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Abstract

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ON THE QUESTION OF A SEMIEMPIRICAL THEORY OF ISOTROPIC HYPERFINE SPLITTING IN THE E.P.R. SPECTRA OF FREE RADICALS

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Analysis of the hyperfine structure of the e.p.r. spectra of free radicals and interpretation of the spectra are possible only on the basis of theoretical considerations. In this respect, simple semiempirical relations connecting the constants of isotropic hyperfine splitting A with the spin densities located on individual atoms are very valuable. As an example one may cite the well-known relation $A_H = Q_H \rho_C^{\pi}$, obtained by McConnell ([1]) for the magnitude of proton hyperfine splitting in aromatic free radicals. In the work of Karplus and Fraenkel ([2]), on the basis of considering π–σ-configurational interaction, an approximate formula was obtained for the splitting constant A on the nucleus of an atom y, participating in several bonds and lying in the nodal plane of the π-orbital of the unpaired electron,

$$A_y = \left(S_y + \sum_i Q_{yx_i} \right) \rho_y^{\pi} + \sum_i Q_{x_i y} \rho_i^{\pi}; \qquad (1)$$

x_i are atoms valence-bonded to y; ρ_y^{π}, ρ_i^{π} are the π-electron spin densities on the corresponding atoms; S_y is a constant due to polarization of the 1s orbitals; Q_{yx_i} and $Q_{x_i y}$ are constants arising from partial unpairing of the electrons of the bonds y—x_i, caused by interaction respectively with the spin densities on the atoms y and x_i. The authors used this formula to interpret the isotropic hyperfine splitting on C^{13} for a series of free radicals in which all atoms y and x_i having nonzero spin density are carbon atoms with sp^2-hybrid orbitals, and obtained good agreement with experiment. In a number of works ([3–6]) formula (1) is also applied in the case when the orbitals forming the bond are nonequivalent, for example for C—N, C—O, C—F bonds. In the present work we wish to draw attention to the fact that such an extrapolation is not always theoretically justified and that a more general formula is necessary.

Fig. 1

Fig. 1

Figure 1: Fig. 1

Let us consider as an example the fragment a—b, which is an element of a conjugated chain (see Fig. 1). The wave function of the delocalized unpaired π-electron may be written in the form $\pi = c_a\pi_a + c_b\pi_b$. The coordinate parts of the wave functions of the ground singlet (φ_0) and excited triplet (φ_1) states have the form

$$\varphi_0 = N_0[\sigma_a(1)\sigma_b(2) + \sigma_b(1)\sigma_a(2) + \gamma\sigma_b(1)\sigma_b(2)],$$

$$\varphi_1 = N_1[\sigma_a(1)\sigma_b(2) - \sigma_b(1)\sigma_a(2)].$$

In the linear approximation of the π–σ-configurational interaction, taking into account three electrons, the contribution of the a—b bond to the constant of hyperfine isotropic splitting at nucleus a is expressed as follows:

$$A_{ab} = Q_{ab}\rho_a^\pi + Q_{ba}\rho_b^\pi \pm Q'_{ab}\sqrt{\rho_a^\pi\rho_b^\pi}, \tag{2}$$

where

$$\rho_a^\pi = c_a^2, \qquad \rho_b^\pi = c_b^2,$$

$$\begin{aligned}
Q_{ab} &= B\{(\pi_a\sigma_a \mid \pi_a\sigma_a) - (\pi_a\sigma_b \mid \pi_a\sigma_b) + \gamma[(\pi_a\sigma_a \mid \pi_a\sigma_b) - S(\pi_a\sigma_b \mid \pi_a\sigma_b)]\},\\
Q_{ba} &= -B\{(\pi_b\sigma_b \mid \pi_b\sigma_b) - (\pi_b\sigma_a \mid \pi_b\sigma_a) - \gamma[(\pi_b\sigma_a \mid \pi_b\sigma_b) - S(\pi_b\sigma_b \mid \pi_b\sigma_b)]\},\\
Q'_{ab} &= 2B\{(\pi_a\sigma_a \mid \pi_b\sigma_a) - (\pi_a\sigma_b \mid \pi_b\sigma_b) + \gamma[{}^1\!/_2(\pi_a\sigma_a \mid \pi_b\sigma_b) + {}^1\!/_2(\pi_a\sigma_b \mid \pi_b\sigma_a)\\
&\qquad - S(\pi_a\sigma_b \mid \pi_a\sigma_b)]\}.
\end{aligned} \tag{3}$$

The coefficient B depends mainly on the density of the σ_a orbital at nucleus a and on the magnitude of the splitting between the singlet and triplet levels of the bond. In formula (2) the sign is chosen according to whether the signs of c_a and c_b are the same or different. For the two-electron integrals the usual notation is adopted:

$$(pq \mid rs) = \int p(1)q(1)\frac{1}{r_{12}}r(1)s(1)\,d\tau_1 d\tau_2;$$

S is the overlap integral of the σ_a- and σ_b-orbitals.

Fig. 2

Figure 2: Fig. 2

Relations analogous to (2) and (3) are also obtained when the bond wave functions are written by the molecular-orbital method. In order to clarify the role of the term Q'_{ab}, calculations were carried out for the ratios $\varepsilon = Q_{ba}/Q_{ab}$ and $\varepsilon' = Q'_{ab}/Q_{ab}$. To determine the influence of hybridization of the σ-orbitals and of the ionicity of the bond on ε and ε', the case of the C–C bond was considered as an example.

The values of the two-center integrals for Slater orbitals corresponding to the internuclear distance $R = 1.465$ Å were taken from the work of Kotani et al. ([7]). For the atomic integrals, semiempirical values given in ([2]) were adopted. Figure 2 shows the curves $\varepsilon(\alpha)$ and $\varepsilon'(\alpha)$, which show the dependence of the ratios of the constants on the hybridization parameter α, obtained for σ_a an sp^2-hybrid orbital, $\sigma_b = \frac{1}{\sqrt{1+\alpha^2}}[p_b + \alpha s_b]$, and $\gamma = 0$. The second two curves $\varepsilon(\gamma)$ and $\varepsilon'(\gamma)$ give the dependence on the bond-ionicity parameter γ for the case in which σ_a and σ_b are both sp^2-hybrid functions. From the results of the calculation it follows that the ratios ε' and ε depend most substantially on the difference in the angular parts of the atomic bond orbitals; for example, the magnitude Q'_{ab}, for the pair sp^2—p, is comparable with Q_{ab}. The ionicity of the bond has a noticeable influence on the ratio of the constants Q only at large values of the parameter γ, i.e., when the bond is strongly ionic. The values of ε and ε' depend substantially on the bond length; thus, for an sp^2—p bond at $R = 1.30$ Å, $\varepsilon = 0.65$, $\varepsilon' = 1.92$; at $R = 1.55$ Å, $\varepsilon = -0.16$, $\varepsilon' = 0.79$.

Fig. 2

We also carried out calculations of ε and ε' for the bonds C–N, C–O, C–F. In all cases, semiempirical values of the atomic integrals ([8]) were used; the estimate of the two-center integrals for Slater orbitals was made by Mulligan' s approximate formula ([9]) and tables ([7]). In the case of a C–N bond at $R = 1.42$ Å and sp^2-hybrid bond orbitals, $\varepsilon = -1.1$, $\varepsilon' \approx -0.01$. For a C–O bond formed by an sp^2-orbital of C and a p-orbi-

that of O at $R = 1.16$ Å, $\varepsilon = 0.42$, $\varepsilon' = 1.34$. The values of ε' for the C–F bond ($R = 1.33$ Å) for several values of the parameters α and γ are given in Table 1.

Consideration of the results of the calculations shows that, for a bond between nonequivalent atoms, especially with different hybridization of the atomic σ-orbitals and with a delocalized π-electron, the contribution of the bond to the hyperfine interaction is determined not by two, but by three parameters of approximately the same order. Thus, for the analysis of the hyperfine structure of EPR spectra of radicals with conjugated bonds containing different or physically nonequivalent atoms, the following semiempirical formula, which is a generalization of (1), may prove useful:

$$A_y = \left(S_y + \sum_i Q_{yx_i} \right) \rho_y^\pi + \sum_i Q_{x_i y} \rho_i^\pi + \sum_i Q'_{yx_i} \left(\pm \sqrt{\rho_y^\pi \rho_i^\pi} \right). \qquad (4)$$

In view of the lack of a sufficient number of experimental data, we were unable to carry out a detailed check of formula (4). Using the theoretically calculated values of the ratios ε and ε', one can substantially reduce the number of independent experimental results needed to determine the constants of formula (4). It should be noted, however, that such a calculation is very sensitive to the bond parameters adopted (bond length, form of the atomic orbitals, etc.) and to the accuracy of the estimation of molecular integrals.

Table 1

$\gamma \backslash \alpha$	0.1	0.3	0.5
0	−0.64	−0.48	−0.32
1.4	−0.85	−0.77	−0.67
∞	−1.40	−1.47	−1.47

In papers [5,10] values are given for the splitting on C^{13} bonded to the O atom for the ion radicals *n*-benzosemiquinone and 2,5-dihydroxysemiquinone, equal respectively to 0.4 and 2.82 oersted. Using the Q and S for C–C bonds given in [2], and the semiempirical values of the spin densities [4], together with the calculated ε or ε', we obtained, respectively, $Q_{\mathrm{CO}} = 21$ oersted, $\varepsilon' = 1.14$, and $Q_{\mathrm{CO}} = 25$ oersted, $\varepsilon = 0.55$. The splitting constant on C^{13} was taken as negative for *n*-benzosemiquinone and positive for 2,5-dihydroxysemiquinone; in formula (4) the minus sign was adopted in accordance with [1]. Taking into account the roughness of the calculation, the agreement of the values of Q_{CO}, ε', and ε may be considered satisfactory. To check the predicted ratios of the constants and their signs, $Q'_{\mathrm{CO}} > Q_{\mathrm{CO}} > Q_{\mathrm{OC}} > 0$, a third independent experiment is necessary.

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Note: Figure translations are in progress. See original paper for figures.