

## Long-range proton hyperfine coupling in bicyclic radicals

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Long-range isotropic proton hyperfine coupling in rigid bicyclic systems is investigated using a non-empirical configuration interaction study of an appropriate  $\sigma$ -bonded fragment in conjunction with a semi-empirical description of a particular spin label. The coupling is found to depend on the symmetry of the highest occupied molecular orbital of the spin label and upon the stereochemistry of  $\sigma$ -bonded moiety. Relationships are obtained linking the hyperfine coupling to the adjacent spin density of the label for both cases wherein the highest occupied molecular orbital is either symmetric or anti-symmetric relative to the reflection plane containing the C-H bond. Numerical calculations are carried out for the particular case of the bicyclo-[2.2.1]heptane semidione radical anion wherein the reflection plane contains the  $\gamma$ -CH<sub>2</sub> group as well as bisecting the molecular orbitals of the spin label.

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### 1. INTRODUCTION

The 'long range' hyperfine coupling constants observed in electron spin resonance are usually those associated with electron-nuclear interactions which occur with nuclei separated by three or more  $\sigma$ -bonds from some principal centre containing an unpaired electron, or some portion of the total unpaired electron density. This type of coupling was first observed in the bicyclic radical systems by Russell and Chang [1]. Russell and his co-workers [2] have clearly established the correct proton assignments to these coupling constants. Subsequently a large number of compounds of great diversity [3-9] have been shown to demonstrate similar effects. The majority are of the bridged polycyclic molecular type attached to a  $\pi$ -electron system which may readily be converted to a paramagnetic valence state, and which acts as a simple spin label. The factor which is common to all systems is a rigid  $\sigma$ -framework which holds the distant nuclei in a fixed position relative to the spin label. The effect is even observed with cyclohexyl radical at temperatures low enough that ring flexure does not occur [10].

This work was undertaken to assess the divergence of opinion [3, 4, 11-14] which exists over the importance of various mechanisms which contribute to the isotropic long-range hyperfine coupling. Two major processes are involved, electron transfer and electron polarization. Of the latter, three types may be distinguished ; the first is 'direct' and results when polarization of the electron pair in the relevant C-H bond arises from a direct 'through space' interaction with the unpaired  $\pi$ -electron density in a  $2p\pi$  orbital of the spin label (figure 1 *a*).

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The second type of polarization is 'indirect' in the sense that polarization of the C-H bond results from direct polarization of one or more of the intervening  $\sigma$ -bonds as shown in figure 1 (b). The third mechanism does not involve any direct polarization of a bond but rather the successive polarization of each  $\sigma$ -bond between the  $\pi$ -centre and the proton of interest. None of these processes involves electron migration into or out of the  $\sigma$ -system. Such effects are referred to as 'electron transfer' processes and result in an accumulation of spin density at a given nucleus due to partial migration of the electronic charge. Contributions to the hyperfine coupling might also be expected to arise from polarizations of inner core electrons. While this type of effect will be important in  $^{13}\text{C}$  hyperfine interaction [15] we will be primarily interested in the proton hyperfine coupling of bicyclic systems and such core polarizations need not be considered. The procedure to be followed is a non-empirical ASMO-CI approach, in which case the configurations corresponding to electron polarization or electron transfer can be readily formulated.

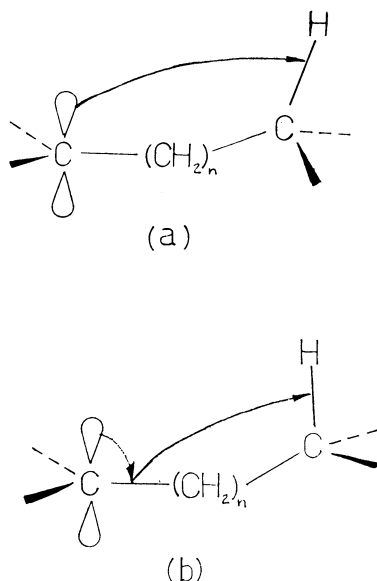


Figure 1. Pathways for  $\pi$ - $\sigma$  spin polarization interactions in a model fragment. (a) Direct polarization. (b) Indirect polarization.

Polarization of  $\sigma$ -bonds is most simply accommodated within M.O. methodology by the inclusion of configurations describing excitations between the bonding and anti-bonding M.O.'s of the intervening  $\sigma$ -bonds. McConnell [16] and Luz [17] have shown that consecutive processes attenuate rapidly along an aliphatic  $\sigma$ -bonded chain, which suggests that totally indirect polarization effects (which arise from multiple excitations) are not important. In fact, multiple excitations enter only as second or higher-order terms so the most important contributions will be due to single excitations, which limit polarization effects to only the relevant C-H bond. The knowledge that electron delocalization effects are small in saturated alkyl chains leads to the conclusion that all indirect effects should be deleted except that diagrammed in figure 1 (a). All of the essential

features of the bicyclic systems can in this approximation be represented by the  $\pi$ - $\sigma$  interactions of a weakly bound C . . . C-H fragment similar to that used so successfully to describe aromatic systems, but incorporating the geometrical factors and  $\pi$ - $\sigma$  distances appropriate to long-range hyperfine interactions of present interest. While the model is somewhat naive, it does allow a fairly rigorous non-empirical calculation to be effected. As far as the mechanisms for the interactions are concerned, this approach is superior to other more empirical formulations which by their nature are restricted to spin polarization or to electron delocalization processes, and to which agreement with experiment is obtained by arbitrary adjustment of the available parameters.

Since the precise geometry of most bicyclic radicals is unknown, we have considered bicyclo[2.2.1]heptane semidione radical anion (BHS), shown in figure 2, using the electron diffraction data for norborane [18]. This leads to the choice of bond lengths C-C, C=C and CH of  $1.555$ ,  $1.40$  and  $1.08 \times 10^{-10}$  m, respectively. The angles  $\psi$ ,  $\phi$  and  $\chi$  are respectively  $96^\circ$ ,  $120^\circ$ ,  $109^\circ 28'$ .

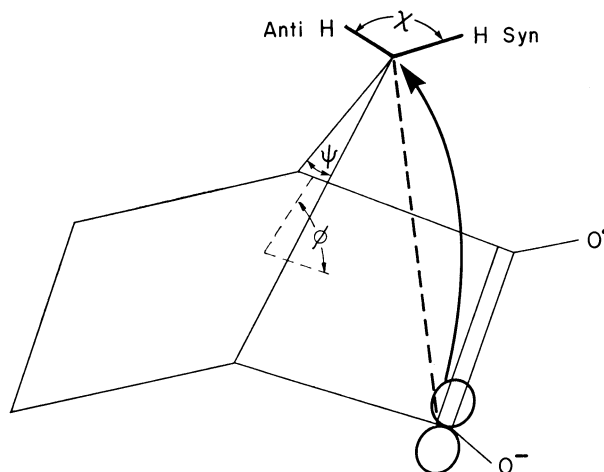


Figure 2. Relevant angular variables for bicyclo[2.2.1]heptane semidione radical anion. The dominant interaction pathway is illustrated.

## 2. COMPUTATIONAL PROCEDURE

The computations follow a procedure devised earlier [19]. The ground-state configuration is given by the normalized Slater determinant.

$$\chi_1 = \|\Pi\sigma_b\bar{\sigma}_b\|. \quad (1)$$

Direct spin polarizations are described by the two singly excited configurations involving the C-H  $\sigma$ -bond

$$\chi_2 = 2^{-1/2}\{\|\Pi\bar{\sigma}_b\sigma_a\| - \|\Pi\sigma_b\bar{\sigma}_a\|\} \quad (2)$$

and

$$\chi_3 = 6^{-1/2}\{2\|\Pi\sigma_b\sigma_a\| - \|\Pi\bar{\sigma}_b\sigma_a\| - \|\Pi\sigma_b\bar{\sigma}_a\|\}. \quad (3)$$

The electron transfer configurations are given by

$$\chi_4 = \|\sigma_a \sigma_b \bar{\sigma}_b\|, \quad (4)$$

$$\chi_5 = \|\Pi \sigma_b \bar{\Pi}\| \quad (5)$$

and

$$\chi_6 = \|\Pi \sigma_a \bar{\Pi}\|. \quad (6)$$

No doubly excited configurations, such as  $\|\Pi \sigma_a \bar{\sigma}_a\|$ , are included. In these equations a bar denotes  $\beta$  electron spin, and the basis set  $[\Pi, \sigma_b, \sigma_a]$  are obtained from the localized M.O.'s of the fragment by a Schmidt orthogonalization procedure wherein

$$\Pi = \{\pi - S_{b\pi} \sigma_b - S_{a\pi} \sigma_a\} \{1 - S_{b\pi}^2 - S_{a\pi}^2\}^{-1/2}. \quad (7)$$

The overlap integrals  $S_{b\pi} = \langle \sigma_b | \pi \rangle$  and  $S_{a\pi}$  are typically very small in long-range coupling situations. The wave function,  $\psi = \sum_{i=1}^6 C_i \chi_i$  for the ground state was determined by an ASMO-CI procedure, and the hyperfine couplings  $A_H$ , determined from  $\mathcal{H}_F$ , the hamiltonian operator for the Fermi contact term,

$$A_H = \langle \psi | \mathcal{H}_F | \psi \rangle \{g_e \beta_e \langle S_Z \rangle \langle I_Z \rangle\}^{-1} = \sum_i \sum_j \langle \chi_i | \mathcal{H}_F | \chi_j \rangle C_i C_j \times \{g_e \beta_e \langle S_Z \rangle \langle I_Z \rangle\}^{-1}. \quad (8)$$

<i>i</i>	<i>j</i>	$C_i$	$C_j$	Hyperfine factor $\Omega_{ij}$	Contribution to the hyperfine coupling (in gauss)
1	1	0.9213	0.9213	$0.3905 \times 10^{-2}$	1.6807
1	2	0.9213	0.3883	0.0	0.0
1	3	0.9213	$0.2252 \times 10^{-2}$	0.5664	0.0596
1	4	0.9213	$-0.1824 \times 10^{-1}$	$-0.7977 \times 10^{-1}$	0.6796
1	5	0.9213	$0.1392 \times 10^{-1}$	$0.3396 \times 10^{-1}$	0.2208
1	6	0.9213	$0.3010 \times 10^{-2}$	0	0
2	2	0.3883	0.3883	$0.3905 \times 10^{-2}$	0.2985
2	3	0.3883	$0.2252 \times 10^{-3}$	0.7704	0.0341
2	4	0.3883	$-0.1824 \times 10^{-1}$	$0.2401 \times 10^{-1}$	-0.0862
2	5	0.3883	$0.1392 \times 10^{-1}$	$0.5641 \times 10^{-1}$	0.1546
2	6	0.3883	$0.3010 \times 10^{-2}$	$0.2401 \times 10^{-1}$	0.0142
3	3	$0.2252 \times 10^{-3}$	$0.2252 \times 10^{-3}$	1.2820	$0.3 \times 10^{-4}$
3	4	$0.2252 \times 10^{-3}$	$-0.1824 \times 10^{-1}$	$-0.1386 \times 10^{-1}$	$0.3 \times 10^{-4}$
3	5	$0.2252 \times 10^{-3}$	$0.1392 \times 10^{-1}$	$0.3257 \times 10^{-1}$	$0.5 \times 10^{-4}$
3	6	$0.2252 \times 10^{-3}$	$0.3010 \times 10^{-2}$	$0.1386 \times 10^{-1}$	$0.5 \times 10^{-5}$
4	4	$-0.1824 \times 10^{-1}$	$-0.1824 \times 10^{-1}$	1.6297	0.2748
4	5	$-0.1824 \times 10^{-1}$	$0.1392 \times 10^{-1}$	0	0
4	6	$-0.1824 \times 10^{-1}$	$0.3010 \times 10^{-2}$	0	0
5	5	$0.1392 \times 10^{-1}$	$0.1392 \times 10^{-1}$	0.2953	0.0290
5	6	$0.1392 \times 10^{-1}$	$0.3010 \times 10^{-2}$	0.6937	0.0147
6	6	$0.3010 \times 10^{-2}$	$0.3010 \times 10^{-2}$	1.6297	0.0075
					SUM = 4.47

Table 1. Contributions made by the various configurations to the hyperfine coupling constant of the syn-proton.

This reduces to

$$A_H = 507.1 \text{ G} \sum_i \sum_j \Omega_{ij} C_i C_j \tag{9}$$

wherein

$$\Omega_{ij} = \rho_{ij}(r_H) \{ |1s(0)|^2 \}^{-1} \tag{10}$$

and  $\rho_{ij}$  is the spin density matrix element†. The simplification of (8) to (9) arises because of the very small values of integrals which are not of the form  $\langle 1s | \mathcal{H}_F | 1s \rangle$ . The matrix elements  $\langle \chi_i | \mathcal{H} | \chi_j \rangle$  for the C . . . CH system were evaluated by the method of Huzinaga *et al.* [20] in which the orbital exponent  $\zeta_C = 1.625$  was used for 2s and 2p orbitals and  $\zeta_H = 1.000$  for hydrogen 1s orbitals. The results for the syn-proton coupling constants for the BHS geometry are given in table 1 wherein the interacting configurations  $i$  and  $j$  are given by columns one and two,  $\Omega_{ij}$  in column five and finally contributions to  $A_H$  in column six. Table 2 gives the corresponding results for an anti-proton in the BHS structure.

$i$	$j$	$C_i$	$C_j$	Hyperfine factor $\Omega_{ij}$	Contribution to the hyperfine coupling (in gauss)
1	1	0.9172	0.9172	$0.3996 \times 10^{-2}$	1.7049
1	2	0.9172	0.3854	0	0
1	3	0.9172	$0.4214 \times 10^{-2}$	0.5664	1.1103
1	4	0.9172	0.1003	$-0.8070 \times 10^{-1}$	-3.7642
1	5	0.9172	$-0.6684 \times 10^{-2}$	$0.3435 \times 10^{-1}$	-0.1068
1	6	0.9172	$-0.5506 \times 10^{-2}$	0	0
2	2	0.3854	0.3854	$0.3996 \times 10^{-2}$	0.3010
2	3	0.3854	$0.4214 \times 10^{-2}$	0.7704	0.6346
2	4	0.3854	0.1003	$0.2429 \times 10^{-1}$	0.4761
2	5	0.3854	$-0.6684 \times 10^{-2}$	$0.5706 \times 10^{-1}$	-0.0746
2	6	0.3854	$-0.5506 \times 10^{-2}$	$0.2429 \times 10^{-1}$	-0.0261
3	3	$0.4214 \times 10^{-2}$	$0.4214 \times 10^{-2}$	1.2820	0.0115
3	4	$0.4214 \times 10^{-2}$	0.1003	$-0.1402 \times 10^{-1}$	-0.0030
3	5	$0.4214 \times 10^{-2}$	$-0.6684 \times 10^{-2}$	$0.3294 \times 10^{-1}$	-0.0005
3	6	$0.4214 \times 10^{-2}$	$-0.5506 \times 10^{-2}$	$0.1402 \times 10^{-1}$	-0.0002
4	4	0.1003	0.1003	1.6297	8.3111
4	5	0.1003	$-0.6684 \times 10^{-2}$	0	0
4	6	0.1003	$-0.5506 \times 10^{-2}$	0	0
5	5	$-0.6684 \times 10^{-2}$	$-0.6684 \times 10^{-2}$	0.2953	0.0067
5	6	$-0.6684 \times 10^{-2}$	$-0.5506 \times 10^{-2}$	0.6937	0.0129
6	6	$-0.5506 \times 10^{-2}$	$-0.5506 \times 10^{-2}$	1.6297	0.0250
					SUM = 6.88

Table 2. Contributions made by the various configurations to the hyperfine coupling constant of the anti-proton.

While the above results establish the relative importance of the various configurations, they are not appropriate to radicals with delocalized  $\pi$ -spin labels. To be applicable to BHS anion it is necessary to modify the description of the  $\pi$ -orbital to account for the fact that the unpaired electron is delocalized over

† G =  $10^{-4}$  T.

several atoms of the spin label. Since some  $\pi$ -centres are somewhat further removed from the syn- and anti-protons in BHS, one can estimate the effects of delocalization by considering the  $\pi$ -molecular orbital to be that of the highest occupied orbital (HOMO) of the label with

$$\pi_r = c_{ir}\phi_i + c_{jr}\phi_j, \quad (11)$$

in which  $\phi_i$  and  $\phi_j$  are the  $2p\pi$  orbitals of the spin label closest to the protons under consideration, while  $c_{ir}$  and  $c_{jr}$  are the normalized LCAO coefficients appearing in the HOMO. In the 'extended' model, use is made of the fact that many of the bicyclic systems have a plane of symmetry which contains both the syn- and anti- $\sigma$  C-H bonds and bisects the  $\pi_r$  MO of the spin label. In BHS the HOMO is symmetrical to this plane and  $c_{ir} = c_{jr}$ . In other labels it could be antisymmetrical with  $c_{ir} = -c_{jr}$  and this has consequences with regard to the mechanisms which can contribute to the long-range hyperfine coupling. In approximate treatments of related systems [21] the hyperfine couplings would be expected to vanish. The fact that non-zero splittings are observed from systems with antisymmetric HOMO's [22] suggests that integrals involving the cross terms  $\phi_i\phi_j$  ( $\phi_i \neq \phi_j$ ) must be retained in the extended model. The effects are due to spin polarization factors alone, since none of the electron transfer configurations contributes in the antisymmetric HOMO case. Considering the magnitude of spin transfer contributions in tables 1 and 2, these configurations must be retained for calculations appropriate to symmetric HOMO's, but since the effects of  $\chi_5$  and  $\chi_6$  are small compared to  $\chi_4$ , only the last has been retained in the 'extended' model. Even so, this configuration cannot be realistically handled following a formal CI procedure, since its contribution is not weighted by the factors  $c_{ir}$  and would thus appear to be independent of the spin density  $\rho = c_{ir}^*c_{ir}$  of the spin label. In order to retain a simple dependence on the spin density of the label and without at the same time demanding detailed information about the electronic structure of the label, the contributing configurations have been partitioned into those describing spin polarization  $\Phi_p$  and  $\chi_4$  for spin transfer. Thus

$$\Phi = u_p\Phi_p + u_4\chi_4 \quad (12)$$

with

$$\Phi_p = \sum_i C_i'\chi_i' \quad (13)$$

and the prime denotes the use of a 'delocalized' MO of (11) rather than a localized A.O. of (7). The coefficients  $u_p$  and  $u_4$  are then determined by a variational procedure. This technique retains the possibility of comparing the hyperfine splittings of syn- and anti-protons of the bicyclo[2.2.1]heptane  $\sigma$ -system bonded to a number of different spin labels in which  $\rho$  is known at the sites of attachment.

Using (12) in (8) yields hyperfine couplings  $A_{H_s}$  and  $A_{H_a}$  for the symmetric and anti-symmetric HOMO's respectively.

### 3. RESULTS

For the symmetric HOMO in BHS,

$$A_{H_s} = \{\rho + R_s^2\}^{-1} \{R_s^2 Q_{44} + \rho^2 Q_{pps} - \rho R_s \operatorname{sgn}(W_{4p}) Q_{4ps}\} \quad (14)$$

with

$$Q_{44} = \frac{8\pi}{3} |1s(0)|^2 g_H \beta_H \Omega_{44} = 826.43 \text{ G (syn)} \quad \text{and} \quad 826.43 \text{ G (anti)}, \quad (15)$$

$$Q_{\text{pps}} = \frac{8\pi}{3} |1s(0)|^2 g_H \beta_H \sum_K \sum_j C_K' C_j' \Omega_{Kj} = 3.541 \text{ G (syn)} \\ \text{and} \quad 0.802 \text{ G (anti)}, \quad (16)$$

$$Q_{4\text{ps}} = \frac{16\pi}{3} |1s(0)|^2 g_H \beta_H \sum_j C_j' \Omega_{4j} = -42.11 \text{ G (syn)} \\ \text{and} \quad -41.62 \text{ G (anti)}, \quad (17)$$

giving

$$A_{\text{Hs}}(\text{syn}) = 1.59 \text{ G} \quad \text{and} \quad A_{\text{Hs}}(\text{anti}) = 4.95 \text{ G}.$$

In these expressions, sgn designates 'sign of' and

$$R_s = \eta_s + (\eta_s^2 + \rho)^{1/2} = 8.54 \times 10^{-3} \text{ (syn)} \quad \text{and} \quad 4.88 \times 10^{-2} \text{ (anti)} \quad (18)$$

with

$$\eta_s = \{ \langle \Phi_p | \mathcal{H} | \Phi_p \rangle - \langle \chi_4 | \mathcal{H} | \chi_4 \rangle \} \{ 2 | \langle \chi_4 | \mathcal{H} | \Phi_p \rangle | \}^{-1} \\ = \{ W_{\text{pp}} - W_{44} \} \{ 2 | W_{4\text{p}} | \}^{-1}. \quad (19)$$

These are all determined with the spin density  $\rho = 0.29 = \rho_i = \rho_j$  being essentially the value obtained by Russell and his co-workers [23, 24] for semidione anions, but somewhat different than that obtained by Amos and Snyder using a somewhat more sophisticated technique [25].

Since the electron transfer configurations do not contribute to the hyperfine coupling for an antisymmetrical HOMO for reasons of symmetry, the partitioning of the contributing configurations is between the ground state and the remaining spin polarization terms. Proceeding in the same manner as used for the symmetric HOMO, one obtains

$$A_{\text{Ha}} = \rho \{ 1 + R_a^2 \}^{-1} \{ Q_{11} - R_a \text{sgn}(W_{1\text{p}}) Q_{1\text{p}_a} + R_a^2 Q_{\text{pp}_a} \}, \quad (20)$$

where

$$Q_{11} = \frac{8\pi}{3} |1s(0)|^2 g_H \beta_H \Omega_{11} = 0 \quad \text{for both syn- and anti-protons}, \quad (21)$$

$$Q_{1\text{p}_a} = \frac{16\pi}{3} |1s(0)|^2 g_H \beta_H \sum_i u_i' \Omega_{1i} = 574.46 \text{ G} \quad \text{for both syn- and anti}, \quad (22)$$

$$Q_{\text{pp}_a} = \frac{8\pi}{3} |1s(0)|^2 g_H \beta_H \sum_i \sum_j u_i' u_j' \Omega_{ij} = 648.84 \text{ G (syn)} \\ \text{or} \quad 653.13 \text{ G (anti)}, \quad (23)$$

$$R_a = \eta_a + (\eta_a + 1)^{1/2} = 1.210 \times 10^{-3} \text{ (syn)} \quad \text{or} \quad 1.585 \times 10^{-3} \text{ (anti)} \quad (24)$$

and

$$\eta_a = \{ \langle \chi_1' | \mathcal{H} | \chi_1' \rangle - \langle \sum_i u_i' \chi_i' | \mathcal{H} | \sum_j u_j' \chi_j' \rangle \} \\ \times \{ 2 | \langle \chi_1' | \mathcal{H} | \sum_i u_i' \chi_i' \rangle | \}^{-1}. \quad (25)$$

From these relationships  $A_{\text{Ha}}(\text{syn}) = -0.20 \text{ G}$  and  $A_{\text{Ha}}(\text{anti}) = +0.26 \text{ G}$ , both computed for a spin density  $\rho = 0.29$ .

## 4. DISCUSSION

Calculation of hyperfine couplings of the magnitude found in the long-range situation is a difficult task even for much smaller molecular systems [26] than those found here. INDO [27, 28] and extended Hückel schemes [12] may be used but emphasize only one type of mechanism over others, with the result that considerable adjustment in the semiempirical parameters may be required. For instance, in BHS, the electron transfer configuration  $\chi_4$  and its cross terms are very important for anti-proton coupling, but spin polarization is more important for syn-coupling in both the localized and delocalized descriptions given above. While it is true that any particular hyperfine contribution to the totals appearing in tables 1 and 2 depends to some extent upon the exact choice of orthogonalization procedure embodied in equation (7), the  $\pi$ - $\sigma$  overlap terms are so small in the present situation that this type of component analysis has even greater validity than in the earlier work [19]. In any event, neither the total hyperfine coupling constant nor its sign is dependent upon the particular orthogonalization scheme that is used.

Experimental information is lacking for radicals of the BHS structure in which the spin label contains an unpaired electron in an antisymmetrical delocalized  $\pi$  orbital. The closest analogy appears to be the semifuraquinone radical [7], in which  $A$  (anti)  $>$   $A$  (syn) and for which our results are in satisfactory agreement. The couplings are smaller than the other radicals cited ( $A_{\text{H}_a} \approx 1$  G) in accord with the fact that neither electron transfer nor ground state-configurations contribute to the overall splittings in cases where  $c_{ir} \approx -c_{jr}$ . The importance of geometry is demonstrated by the fact that the sign of the hyperfine interaction changes in going from anti- to the syn-orientation, due in large part to the sign of the matrix element  $\langle \chi_1 | \mathcal{H} | \Phi_p \rangle$ . In radicals such as BHS anion with a symmetric HOMO, it is the matrix element  $\langle \chi_4 | \mathcal{H} | \Phi_p \rangle$  which plays an important role in determining the magnitude of the hyperfine couplings for the syn- and anti-protons. The results we have calculated,  $A_{\text{H}}$  (anti) = 4.95 G and  $A_{\text{H}}$  (syn) = 1.59 G should be directly comparable to the experimental results for BHS. These are 6.47 and 0.41 G respectively, for which the agreement must be considered to be satisfactory. The importance of electron transfer configurations such as  $\chi_4$  has been overlooked in some calculations [17, 29], but according to the results of the present non-empirical study, should have been retained. They are especially important for C-H bonds near the anti-orientation where the contribution is sizeable.

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