the contribution to the spin densities can be important due to the mechanism of the σ—π-exchange polarization of the π-electron system.[2] According to the perturbation theory, for the spin populations of the π-AO of the ligand, in the second stage of calculations we have

$$\rho_{\mu\mu}^{\pi} = -(1/2)\pi_{\mu n} \cdot æ_{N,n} \cdot \rho_N^0, \qquad (24)$$

where $æ_{N,n}$ is the one-centered exchange integral for the φ_N σ-AO and φ_n π-AO of the coordinated atom. Unlike Eqs. (21) and (22), the energy of the orbital of the unpaired electron does not enter Eq. (24), *i.e.*, the character of the spin polarization of the π-system is independent of ε_a.

Thus, the problem of calculation of spin densities in paramagnetic complexes is substantially simplified, because it is reduced to the determination of MO of ligands. This was favored by approximations on which the model was based: (1) neglecting resonance integrals for the AO of the ion and all AO of the ligand except the coordination hybrid φ_N σ-AO and (2) calculation of the MO of the ligand without taking into account the φ_N-AO of the unshared electron pair of the coordinated N atom. It should be emphasized that these approximations belong to those that are most often used in semiempirical methods. At the same time, the factors that are absent in free radicals related to ligands by similarity in IHFC are ruled out.

It was of interest to test the model formulated for particular radicals. Therefore, a phenyl radical was calculated in terms of the RHT method[2] for the one-centered resonance integral proportional to ω^2 for the hybrid σ-AO of the unpaired electron. The values of spin populations ($\rho_{\mu\mu}^H$) and relative damping coefficients ($K = \rho_{\mu\mu}^H/\rho_{\sigma\sigma}$) obtained for the φ_H-AO of the H atoms by the perturbation theory with the normalized wave function (Ψ_0) are presented in Table 4. A nontrivial conclusion follows from the analysis of data in Table 4: the perturbation theory should result in the same qualitative results for free radicals as the more exact MO LCAO schemes, since damping coefficients of spin populations of AO change as ω^2 in the whole $0 < \omega < 1$ region. Analogous calculations of the π-benzyl radical confirmed this conclusion.

It should be emphasized that the conclusion about the applicability of the perturbation theory to free radicals is basic for understanding reasons for the correlation observed,[5] because the spin density distributions in organic ligands of paramagnetic complexes can be determined, beyond a doubt, in terms of the perturbation theory. Let us consider particular results obtained for several ligands using the model described above.

Pyridine. The absolute spin populations of the AO of the H atoms were calculated by Eq. (21) for the variable ε_a parameter and $\omega = 0.075$, which was estimated[16] from IHFC with the ^{14}N nuclei in the $[Co(NC_5H_5)_6]^{2+}$ complex. The theoretical and experimental ρ_H values are presented in Table 5. It can be seen that satisfactory

Table 5. Spin populations (ρ) for pyridine

$\lvert\varepsilon_a\rvert$/eV	$\rho_H^o \cdot 10^2$	$\rho_H^m \cdot 10^3$	$\rho_H^p \cdot 10^3$
11	0.31	15.0	22.0
15	0.26	0.64	0.33
16	0.17	0.36	0.17
17	0.13	0.26	0.12
*	0.10	0.28	≈0

* Experimental data.

agreement between the experiment and theory is achieved when $|\varepsilon_a| \approx 17$ eV, which does not contradict known data on the ionization potentials of valence states of Co and Ni atoms.

The contribution to the spin populations ($\rho_{\mu\mu}^{H}$) of the hydrogen AO from the mechanism of the exchange σ—π-polarization (ρ_{cp}) can be determined from Eq. (24) and the McConnel relation.[2] Calculation with the standard one-centered exchange integrals gives $\rho_{cp}^{o} = -0.6 \cdot 10^{-4}$, $\rho_{cp}^{m} = 0.3 \cdot 10^{-5}$, and $\rho_{cp}^{p} = -0.4 \cdot 10^{-4}$ for *ortho-*, *meta-*, and *para*-protons, respectively. Thus, even for a "remote" proton in the *para*-position, the IHFC observed is completely caused by the σ-electronic structure of pyridine, and the role of the π-system is comparatively small. This follows from the analysis of the whole available experimental material for a complex of nickel acetylacetonate (Ni(acac)$_2$) with pyridine.

Picolines. The spin populations of the AO of the H atoms of the methyl group participating in hyperconjugation with the π-electron system should be approximately proportional to the spin populations of the π-AO of the adjacent C atoms to which a substituent is added in α-, β-, and γ-picolines. Therefore, in this case, the contribution caused by the σ—π-spin polarization is most important (see Eq. (24)). In terms of the hyperconjugation model, the determined ratios of spin populations of the AO of the H atoms in the freely rotating Me groups ($\rho_{cp}^{o}/\rho_{cp}^{p} = 1.2$ and $\rho_{cp}^{m}/\rho_{cp}^{p} = -0.042$) agree qualitatively with the experimental values ($\rho_{H}^{o}/\rho_{H}^{p} = 1.6$ and $\rho_{H}^{m}/\rho_{H}^{p} = -0.56$). The effects of delocalization of an unpaired electron in the σ-system of picolines should be taken into account to improve the quantitative coincidence.

Aniline. Based on Eq. (22), after simple transformations, we can obtain for *ortho-* and *para*-positions the ratio of spin populations of the π-AO (ρ_{C}^{π}), which determine IHFC with protons in the paramagnetic complex of Ni(acac)$_2$ with aniline:

$$K = [1 - (\alpha - \varepsilon_a)^2/(2\beta^2)]^2, \qquad (25)$$

where α and β are the standard Coulomb and resonance integrals for benzene. Inserting $\varepsilon_a \approx \alpha$ or $\varepsilon_a \approx \alpha \pm 2\beta$ into Eq. (25), we obtain the experimental value $K \approx 1$. Taking into account that the IHFC features inherent in the benzyl radical appear in aniline, $\varepsilon_a \approx \alpha$ should most likely be chosen.

* * *

Thus, establishing correlations facilitates interpretation and systematization of experimental data on the spin delocalization obtained by different magnetic resonance methods and favors deeper understanding of the physical picture of the spin density distribution in chemical compounds. The correlations established make it possible to justify using comparatively simple but fairly efficient quantum-chemical schemes of analysis of magnetic resonance parameters of complex paramagnetic systems.

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Received April 22, 1997