

Relationships for the Computation of Long-Range Proton Hyperfine Coupling Constants Derived from π -Electron Spin Labels

FREDERICK W. KING

Department of Chemistry, Queen's University, Kingston, Ontario, Canada

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Long-range proton hyperfine coupling constants derived from both cationic and anionic spin labels are calculated. The relationships employed are based on a non-empirical CI treatment of the σ - π interactions. Both positive and negative γ -proton coupling constants may be obtained.

There have been numerous reports on the observation of long-range proton hyperfine couplings (1-4). Despite a few semiempirical (5-12) and *ab initio* (13, 14) studies on specific molecules, to date, no useful procedure has been proposed which permits the prediction of the size of long-range proton hyperfine coupling constants based on the π -electron spin density distribution of the attached label. The purpose of this note is to outline and employ fairly simple relationships for the calculation of long-range coupling constants.

The basis for the model from which the equations are derived has been discussed (14). A modified form of the model has been employed previously for the calculation of the angular dependence of the β -proton hyperfine couplings (15). There are several approximations involved in this model which we outline briefly. Consecutive through-bond spin polarization is ignored since this is at least a second-order mechanism, based on a perturbation theory argument. Other through-bond effects, such as spin polarization of one of the intervening bonds and then a subsequent interaction with the center of interest are not retained. Configurations characterizing electron migration to the spin label have been calculated to be insignificant (14) for the bicyclo[2.2.1]heptane semidione radical anion, and it has been assumed that this holds true for the spin labels considered here. Only nearest neighbour spin label centers are considered in the σ - π interactions between the σ -framework and the spin label. The nonorthogonal nature of the σ - π interactions in these systems makes it impossible to attach a precise meaning to each distinct mechanism. However, earlier work (15) has shown that there is considerable advantage to be gained from *partitioning* the hyperfine coupling into various mechanisms in order to carry out a component analysis of the hyperfine coupling.

The model takes account of the inclusion of the following mechanisms: through-space spin exchange (to the σ -moiety); through-space (*direct*) spin polarization (*excitation spin decoupling*) and a contribution arising from a *direct ground-state* mechanism. The ground state mechanism arises from the fact that there is already an admixture of σ -orbital character with the π -orbital of the spin label, when an orthogonal

basis is constructed. The orthogonalization scheme is not unique. With these contributions, the partitioning of the appropriate secular equation into various mechanisms, leads to a result for the hyperfine coupling constant in terms of various hyperfine Q factors. There are two distinct situations which arise. For the case when the highest occupied molecular orbital (HOMO) of the spin label is symmetric with respect to the plane bisecting the spin label and containing the CH_2 protons (*7-anti*, *7-syn*) of interest, the hyperfine coupling constant A_H is given by

$$A_{Hs} = (\rho + R_s^2)^{-1} \{R_s^2 Q_{tts} + \rho^2 Q_{pps} - \rho R_s \text{sgn}(W_{tp}) Q_{tps}\}, \quad [1]$$

where

$$R_s = \eta_s + (\eta_s^2 + \rho)^{1/2}. \quad [2]$$

In Eq. [1], the hyperfine Q factors denote: spin transfer contributions Q_{tts} , mixed spin polarization (*direct*)-spin transfer contributions Q_{tps} and pure spin polarization (*ground state* term included) contributions Q_{pps} . ρ is the spin density at the nearest site of the spin label, η_s is a purely electronic factor, $\text{sgn}(W_{tp})$ designates the sign of the matrix element connecting the configurations denoting spin exchange and *direct* spin polarization and the subscript s is employed to indicate symmetric HOMO. For the case where the HOMO is antisymmetric, the hyperfine coupling is given by

$$A_{Ha} = \rho(1 + R_a^2)^{-1} \{R_a^2 Q_{ppa} + Q_{gga} - R_a \text{sgn}(W_{gp}) Q_{gpa}\}, \quad [3]$$

where

$$R_a = \eta_a + (\eta_a^2 + 1)^{1/2}. \quad [4]$$

In Eq. [3], the Q factors now denote: purely *direct* spin polarization (*excited*) contributions Q_{ppa} , *ground-state* term Q_{gga} , and mixed *ground-state* term—spin polarization Q_{gpa} . The subscript a indicates antisymmetric HOMO. η_a is a purely electronic term and $\text{sgn}(W_{gp})$ has a similar meaning as described above. Equations [1] and [3] have been presented for the symmetric situation in which the adjacent spin densities are equal, $\rho_1 = \rho_2 = \rho$, which is the frequently encountered situation. If we now concern ourselves only with the *7-syn* and *7-anti* protons and employ the assumption that the stereochemical environment of those protons is not greatly perturbed on changing from one spin label to another, then all the parameters of Eqs. [1] and [3] may be calculated and assumed transferable, since they are only dependent upon the stereochemistry. Table 1 presents the Q parameters obtained from a nonempirical CI calculation. The principal distinction which symmetry dictates, is the complete absence of any spin transfer

TABLE 1
HYPERFINE Q FACTORS FOR SYMMETRIC AND ANTISYMMETRIC HOMO

	<i>7-syn</i>	<i>7-anti</i>		<i>7-syn</i>	<i>7-anti</i>
Q_{tts}	826.43	826.43	Q_{ppa}	648.84	653.13
Q_{pps}	3.541	0.8024	Q_{gga}	0.	0.
Q_{tps}	-42.11	-41.62	Q_{gpa}	574.46	574.46
$\text{sgn}(W_{tp})$	+1	-1	$\text{sgn}(W_{gp})$	+1	-1
η_s	-16.969	-2.947	R_a	1.210×10^{-3}	1.585×10^{-3}

mechanism, for the case in which the HOMO is antisymmetric, since the appropriate matrix elements vanish identically. For the same reason Q_{gga} is now zero, i.e., the ground-state description gives rise to no hyperfine splitting.

In Tables 2 and 3, the results for the calculated hyperfine coupling constants are presented. For the spin densities reported in tables 2 and 3, the Hückel values based on the following parameters $\beta_{CO} = 1.5\beta$, $\beta_{CN} = 0.9\beta$, $\alpha_O = \alpha_C + 1.4\beta$, $\alpha_N = \alpha_C + 0.9\beta$, $\alpha_{C'}$ (adjacent to O) = $\alpha_C - 0.14\beta$ and $\alpha_{C'}$ (semiduraquinone) = $\alpha_C - 0.7\beta$ have been

TABLE 2
CALCULATED 7-*syn* AND 7-*anti* PROTON COUPLING CONSTANTS (IN GAUSS) FOR SOME RADICAL ANIONS

Spin label	Spin density at adjacent site	Calculated		Observed ^c	
		7- <i>syn</i>	7- <i>anti</i>	7- <i>syn</i>	7- <i>anti</i>
Semidione (I)	0.294 (s) ^b	1.62	5.01	0.41	6.54 ^d
Semiquinone (II)	0.110 (a)	-0.08	0.10	0	0.66 ^e
Semifuraquinone (III)	0.299 (a)	-0.21	0.27	0.47	1.03 ^f
Dicyanoethylene (IV)	0.146 (a)	-0.10	0.13	—	—
2,5-semidione (V) ^e	0.238 (a)	-0.17	0.22	—	—

^a Assumed bound as a spin label across 3-4 bond.

^b Symmetry of HOMO designated as a for antisymmetric, s for symmetric.

^c Only absolute values of the coupling constant reported.

^d Data from G. A. Russell and K.-Y. Chang, *J. Amer. Chem. Soc.* **87**, 4381 (1965).

^e Data from S. F. Nelsen and B. M. Trost, *Tetrahedron Lett.* 5737 (1966).

^f Data from S. F. Nelsen and E. P. Seppanen, *J. Amer. Chem. Soc.* **89**, 5740 (1967).

TABLE 3
CALCULATED 7-*syn* AND 7-*anti* PROTON COUPLING CONSTANTS (IN GAUSS) FOR SOME RADICAL CATIONS

Spin label	Spin density at adjacent site	Calculated	
		7- <i>syn</i>	7- <i>anti</i>
I	0.088 (a)	-0.06	0.08
II	0.250 (s)	1.37	4.28
III	0.384 (s)	2.11	6.49
IV	0.212 (s)	1.17	3.64
V	0.373 (s)	2.05	6.31

employed. The agreement between calculated and experimental is in general, satisfactory. The 7-*syn* proton coupling for the semidione radical anion is poorly predicted, however the 7-*anti* coupling is reasonably close to the experimental value. For the cationic systems calculated, no experimental results have yet been reported. Nelsen and Hintz (3) have measured one cationic long-range coupled radical, however for the system

studied, it is unlikely that it behaves in the typical manner of the π -electron spin labels considered here. It will be interesting to see these systems prepared, since there are quite distinctive changes predicted when going from anion to cation for the same spin label. These changes (Tables 2 and 3) are consistent with expectations based on the change of more symmetry of the HOMO.

Equations [1] and [3] are not restricted to the prediction of only positive hyperfine coupling constants, a difficulty which has been associated with some of the semiempirical calculations of the γ -proton couplings in alkyl radicals, for which both positive and negative coupling constants have been measured. Some of the semiempirical expressions seem to be applied out of context. In our opinion, certain mechanisms are more favored by highly constrained stereochemical arrangements and these are not considered in all the alkyl-model expressions. Such a mechanism is the through-space spin exchange contribution. Thus to apply such alkyl model expressions for γ -couplings in bicyclic radicals is questionable.

A satisfactory justification for the three underlying assumptions of the model, can be given. The neglect of consecutive through-bond spin polarization contributions is justified on the grounds that, in the alkyl radicals, such a contribution is only approximately 0.5 G, and this is derived from an essentially nonlocalized unpaired spin. If a delocalized spin distribution is considered as in the spin labels, then the expected splitting would be less than 0.1 G, and this idea is substantiated by various studies which have shown that the coupling constants of protons of alkyl groups bonded to essentially π -electron radicals are very small or unobservable beyond the nearest (α -) proton. *Back transfer* to the spin label was found to be such an insignificant contribution for the bicyclo[2.2.1]heptane semidione radical anion, that its neglect should be certainly valid for all the spin labels considered here. For electron deficient spin labels, such as the cationic spin labels, the assumption may be less accurate. However, due to the lack of data for these systems this approximation has not been examined in detail. Inclusion of such terms would result in additional Q factors in Eq. [1]. The neglect of nonadjacent spin label centers in calculating the interactions between the σ -framework and the spin label is argued on the grounds that the appropriate matrix elements linking the two moieties fall off rapidly with distance. Although most of the additional matrix elements are small, it is of course tacitly assumed that the total sum of all such contributions is small, which would appear to be a valid approximation.

The present difficulty is of course the calculation of the Q factors for the various σ -frameworks. To apply Eqs. [1] and [3] to other σ -structures, e.g., bicyclo[2.2.2]octane derivatives, new Q factors are required to account for the modified stereochemistry. General Q factors exhibiting explicit dependence on the various angular variables could be given, however they would be far too complex to be useful. It thus seems preferable to evaluate Q factors for the principal σ -frameworks. As an alternative, it may be possible to fit experimental results to Eqs. [1] and [3] to obtain estimates of the appropriate Q factors. Unfortunately there is lacking, a suitable sequence of compounds in which the spin density distribution at the adjacent π -center spans a wide range for the same σ -moiety.

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