

THE UNIVERSITY OF CALGARY

THE MECHANISM OF LONG-RANGE PROTON HYPERFINE COUPLING
IN THE RIGID BICYCLIC ORGANIC RADICALS

by

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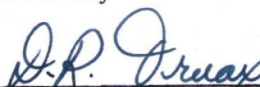
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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "The Mechanism of Long-range Proton Hyperfine Coupling in the Rigid Bicyclic Organic Radicals" submitted by Frederick W. King in partial fulfillment of the requirements for the degree of Master of Science.



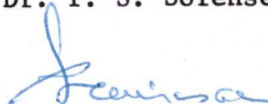
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ABSTRACT

This thesis elucidates the principal mechanisms of long-range proton isotropic hyperfine coupling for the bicyclo[2.2.1]heptane semidione radical anion. The approach involves a non-empirical configuration interaction study of a suitable σ -bonded fragment coupled with a semiempirical description of the spin label.

The effect of different spin labels for this σ -fragment is investigated. The mechanism of coupling is found to depend critically on the symmetry of the highest filled molecular orbital of the spin label, and on the stereochemistry of the σ -bonded moiety.

Relationships are obtained connecting the hyperfine coupling and the spin density on the spin label, for both the cases where the highest filled molecular orbital of the spin label is symmetric or antisymmetric with respect to the reflection plane of the molecule, which contains the CH_2 group under consideration and bisects the spin label.

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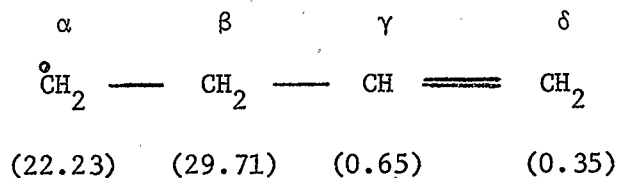
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CHAPTER I

INTRODUCTION

Long-range hyperfine coupling constants observed in electron spin resonance spectra are those which occur between nuclei separated by three or more σ -bonds from some principal centre containing an unpaired electron, or some portion of the unpaired electron density. This description of long-range coupling tends to imply that the number of intervening bonds is of critical importance, however, it shall be clearly illustrated in this thesis that this is not entirely correct.

A wealth of information from electron spin resonance studies of organic radical systems in solution has revealed a basic pattern for the magnitude of various hyperfine interactions. It is apparent from the vast amount of experimental data, that hyperfine couplings which fall into the category defined above are either experimentally unobservable or very small in magnitude. Numerous examples illustrate this remark; for example the 3-butenyl radical [1] clearly demonstrates the appreciable attenuation of hyperfine



interactions along the chain. The δ -coupling reported is for one proton only and it is not known which of the δ protons gives rise to the splitting. The numerical values are in units of gauss. Many other illustrations may be located in the literature [2-4].

A certain class of radical systems [5,6] were accidentally discovered to show rather anomalously large hyperfine coupling for certain protons removed three bonds 'from the nearest atom with a fraction of the unpaired electron'. It was clearly noted that the unusually strong hyperfine splittings were not characteristic of several related radicals investigated by the same authors [7]. A typical example of the experimentally observed results are those obtained by Russell and Chang in the original work [5], part of which is illustrated below in Figure 1.1.

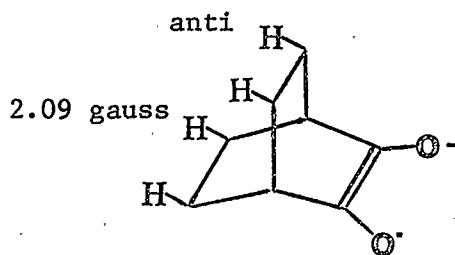


Figure 1.1 Bicyclo [2.2.2] octane semidione radical anion.

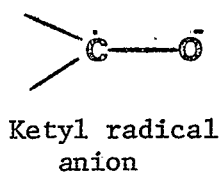
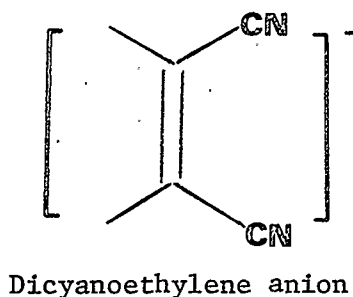
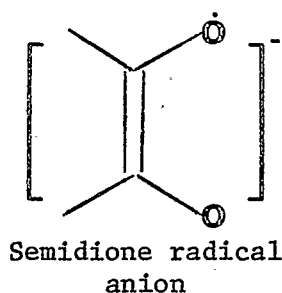
The size of the anti-hyperfine coupling is roughly an order of magnitude greater than the corresponding γ -coupling observed in most unconstrained radical systems. The splitting due to the bridgehead and syn-protons is very small.

Since this initial discovery, a large number of compounds of great diversity have been found to reveal similar long-range couplings. Despite the variety, the majority of systems are of the bridged polycyclic molecular type. Other molecules which do not fall directly into this category are those which have, or are forced to have, a frozen geometrical configuration, such as the cyclohexyl radical at low temperature [1].

Long-range splittings have been observed almost exclusively for protons, the exception being fluorine in perfluorocyclobutanone ketyl [8] and a few other similar systems [9]. Nuclei other than hydrogen have attracted far less attention.

The experimental work of Russell and co-workers [5,6,10-13] has established beyond doubt the correct assignment of the hyperfine splitting constants for the principal systems which they studied. These workers resorted to an investigation of many methylated derivatives and isotopically substituted compounds of known configuration. However, most subsequent investigators arbitrarily based their assignments on the work of Russell's group, even though

somewhat different geometrical systems were involved. Additional confirmatory work has been performed by Kosman and Stock [14,15]. Most of these investigations have been carried out with molecules which are derivatives of relatively easily reduced π -electron systems which act as sources of unpaired spin density. These can be considered to be "spin labels".[†] The only labels which have been employed in long-range studies are illustrated in Figure 1.2.



[†] In this thesis, a spin label will be broadly defined as any molecular species which exists as a non-singlet ground state entity and is capable of being bonded to other molecular species in some manner which does not affect the paramagnetic properties of the label.

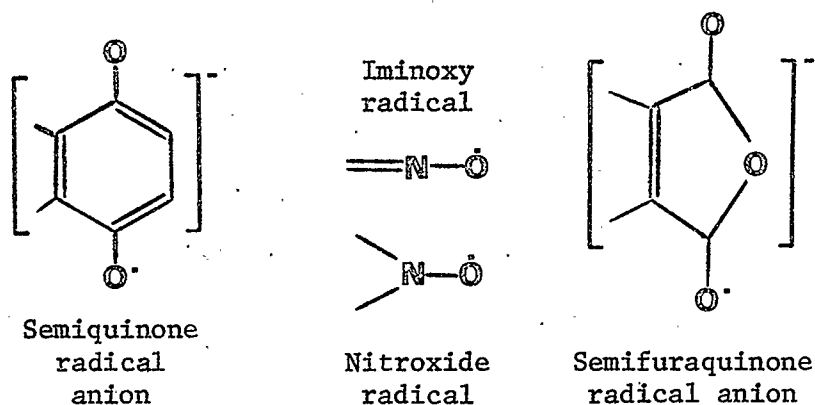


Figure 1.2 Spin Label Systems.

The semidiones [5,6,10-13, 16-20] and semiquinones [14,15,18,21-23] are the most thoroughly investigated of these labels, while the others have received only cursory attention [24-27]. The only other technique by which radicals exhibiting long-range coupling have been generated is by irradiation, where both U.V. [28-30] and γ -irradiation [31,32] have been employed. Some quite unexpected assignments have been made in this latter group of work and the appropriate comments on these assignments will be made in a later chapter. Experimental values where relevant, will appear in the discussion section.

Two papers deserve special mention at this point. The first [33] concerns nuclear magnetic resonance work on the system shown in Figure 1.3. This elegant work illustrates how N.M.R. may be

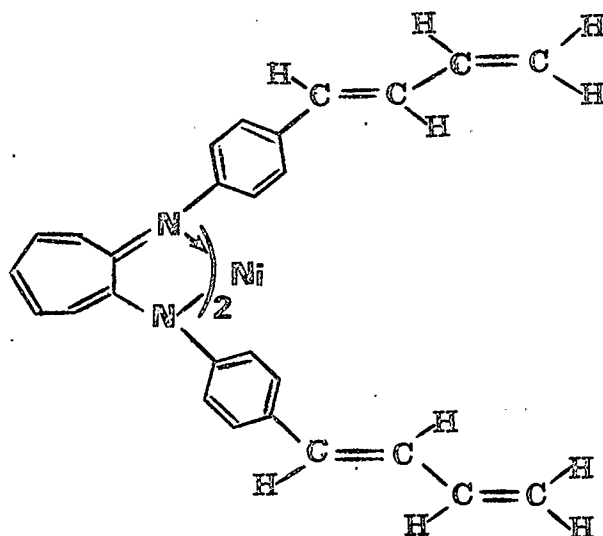


Figure 1.3 Ni (II) N, N'-bis-(p-1,3-butadienylphenyl)
aminotroponeimineate.

used to monitor the migration of 'unpaired spin density' by measurement of the paramagnetic shift of the protons at different positions. The apparent transference of spin over several bonds in systems of this type should not be considered highly unusual, since the entire ligand is conjugated and it is readily apparent from our previous definition, that the anomaly of long-range coupling is connected in some way with a localized (σ) bonding description. However, such nuclear magnetic resonance studies have the advantage over ESR measurements that they predict the sign as well as the magnitude of the hyperfine coupling. The second paper [26], presents an N.M.R. study of a bicyclic nitroxide radical. Although the work is incomplete, the authors do manage to ascribe a

sign to the anti-proton coupling constant. Evidence as to the sign of the long-range couplings based on ESR studies has not been forthcoming. So this N.M.R. evidence will prove of considerable value. This point will be discussed at a later stage.

Before proceeding to outline the procedure for rationalizing the experimental data (Chapter 2) it would seem appropriate to outline briefly the scope of this thesis. The present work is concerned only with proton hyperfine interactions. With the immense diversity of compounds which might attract our particular attention as a possible starting point, it was apparent that some criterion for selection was needed. Since the 'exact' geometry of all of these radical systems is unknown and is in fact likely to remain so for some time, our selection has been based partly on the availability of known geometry for similarly related systems. More important however, in directing our choice was the fact that the best available techniques for calculating magnetic resonance parameters are likely to be quite ineffective for calculating such small values of splitting constants as are required here. This immediately leads to the choice of the bicyclo [2.2.1] heptane semidione radical anion, Figure 1.4. This system exhibits one of the largest anti-proton coupling constants observed for any spin label, while at the same time has a sizeable syn-coupling, and is thus likely to be the most attractive choice for study.

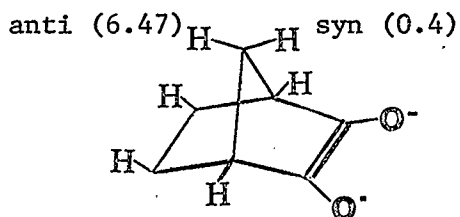


Figure 1.4. Bicyclo [2.2.1] heptane semidione radical anion.

The thesis is directed primarily towards the study of this system. Since the bicyclic structure is present in the vast majority of systems observed experimentally, the conclusions reached for the bicyclo [2.2.1] heptane semidione system will be of general validity for the other systems. Also examined will be the effect of substituting different spin labels into the bicyclo heptane system, and this will be discussed as far as experimental data is available on the relevant compounds.

CHAPTER II

THEORETICAL DESCRIPTION OF MODELS AND COMPUTATIONAL PROCEDURE

A. Mechanism of Hyperfine Coupling

In this section the various mechanisms which have been applied to calculate hyperfine coupling constants will be examined. Particular emphasis will be placed on those methods which are of explicit applicability to the systems studied in this thesis.

(a) Fermi contact interaction

Experimental results for hyperfine couplings are found to be 'successfully explained' on the hypothesis that electron and nuclear spins interact via a magnetic dipole-dipole interaction, an orbital-dipole interaction or a Fermi contact interaction. Spin-orbit interactions have been excluded since these are known to give rise to very small effects [34] for the type of compounds which are of concern here. Furthermore, the experimental data to be described were obtained from radical systems in non-viscous liquid media. Under these conditions, the molecules undergo a rapid tumbling motion with the result that the dipolar contribution vanishes [35]. Thus the

term 'hyperfine coupling' will be taken to mean only isotropic hyperfine coupling for the rest of this thesis.

It appears that the Fermi contact contribution provides the dominant term for the 'explanation' of hyperfine interactions. It has therefore been assumed that interaction terms other than the Fermi contact contribution are unimportant in consideration of the molecular systems of interest here.

The Hamiltonian operator for the Fermi contact term takes the form

$$H_F = \frac{8\pi}{3} g_e \beta_e \sum_N g_N \beta_N \sum_k \delta(r_{kN}) S_k \cdot I_N \quad (2.1)$$

where $\delta(r_{kN})$ is the Dirac delta function, which here expresses the property that H_F operates on the wave function only at the nuclei (contact) while g_e and g_N are the electron and nuclear g factors respectively, β_e and β_N are respectively the electronic and nuclear Bohr magneton, S_k denotes the spin of electron k and I_N the spin of nucleus N . A lucid derivation of the contact term can be found in the work of Blinder [36].

The form of equation (2.1) can be simplified when the Zeeman energy is very large compared to the hyperfine interaction. This is the high field approximation, i.e. both I and S are decoupled and in-

dependently quantized in the direction of the applied field as in the Paschen-Back effect. If hyperfine interaction is identified with a particular nucleus N, equation 2.1 becomes

$$H_F = \frac{8\pi}{3} g_e \beta_e g_N \beta_N I_N \sum_k S_{kz} \delta(r_{kN}) \quad (2.2)$$

where the axis of quantization has been arbitrarily chosen as the z axis. Justification for neglect of second order terms such as $S_x I_x$ etc., is based on the high field approximation which is readily demonstrable in the typical experimental situation.

The term H_F is empirical in the sense that it tells nothing about the actual mechanism of coupling, and is simply the operator representation of the isotropic hyperfine interaction. The process by which coupling takes place is determined on the basis of physical intuition and the use of naive model systems. It's relative applicability is then judged by how well the experimental facts are correlated with the theoretical expectations.

The hyperfine coupling of a particular nucleus N is given by

$$A_N = \langle \psi | H_F | \psi \rangle / (g_e \beta_e \langle S_z \rangle \langle I_z \rangle) \quad (2.3)$$

where $\langle S_z \rangle$ is the expectation value of the total spin of the fragment

of interest, $\langle I_z \rangle$ the expectation value of the nuclear spin N , and the $g_e \beta_e$ is a conversion factor so that the hyperfine coupling A_N is expressed in gauss.

The hyperfine couplings observed for aromatic systems attracted a fair amount of interest due to the somewhat paradoxical situation which existed. In these systems the odd electron is 'confined' to a π -molecular orbital, with the result that there is zero unpaired electron density at the in-plane aromatic protons and consequently the contact hyperfine interaction should vanish. The initial suggestion [37] that the hyperfine coupling was due to out of plane vibrations was later shown to be incorrect [38], although this may account in part for the temperature dependence of such couplings.

It was pointed out simultaneously by McConnell [39], Bersohn [40] and Weissman [41] that the approximate order of magnitude of hyperfine couplings could be predicted, based on the assumption that the unpaired electron produced an appreciable electron spin polarization of the hydrogen 1s atomic orbitals at the aromatic protons. Based on the assumption that the σ - π exchange interaction can be treated as a first-order perturbation, McConnell was able to show that for proton hyperfine coupling, a relationship of the form

$$A_N = Q\rho_N \quad (2.4)$$

was suitable for qualitative and semiquantitative estimates. Q is a semiempirical constant and ρ_N is the 'spin density in the $2p\pi$ orbital on the carbon atom' bonded to the hydrogen nucleus N . The spin density associated with a particular atomic orbital may be intuitively related to the difference between the populations of electrons of α spin and those of β spin. ρ_N will be negative whenever the population of electrons with spin β exceeds those with spin α . In the present thesis, ρ can generally be taken to be positive.

Within the orbital approximation, several formulae for the fractional population of unpaired spin density have been given [42,43]. Attempts to relate the hyperfine coupling to fractional spin populations on several of the nearest π -centres must all be rigorously discounted. This is due to the fact that the concept of unpaired spin density not directly associated with any particular atom, i.e., in the overlap region, has been entirely neglected. This will only be a sound approximation when the appropriate overlap integrals are negligible. Some work in the direction of including non-atomic contributions to the spin density matrix has been attempted [44].

For the purposes of relating the hyperfine coupling to the spin density on the spin label, one can assume a naive definition for spin density on centre i ,

$$\rho_i = c_{ir}^* c_{ir} \quad (2.5)$$

where c_{ir} are the expansion coefficients in the LCAO (linear combination of atomic orbitals) approximation, and the unpaired electron occupies the r th molecular orbital. A probability density $\rho(r_N)$ can be defined so as to give a measure of the unpaired spin density at the nucleus N , by

$$\rho(r_N) = \langle \psi | \sum_k \sigma_{zk} \delta(r_{kN}) | \psi \rangle \quad (2.6)$$

where σ_z is the Pauli spin operator, defined such that

$$\sigma_{zk} \alpha_k = \alpha_k \quad \sigma_{zk} \beta_k = -\beta_k \quad (2.7)$$

The simple relationship in equation 2.4 was found inadequate for numerous systems and further semiempirical extensions of this equation have since appeared [45,46]. Nuclei other than hydrogen also give rise to hyperfine couplings which may be related to the spin density by extended versions of equation 2.4 [47], based on the work of Karplus et al. on carbon-13 hyperfine splittings [48]. All of this work is essentially based on the assumption that spin polarization is the major mechanism responsible for coupling. Other systems have been studied where it has been 'shown' that spin polarization was not the dominant mechanism [49]. The general mechanisms which will be appropriate to

the bicyclo [2.2.1] heptane semidione system are discussed in the next section.

(b) Spin polarization

Spin polarization arises from the 'exchange' interaction[†] between the singly occupied π -orbital and the electrons of the σ -bonding system. To illustrate this, consider a C-H fragment. In the approximation of perfect pairing we would consider structures (a) and (b) to be equally important.

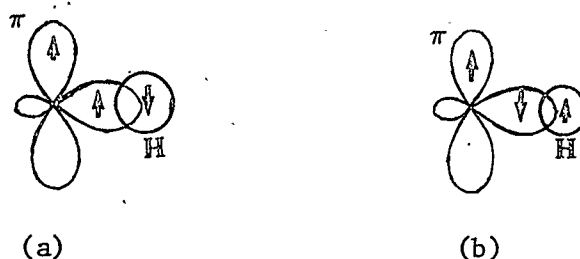


Figure 2.1 Polarization in C-H fragment.

If the interaction between σ - and π -electrons is taken into account, the (a) structure will energetically be more favoured than the other, as

[†] Hence the synonym for spin polarization is exchange polarization. This nomenclature is somewhat loose (although commonly used), since other non-exchange terms also contribute to the coupling in general.

determined by the size of various exchange integrals. This fact implies that the electrons of the C-H bond are slightly polarized. The π -electrons thus induce a departure from perfect pairing which results in a finite unpaired spin density at both the hydrogen and carbon nuclei.

The process can be clearly applied to systems with more than one intervening bond. For such systems, three different spin polarization processes may be distinguished. The first mechanism is the direct polarization of the electrons of the C-H bond of interest as a result of the unpaired π -electron density.

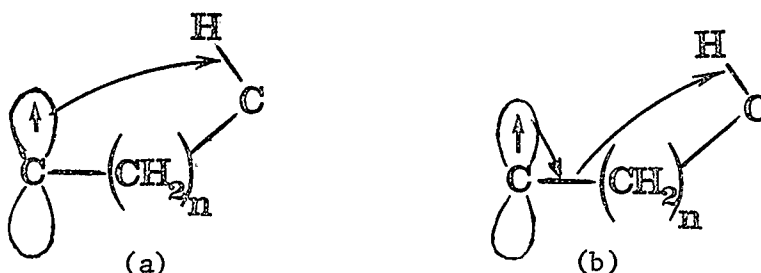


Figure 2.2 Delocalization pathways.

This is depicted in Figure 2.2(a). The second contribution arises from terms representing spin polarization of 'mixed' direct-indirect character, i.e. polarization of one of the intervening bonds and subsequent polarization of the C-H bond as a result of the induced polarization at the intermediate centre as shown in Figure 2.2(b). There

may be many such terms depending on the size of n and on the molecular configuration. The third mechanism is a purely indirect process whereby each bond between the π - system and the hydrogen atom is polarized. All exchange polarization processes involve only an electron pair decoupling process and do not induce π -electron migration into the σ -system. However, both polarization and transfer processes may operate at the same time as will be seen below.

(c) Electron transfer processes

Electron transfer processes refer to those situations which cause unpaired spin density to be induced at a certain centre, either by fractional migration of electrons away from or towards the particular center. These processes depend critically on the particular orbitals involved in the delocalization mechanism. Electron delocalization will be considered to be important for a particular orbital when the process leads to a non-vanishing contact hyperfine contribution.

The most common migration path is through the classical bonding pathway, i.e. an indirect process. Electron delocalization may also take place via a direct route between 'non-bonded' atoms. This process is governed by the geometry of the situation which in turn

determines the relative overlap of orbitals centred on the non-bonded centres. Electron delocalization will depend on the relative electronegativities of the different centres.

These processes are similar to those often referred to as 'hyperconjugation' in the literature. In a restricted sense, hyperconjugation is associated with electron delocalization. However, in a more general way, hyperconjugation may be taken to include other interactions between atoms; eg. non-conventional pairing schemes. Hyperconjugation then includes both electron transfer and spin polarization mechanisms. In view of the general confusion regarding this term, it appears preferable to avoid its use and retain only the terms electron delocalization and spin polarization.

Direct interactions result when the unpaired electron is in an orbital which has finite probability at the nucleus under consideration. The expressions 'local-direct', 'non-local-direct' and 'distant-direct' may be taken to mean that the orbital containing the odd electron is situated on the nucleus, its neighbour or a distant centre respectively.

For those cases where there is an 'electron-paired' inner core, contributions to the hyperfine coupling will arise from inner core polarization. This amounts to an exchange polarization of the inner core electrons by the 'unpaired electron' in the outer shell.

(d) Relative importance of contributions

The general importance of each of the outlined mechanisms depends on factors such as stereochemistry, type of atom under consideration and substituent effects. The work of McConnell [34,39] and Luz [50] pointed out that consecutive spin polarization (indirect process) along a chain will be quickly attenuated after the first bond. This can be seen by treating the $\sigma - \pi$ interaction as a small perturbation. For consecutive polarization, the only process by which this mechanism can be accommodated into simple molecular orbital methodology is to include descriptions of the system containing multiple excitations from bonding to antibonding molecular orbitals of the intervening bonds of the chain. Multiple polarizations will therefore enter only as second-and higher-order terms. The most important contribution will accordingly arise from terms involving single excitations, and this automatically restricts the polarization to only one bond. Transmission of exchange decoupling in saturated systems does not depend on the dihedral angles of the system. Geometrical dependence enters via the bond length between adjacent atoms.

Essentially the same ideas will apply to mixed-direct-indirect contributions to hyperfine coupling. However, in this case the geometry of the entire framework of the saturated system will be involved. Mixed-direct-indirect terms will only be expected to give

rise to a fairly small collective contribution to the first-order hyperfine coupling, and only in those cases where the geometry is highly favourable.

Indirect spin polarization processes over more than one bond have received little attention. Colpa and de Boer [49] have made a naive estimate for the C-C-H radical, and showed that such processes are much too small to explain the experimental results. This conclusion is intuitively correct and will apply even more appropriately to the extended saturated systems studied here. Direct polarization will be highly dependent on geometrical considerations. For the saturated system C_4H , orientated as shown in Figure 2.3(a), the direct exchange coupling will be negligible.

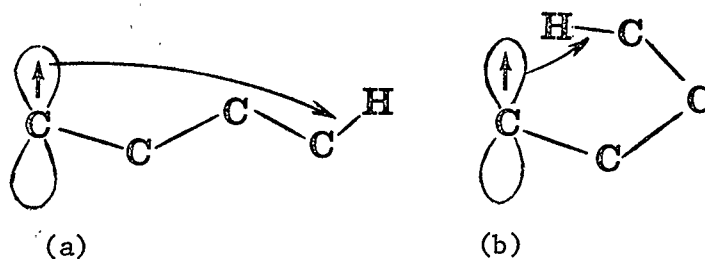


Figure 2.3 Possible orientations for C_4H fragment.

For the orientation in Figure 2.3(b) however, the geometry is such that a reasonable interaction may occur as illustrated. These types of inter-

actions have been essentially neglected, apparently due to the fact that the appropriate integrals do not appear in the literature. Saturated systems, such as depicted in Figure 2.3(a) will not have a very large hyperfine interaction resulting from this mechanism. On the other hand, oriented systems such as the bicyclic derivatives may have some C-H bonds constrained in a geometry resembling Figure 2.3(b) and may have a reasonable portion of the observed hyperfine coupling produced through direct exchange coupling.

Spin delocalization processes can be accounted for in a simple molecular orbital description by 'promoting' an electron from a localized orbital in one part of the molecule to an orbital characteristically localized in another portion of the molecule. This redistribution of charge will depend upon the extent of overlap between the participating orbitals. Overlap dependence is or appears to be the factor governing delocalization processes and this is explicitly dependent on the stereochemistry of the system. The spin delocalization and spin polarization processes provide the pathway for the hyperfine coupling which may then be categorized in terms of local-direct, non-local-direct and distant-direct contributions. Only the local-direct contributions are sufficiently large to explain the experimental results.

For consideration of proton hyperfine couplings, core

polarization terms are not important, although they cannot be neglected for example, in the calculation of carbon-13 hyperfine splittings.

(e) Mechanisms included in semiempirical procedures

The simplest systems studied by ESR containing an interacting π - and σ -electron system are the methyl substituted aromatic radicals. A number of calculations [40,49,51] have shown that methyl-group spin densities in approximate agreement with experiment are obtained by use of either valence bond or Huckel molecular orbital methods using reasonable values for the required integral parameters. The success of these alternative theoretical approaches is encouraging, if predictive power and agreement with experiment are the gauges of success. On the other hand, if the mechanism of coupling is to be understood, then such schemes are unsatisfactory since the use of semiempirical parameters does not allow the separation of factors required in such an analysis.

The mechanism involved in the transfer of the unpaired spin to the methyl group in the valence-bond and Huckel molecular orbital calculations is fundamentally different in character. In the former, the π -electron spin delocalization into the methyl group is produced entirely by exchange polarization, while in the latter, it is a consequence solely of electron transfer.

Colpa and de Boer [49] have suggested that exchange polarization makes only a minor contribution to hyperfine coupling in the C_2H fragment. This observation may be correct for the system they investigated, however it is not true for the constrained bicyclic radical systems. In view of the approximations involved in the semi-empirical scheme employed by Colpa and de Boer, their final conclusions are, in any case, somewhat suspect.

B. Molecular Models

As already outlined in the introduction, the bicyclo [2.2.1] heptane semidione radical anion (BHS) seems to be the logical molecular system to study. The physical size of this system, however precludes the possibility of performing a fairly rigorous nonempirical calculation, although a few molecules of comparable size have been investigated in some laboratories. In view of the enormous difficulty of working with such large molecules it is necessary to make some approximations which can, however, be made in the light of the preceeding discussion of the relative importance of different mechanisms contributing to long-range coupling of interest in the semidiones.

The primary concern is obtaining a description of the large anti-coupling proton constant and comparing it to the syn-coupling constant on the same atom. Furthermore, the coupling would vanish in

the absence of the spin label system, so the essential ingredients of the fragment investigated must include these features. Two simple models have been chosen to describe the BHS system.

(a) Model I

In this model, the fragment examined represents the simplest possible molecular system. This consists of a π -orbital situated on that centre of the spin label nearest to the protons under consideration. The interaction between the π -orbital with the C-H bond oriented in each of the anti-proton and syn-proton conformations is then investigated. This approximate representation of BHS amounts to a weakly bound $C\cdots C-H$ system. While it is recognized that this is a somewhat naive model, it does have some theoretical justification as outlined in the following section.

Although some bicyclic derivatives have a conjugated system aside from that belonging to the label, the majority do not. In these doubly conjugated systems, hyperfine coupling may result from an indirect process involving spin transfer to the secondary π -centres followed by a 'back-sided' interaction. If nonclassical structures such as 'observed' in the norbornyl cationic systems are excluded for the BHS molecule, then there are essentially no interactions leading to a sizeable coupling arising from the back skeleton of the BHS system.

Because indirect spin polarization is of second-and higher-order for the BHS molecule, the bonding between the spin label π -orbital and the relevant C-H bond is not important, in the sense of contributing to the hyperfine coupling of the syn- and anti-protons. Indirect electron delocalization along the path of the σ -bonds will be negligibly small in most cases (including BHS), but could conceivably change with the substitution of certain groups which might change the geometry or the characteristics of the intermediate bonds. The main problem not treated in model I will be the effect of interactions between the C-H bond electrons and the other orbitals of the spin label. This question will be taken up at a later stage. Finally, it should be noted that considerable success is achieved by representing aromatic systems by the simple C-H fragment [34], and model I is the closest analogy one can choose for the long-range interactions of interest here. It must be emphasized that the paramount effect in the BHS type system is that the particular bonding arrangement keeps the $C\cdots C-H$ fragments in a relatively rigid orientation to each other. It should be apparent that the unusually rigid nature of the σ -framework and particular stereochemical location of the syn- and anti-protons may well be the cause of the experimental observations concerning the proton hyperfine structure. This will be discussed further at a later stage.

(b) Model II

In this model essentially the same fragment is used as before, except that both anti- and syn-protons are considered together. The interaction is then described by means of a suitable combination of both syn- and anti-hydrogen 1s charge clouds with an orbital of appropriate symmetry on the adjacent carbon. The interactions of this subsystem with the π -orbital of the spin label are then investigated. The fragment of interest now resembles a weakly bound 'allyl' system.

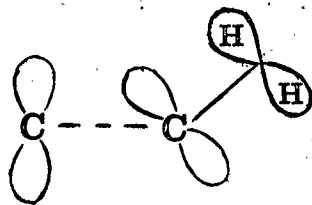


Figure 2.4 Fragment for model II.

For reasons which will become apparent in the next section, the individual values of the proton hyperfine couplings for the syn- and anti-protons are not obtained from this model; only the sum is calculated. For this reason a less rigorous investigation of this particular model was employed. Model II provides a somewhat independent comparison based on the use of a different fragment for testing the reliability of the results based on model I. There is precedent for the use of a

fragment similar to the one used in model II [52].

(c) Theoretical description of models

For model I the molecular orbitals describing the fragment will be denoted as π for the π -molecular orbital of the spin label, and b and a for the bonding and antibonding molecular orbitals respectively of the C-H bond. The latter molecular orbitals will be defined in terms of atomic orbitals,

$$b = [1s_h + hy_c] \{2[1 + S_{(1shy)}]\}^{-1/2} \quad (2.8)$$

$$a = [1s_h - hy_c] \{2[1 - S_{(1shy)}]\}^{-1/2} \quad (2.9)$$

where $1s_h$ denotes a hydrogen $1s$ atomic orbital; $S_{(1shy)}$ is the overlap integral

$$S_{(1shy)} = \langle 1s_h | hy_c \rangle^+ \quad (2.10)$$

wherein hy_c denotes a hybrid type orbital and the subscript denotes the atom on which it is centered,

$$hy_c = \frac{1}{2}[(2s_c) + \sqrt{3}(2p_c)] \quad (2.11)$$

[†] The notation $\langle \chi_A | \chi_B' \rangle = \int \chi_A(i) \chi_B'(i) d\tau_i$ is employed.

The zeroth-order (ground state) configuration of the fragment will be given by the following Slater determinant, the notation for which is represented by $\|\cdots\|$, so that

$$\psi_g \equiv \psi_1 = \|\pi b \bar{b}\| \quad (2.12)$$

where the bar in equation 2.12 denotes spin β and no bar denotes spin α . Singly excited $\pi\text{-}\sigma^*$ configurations can be described which are based on the representation of the ground state ψ_1 as given by equation 2.12.

Thus,

$$\psi_2 = \frac{1}{\sqrt{2}} [\|\pi b \bar{a}\| - \|\pi \bar{b} a\|] \quad (2.13)$$

$$\psi_3 = \frac{1}{\sqrt{6}} [2\|\pi \bar{b} a\| - \|\pi b \bar{a}\| - \|\pi b \bar{a}\|] \quad (2.14)$$

These functions are eigenfunctions of S_z ($=\frac{1}{2}$) and S^2 ($=3/4$). Configurations corresponding to electron transfer may also be defined. For electron transfer away from the spin label, i.e. from the π -molecular orbital' one has

$$\psi_4 = \|\pi a \bar{b}\| \quad (2.15)$$

while for electron transfer to the spin label, configurations such as

$$\psi_5 = \|\pi b \bar{\pi}\| \quad (2.16)$$

$$\psi_6 = \left\| \pi a \bar{\pi} \right\| \quad (2.17)$$

are employed. The configurations described by equations 2.15 to 2.17 may be referred to as intramolecular charge transfer configurations.

Doubly excited configurations such as $\left\| \pi a \bar{a} \right\|$, $\left\| a b \bar{a} \right\|$, $\left\| \pi a \bar{\pi}^* \right\|$ etc. have not been included. Such configurations will not contribute appreciably to a first order estimate of the hyperfine coupling.

For model II the following molecular orbitals are defined; A denotes the anti-bonding orbital for the CH₂ system, and B the corresponding bonding orbital. These are defined by

$$B = [\phi_1 + \phi_2] \{2[1 + S_{\phi_1\phi_2}]\}^{-1/2} \quad (2.18)$$

$$A = [\phi_1 - \phi_2] \{2[1 - S_{\phi_1\phi_2}]\}^{-1/2} \quad (2.19)$$

where

$$\phi_1 = [1s_a - 1s_s] \{2[1 - S_{as}]\}^{-1/2} \quad (2.20)$$

and ϕ_2 is a 2p π orbital of appropriate symmetry on the carbon of the CH₂ fragment, $S_{\phi_1\phi_2}$ is the overlap integral for the orbitals ϕ_1 and ϕ_2 , and S_{as} is the overlap integral for the two hydrogen 1s orbitals

centred on the anti-proton (subscript a) and syn-proton (subscript s). The other 'molecular orbital' is taken as the π -orbital on the spin label. This basis set amounts to using orbitals of a nonlocalized character.

For model II, included are configurations similar to those employed for model I. The configurations representing the zeroth-order state function and the singly excited configurations are

$$\Phi_1 = \parallel \pi \bar{B} \bar{B} \parallel \quad (2.21)$$

$$\Phi_2 = \frac{1}{\sqrt{2}} [\parallel \pi \bar{B} \bar{A} \parallel - \parallel \pi \bar{A} \bar{B} \parallel] \quad (2.22)$$

$$\Phi_3 = \frac{1}{\sqrt{6}} [2 \parallel \pi \bar{B} \bar{A} \parallel - \parallel \pi \bar{A} \bar{B} \parallel - \parallel \pi \bar{A} \bar{A} \parallel] \quad (2.23)$$

and those configurations denoting electron transfer are

$$\Phi_4 = \parallel A \bar{B} \bar{B} \parallel \quad (2.24)$$

$$\Phi_5 = \parallel \pi \bar{B} \bar{\pi} \parallel \quad (2.25)$$

$$\Phi_6 = \parallel \pi \bar{A} \bar{\pi} \parallel \quad (2.26)$$

C. Outline of the Computational Schemes

In the present section we shall outline the procedures employed in the calculations. For model I, the variational procedure was employed while for model II, a perturbation theory approach was followed. The reasons for these choices has already been outlined.

The non-relativistic Hamiltonian operator for a molecule of N nuclei and n electrons is in atomic units[†]

$$H = -\frac{1}{2} \sum_i^n \nabla_i^2 - \frac{1}{2} \sum_{\mu}^N \frac{\nabla_{\mu}^2}{m_{\mu}} - \sum_{\mu}^N \sum_i^n \frac{Z_{\mu}}{r_{\mu i}} + \sum_{\mu < \lambda}^N \sum_{\mu < \lambda}^N \frac{Z_{\mu} Z_{\lambda}}{r_{\mu \lambda}} + \sum_{i < k}^n \frac{1}{r_{ki}} \quad (2.27)$$

The terms in the Hamiltonian are (from left to right), the kinetic energy of the electrons, the kinetic energy of the nuclei, the electron-nuclear potential energy, the nuclear mutual potential energy and finally the electron mutual potential energy. The Schrodinger equation which this Hamiltonian satisfies can be written

$$H \Psi(r, R) = E \Psi(r, R) \quad (2.28)$$

where E is the 'total energy' of the system. The wave function $\Psi(r, R)$ depends upon both the electronic co-ordinates r and the nuclear co-

[†] The energy unit, hartree = 27.2107 ev., and the unit of length, bohr = 0.529165×10^{-8} cm.

ordinates R .

The Born-Oppenheimer approximation was employed, which allows the total wave function of the molecule to be written as

$$\Psi(r, R) = \Psi_R(r) \Phi(R) \quad (2.29)$$

The function $\Psi_R(r)$ is the electronic wave function and depends parametrically upon the nuclear co-ordinates. $\Phi(R)$ is the nuclear wave function. The Hamiltonian operator for the electrons is conveniently written as

$$H_e = \sum_i^n h(i) + \sum_{i < j}^n \frac{1}{r_{ij}} \quad (2.30)$$

where the mono-electronic operators for the kinetic energy and nuclear electron potential energy have been collected together, i.e.,

$$h(i) = -\frac{1}{2} \nabla_i^2 - \sum_{\mu}^N \frac{Z_{\mu}}{r_{\mu i}} \quad (2.31)$$

The electronic energy $E(R)$ is then given by the solution of

$$\left\{ \sum_i^n h(i) + \sum_{i < j}^n \frac{1}{r_{ij}} + \sum_{\mu < \lambda}^N \frac{Z_{\mu} Z_{\lambda}}{r_{\mu \lambda}} \right\} \Psi_R(r) = E(R) \Psi_R(r) \quad (2.32)$$

The solution of the set of differential equations given by (2.32) is not possible for more than one electron, so that approximate methods must be employed. The first procedure used for obtaining approximate solution for (2.32) is the variational method.

In order to implement this technique, one requires a linear combination of some set of basis functions in terms of which the state functions may be expanded. In the case of model I, the state functions may be written as

$$\chi_J = \sum_{K=1}^6 c_{KJ} \psi_K \quad (2.33)$$

where the ψ_K are the configurations given by (2.12) to (2.17) and the c_{KJ} are the variational coefficients to be determined by the solution of the set of linear equations which are given by

$$\sum_{K=1}^6 c_{KJ} (H_{KL} - E_J S_{KL}) = 0 \quad (L = 1, \dots, 6) \quad (2.34)$$

wherein

$$S_{KL} = \int \psi_K^* \psi_L d\tau \quad (2.35)$$

and

$$H_{KL} = \int \psi_K^* H \psi_L d\tau \quad (2.36)$$

H_e is the electronic Hamiltonian defined by the left hand side of equation 2.32. The non-trivial solutions of the simultaneous equations, 2.34 are obtained from the solution of the secular equation.

$$\det | H_{KL} - E_J S_{KL} | = 0 \quad (2.37)$$

With the coefficients C_{KJ} of equation 2.33 in principle determined, it merely remains to substitute equation 2.33 into equation 2.3 to determine the hyperfine coupling. Thus the hyperfine coupling will be given by the equation

$$A_H = [g_e \beta_e \langle S_z \rangle \langle I_z \rangle]^{-1} \sum_{K=1}^6 \sum_{L=1}^6 C_{K1} C_{L1} \langle \psi_K | H_F | \psi_L \rangle \quad (2.38)$$

The subscript 1, denoting the lowest energy eigenstate will be neglected from now on.

For model II, a less rigorous solution of (2.32) is obtained. The idea applied here is that the conjugated spin label and the σ -framework of the bicyclic fragment are essentially independent entities, and the interactions between the two systems may be treated

as a small perturbation of the entire system. The ground state description is given by equation 2.21. The other configurations, equations 2.22 to 2.26 are then admixed with the perturbation given by

$$H_p = \sum_{i < j}^n \frac{1}{r_{ij}} \quad (2.39)$$

The improved wave function, χ_I is then given (to first-order) by

$$\begin{aligned} \chi_I = \Phi_g + \lambda \sum_{k \neq g}^6 \{ <\Phi_k | H_p | \Phi_g > - <\Phi_k | \Phi_g > <\Phi_g | H_p | \Phi_g > \} \\ \times \{ \Phi_k - <\Phi_g | \Phi_k > \Phi_g \} \times \{ E_g - E_k \}^{-1} \end{aligned} \quad (2.40)$$

as outlined in appendix I. The parameter λ measures the order and is set equal to unity in calculations. The hyperfine coupling is then obtained by substituting χ_I into the equation for the hyperfine coupling (2.3),

$$\begin{aligned}
 A_H = & \left\{ \langle \Phi_g | H_F | \Phi_g \rangle + 2 \sum_{k \neq g}^6 \left\{ \left[\langle \Phi_g | H_F | \Phi_k \rangle \langle \Phi_k | H_P | \Phi_g \rangle \right. \right. \right. \\
 & - \langle \Phi_k | H_P | \Phi_g \rangle \langle \Phi_g | \Phi_k \rangle \langle \Phi_g | H_F | \Phi_g \rangle \\
 & - \langle \Phi_g | H_P | \Phi_g \rangle \langle \Phi_g | \Phi_k \rangle \langle \Phi_k | H_F | \Phi_g \rangle \\
 & \left. \left. + \langle \Phi_g | H_P | \Phi_g \rangle \langle \Phi_g | \Phi_k \rangle^2 \langle \Phi_g | H_F | \Phi_g \rangle \right] \right. \\
 & \left. + \frac{1}{2} \sum_{\ell \neq g}^6 \left[\langle \Phi_k | H_P | \Phi_g \rangle \langle \Phi_g | H_P | \Phi_\ell \rangle \langle \Phi_k | H_F | \Phi_\ell \rangle \right. \right. \\
 & \left. \left. + \text{further smaller terms} \right] (E_g - E_\ell)^{-1} \right. \\
 & \left. \times \left\{ (E_g - E_k)^{-1} \right\} (g_e \beta_e \langle S_z \rangle \langle I_z \rangle)^{-1} \right. \quad (2.41)
 \end{aligned}$$

(a) Calculation of matrix elements

The hyperfine coupling for both of the above procedures is clearly seen to be dependent on different matrix elements of the form (a) $\langle \Psi_k | \Psi_\ell \rangle$, (b) $\langle \Psi_k | H_e | \Psi_\ell \rangle$ and (c) $\langle \Psi_k | H_p | \Psi_\ell \rangle$.

In this section a procedure is outlined for obtaining the values for these terms. A slight digression at this point is necessary in order to describe the calculation of matrix elements and also to rationalize some of the preceding remarks in this chapter.

The simple treatment of McConnell and others of the C-H fragment has one very important advantage; at the level of approximation that was used, the π -system and the σ -system[†] are rigorously separable into two distinct groups. In such a case, the π - σ interaction is assumed small, and hence may be treated as a perturbation. The form of the perturbation used by McConnell was

$$H_p = \sum_{i < j}^n \frac{1}{r_{ij}} \quad (2.42)$$

The description of both model fragments in this work is based on an initial basis set of non-orthogonal orbitals, ie.,

$$\begin{aligned} \langle \pi | a \rangle &\neq 0 & \langle \pi | b \rangle &\neq 0 \\ \langle \pi | A \rangle &\neq 0 & \langle \pi | B \rangle &\neq 0 \end{aligned} \quad (2.43)$$

although

$$\langle b | a \rangle = 0 \quad \langle A | B \rangle = 0 \quad (2.44)$$

The non-orthogonality problem enters into the calculation of the matrix elements

$$\langle \Psi_k | \sum_{i < j}^n \frac{1}{r_{ij}} | \Psi_\ell \rangle.$$

[†] The terms ' σ -electron' and ' π -electron' have only a precise meaning when the electronic wavefunction of the molecule is treated by a particular quantum mechanical approximation.

An orthogonal basis set can be constructed from any non-orthogonal basis set in a straight forward manner. The procedure of constructing such an orthogonal basis set has a slight conceptual drawback. For the non-orthogonal basis set, each orbital can be identified with a certain contribution towards the hyperfine coupling; for example, the contribution of the π -orbital towards the hyperfine coupling of the syn- and anti-protons (distant-direct contribution) has been estimated (see next chapter) and found to be negligible. However, in the construction of an orthogonalized set, the π -orbital takes on hydrogen 1s character. This is an undesirable side effect, since it does not allow one to delete a large number of integrals of the form $\langle \pi | H_F | 1s \rangle$ etc., which give rise to negligible contributions toward the hyperfine coupling for the non-orthogonal set. From this point onwards, the orthogonalized π -orbital used in describing the spin label will no longer rigorously imply purely ' π -character', although it still remains a useful idea in a loose sense.

For the calculation using model I, the basis set $[\pi, b, a]$ has been replaced by the Schmidt orthogonalized basis set $[\Delta, b, a]$ where Δ is given in terms of the initial basis set by

$$\Delta = [\pi - \langle b | \pi \rangle b - \langle a | \pi \rangle a] [1 - \langle b | \pi \rangle^2 - \langle a | \pi \rangle^2]^{-1/2} \quad (2.45)$$

For the calculations using model II, the non-orthogonal basis set was employed and equation 2.40 was then used to determine the hyperfine coupling.

The general matrix elements I_1 , I_2 are given by

$$I_1 = \int \|\psi_1 \bar{\psi}_2 \cdots \psi_{N-1} \bar{\psi}_N\| \sum_i h(i) \|\psi'_1 \psi'_2 \cdots \psi'_{N-1} \bar{\psi}'_N\| d\tau_1 \cdots d\tau_N \quad (2.46)$$

$$I_2 = \int \|\psi_1 \bar{\psi}_2 \cdots \psi_{N-1} \bar{\psi}_N\| \sum_{i < j} \frac{1}{r_{ij}} \|\psi'_1 \psi'_2 \cdots \psi'_{N-1} \psi'_N\| d\tau_1 \cdots d\tau_N \quad (2.47)$$

where the set of spin orbitals $\psi(i)$ differs from the set, $\psi'(i)$ in that each of the ψ 's is either identical with the corresponding ψ' or orthogonal to all of them as well as being orthogonal to the other ψ 's as is the case for a completely orthogonal set. The standard results [53] are then obtained.

$$I_1 = \int \psi_n(i) h(i) \psi'_n(i) d\tau_i \quad (2.48)$$

if the set differs only by $\psi'_n \neq \psi_n$ and

$$I_1 = \sum_n \int \psi_n(i) h(i) \psi_n(i) d\tau_i \quad (2.49)$$

if the determinants are identical.

The results for I_2 are

$$I_2 = [\psi_i \psi_i' | \psi_j \psi_j'] - [\psi_i \psi_j' | \psi_j \psi_i'] \quad (2.50)$$

if the determinants differ only by $\psi_i' \neq \psi_j$ and $\psi_j' \neq \psi_i$.

$$I_2 = \sum_{j \neq i} \{ [\psi_i \psi_i' | \psi_j \psi_j] - [\psi_i \psi_j | \psi_j \psi_i'] \} \quad (2.51)$$

when the determinants differ only by $\psi_i' \neq \psi_i$ while

$$I_2 = \sum_i \sum_j \{ [\psi_i \psi_i | \psi_j \psi_j] - [\psi_i \psi_j | \psi_j \psi_i] \} \quad (2.52)$$

if the determinants are the same. Use has been made of the notation

$$[\chi_i \chi_j' | \chi_k'' \chi_\ell'''] = \iint \chi_i(1) \chi_j'(1) \frac{1}{r_{12}} \chi_k''(2) \chi_\ell'''(2) d\tau_1 d\tau_2 \quad (2.53)$$

and the subscripts on the spin orbitals refer to the centres on which the orbitals are located.

For the case of a non-orthogonal set, the matrix elements are obtained in the following way. A general Slater determinant of non-orthogonal spin orbitals, $\|\psi_1 \psi_2 \cdots \psi_N\|$ has for the general element

$$H_{mn} = \int \psi_m^* H \psi_n d\tau \quad (2.54)$$

$$= \frac{1}{\sqrt{N_m! N_n!}} \sum_P \sum_{P'} (-1)^{P+P'} \times \int \psi_{P'}^*(1) \cdots \psi_N^*(N) H \psi_1(1) \cdots \psi_N(N) d\tau_1 \cdots d\tau_N \quad (2.55)$$

where the determinants have been expanded. Multiplication of equation 2.55 by $(P')^{-1}$ reduces equation 2.55 to the form where only the diagonal term of the first determinant need be considered.

$$H_{mn} = \frac{N!}{\sqrt{N_m! N_n!}} \sum_{P''} (-1)^{P''} \int \psi_1(1) \psi_2(2) \cdots \psi_N(N) H P'' \psi_1'(1) \cdots \psi_N'(N) d\tau_1 \cdots d\tau_N \quad (2.56)$$

So H_{mn} will contain terms such as

$$\langle \psi_1(1) | \psi_1'(1) \rangle \cdots \langle \psi_N(N) | \psi_N'(N) \rangle \int \psi_i(i) \psi_j(j) \frac{1}{r_{ij}} \psi_i(i) \psi_j(j) d\tau_i d\tau_j \quad (2.57)$$

It is clear from equation 2.56 that for the non-orthogonal set that there will be $N!$ possible permutations; the inclusion of spin orthogonality reduces the number of terms considerably. For the case where the number of orbitals of spin α is N and the number of orbitals

of spin β is N_β ($N_\alpha + N_\beta = N$), then the upper bound to the number of non-zero permutations is $(N_\alpha!)(N_\beta!)$, which is a considerable reduction compared to $N!$. Furthermore, if some of the molecular orbitals are in effect orthogonal, then the number of terms will be further reduced, since if the orthogonal function appears as a premultiplicative factor (ie., as an overlap integral), then the whole term vanishes.

The matrix elements are determined when the integrals given by equations 2.48 to 2.52 are known. The integrals can be divided into the following general types

$$\int \chi_A(i) \chi'_B(i) d\tau_i \quad \text{overlap,}$$

$$\int \chi_A(i) \left(\frac{-\nabla^2}{2} \right) \chi'_B(i) d\tau_i \quad \text{kinetic energy,}$$

$$\int \chi_A(i) \frac{1}{r_{iC}} \chi'_B(i) d\tau_i \quad \text{nuclear attraction,}$$

$$\iint \chi_A(i) \chi'_B(i) \frac{1}{r_{ij}} \chi''_C(j) \chi'''_D(j) d\tau_i d\tau_j$$

electron repulsion.

Each of these types can be subdivided further according to the number of distinct centres involved. The electronic repulsion integrals have a further subdivision into coulomb, exchange and hybrid (mixed cou-

lomb-exchange) according to whether the charge clouds ($\chi_A(i)\chi'_B(i)$) are based on a single centre or are distributed over two centres.

In order to evaluate these integrals one must assume a functional form for the χ_A 's. The most commonly used form is that due to Slater. For an orbital χ_A centred at the point A, where A is described by the spherical polar co-ordinates (r_a, θ_a, ϕ_a) , then the functional form χ_A is taken to be

$$\chi_A = r_a^{n_a-1} \exp[-\zeta_a r_a] P_{\ell_a}^{m_a}(\cos \theta_a) \cos m_a \phi_a \quad m_a \geq 0 \quad (2.58)$$

$$\chi_A = r_a^{n_a-1} \exp[-\zeta_a r_a] P_{\ell_a}^{m_a}(\cos \theta_a) \sin(|m_a| \phi_a) \quad m_a < 0 \quad (2.59)$$

Here n_a , ℓ_a and m_a are quantum numbers characterizing χ_A ; ζ_a is an adjustable parameter called the orbital exponent which controls the scale of χ_A . The associated Legendre functions $P_{\ell}^m(x)$ appearing in equations 2.58 and 2.59 are defined by

$$P_{\ell}^m(x) = [(-1)^m (1-x^2)^{|m|/2} / 2^{\ell} \ell!] \left(\frac{d}{dx} \right)^{\ell + |m|} (x^2 - 1)^{\ell}$$

for $|x| \leq 1$ (2.60)

Substitution of equations 2.58 and 2.59 into the integral forms of equation 2.55 yields what has been called the "Bottleneck of quantum chemistry". Some of the integrals (namely all integrals up to and including two centres) were programmed for the IBM 360/50 by the procedures developed by Roothaan, Ruedenberg and Jaunzemis [54-57]. Quantum Chemistry Program Exchange supplied versions of integral routines for some of the multicentre integrals but unfortunately these routines were unusable due to programming errors. Accordingly, a program due to Huzinaga and co-workers [58] was obtained[†] and used to obtain multicentre integrals. After preliminary calculations in the absence of multicentre integrals, certain features of the Huzinaga scheme made it an attractive choice for obtaining all the integrals.

The main features which emerge from the calculations of the integrals for the schemes given in references [54-57] is that they represent somewhat inefficient computational schemes, especially the procedure followed for computation of hybrid integrals. However, it was found that these procedures were very fast in terms of actual computer time used relative to other programs.

D. Extension of Model I

Model I, as described previously is insufficient in

†

The program was supplied by Mr. H. N. W. Lekkerkerker who we most cordially thank.

one essential detail; namely, it does not describe the conjugated spin label to the extent that is required. It has already been pointed out that the inclusion of a number of the spin label centres would quickly make the problem intractable. We have been content to include only the adjacent centres of the spin label. In this case the π -molecular orbital becomes

$$\pi \approx [c_i \phi_i + c_j \phi_j] / \sqrt{N} \quad (2.61)$$

where ϕ_i and ϕ_j are $2p\pi$ atomic orbitals, c_i and c_j are the LCAO coefficients and N , the normalization constant. Equation 2.61 will be expected to provide a fairly satisfactory approximation, since all other centres of the spin label are somewhat further removed from the syn- and anti-protons of the σ -portion of the molecule. Hence, interaction with this part of the molecule will be a good deal smaller.

The main feature which is exploited in the extended model is the dependence of the hyperfine coupling on the symmetry of the highest occupied molecular orbital of the spin label. This allows a comparison to be made with other bicyclo [2.2.1] heptane radical anion systems. These latter systems give rise to somewhat smaller coupling constants, so that other effects may be of greater relative importance.

A simple model first employed by Whiffen arose in connection with the anomalously large proton hyperfine splitting of the

CH₂ group in the cyclohexadienyl radical [59], Figure 2.5.

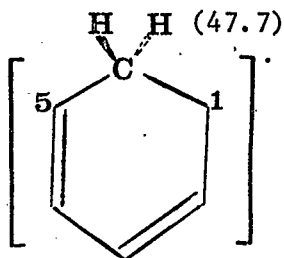


Figure 2.5 Cyclohexadienyl radical

Whiffen suggested that the interactions at the CH₂ protons did not result from a simple sum of the spin populations at C₁ and C₅. It was proposed that the hyperfine coupling was proportional to the square of the sum of the LCAO coefficients, ie., $[c_1 + c_5]^2$, which amounts to a factor of 4p in the Huckel formulation, where $c_1 = c_5$, as is the case for the cyclohexadienyl radical.

Whiffen's idea for the hyperfine coupling can be visualized quite readily using perturbation theory. The hyperfine coupling will be proportional to terms of the following form,

$$A \propto \langle \psi_k | H_p | \psi_g \rangle \langle \psi_g | H_F | \psi_k \rangle \quad (2.62)$$

So if terms containing π -molecular orbitals are expanded according to equation 2.61 and substituted in equation 2.62, then with the approxi-

mation of certain cross terms, the hyperfine coupling is of the form

$$A \propto (c_i + c_j)^{2n} \langle \psi_k | H_P | \psi_g \rangle \langle \psi_g | H_F | \psi_k \rangle \quad (2.63)$$

where the prime denotes matrix elements containing $2p\pi$ atomic orbitals, and n is dependent upon the particular form of ψ_k and ψ_g . The superscript n depends on whether π appears in ψ_k , i.e. no π , $n = 1$. and so on. Whiffen restricts himself to the case where $n = 1$. This in general, is not always true as can be seen by including spin transfer states of the form $\parallel \pi b \pi \parallel$ etc. For the case where $c_i = c_j$ i.e. symmetric combination of orbital across the mid-plane between $C_i - C_j$, the the hyperfine coupling takes the form

$$A \propto 4 \rho_i^n \langle \psi_k | H_P | \psi_g \rangle \langle \psi_g | H_F | \psi_k \rangle \quad (2.64)$$

For the case where $c_i = -c_j$, the antisymmetric combination across

$C_i - C_j$

$$A \approx 0 \quad (2.65)$$

Whiffen's model has been used reasonably successfully for several systems where equation 2.64 applies [59] and to some systems [60] where equation 2.65 is applicable.

Returning now to the rigid bicyclic structures, it is necessary to investigate the cross terms which were 'neglected' in obtaining the result in equation 2.65. The reason for this is because systems where the highest occupied level is antisymmetric across the plane of symmetry of the molecule actually give rise to experimentally observed splittings. These splittings are usually in the range 0.5 - 1.5 gauss for $|A_H(\text{anti})|$ and 0 - 0.5 gauss for $|A_H(\text{syn})|$ [15,24].

Splittings of this order would not be obtained from Whiffen's model which, for the case where $c_i = -c_j$, the contribution is zero.

The symmetry of the highest occupied molecular orbital (HOMO) of the spin label has considerable influence on the possible mechanisms which may contribute to long-range coupling. When the HOMO of the spin label is antisymmetric, then all matrix elements between configurations describing exchange polarization and configurations representing spin transfer vanish. Thus for the antisymmetric case[†] the hyperfine coupling must arise from a spin polarization process in which case only the configurations in equations 2.12 to 2.14 will appear. The importance of this symmetry constraint will become apparent in the section describing the numerical results.

The question of obtaining the LCAO coefficients which appear in equation 2.61 is now discussed. For the present work, the

[†] The words antisymmetric and symmetric will from now on be used to imply the character of the HOMO.

c 's are obtained by the simplest possible procedure, i.e., the Huckel method. This approximation introduces considerable semiempirical character into the calculations. It is a straight forward process to replace the Huckel approximation by some more sophisticated method, for example the unrestricted Hartree-Fock self-consistent field procedure for obtaining the c_i coefficients. Such a process could still be used in a semiempirical manner, but the simple approximate Huckel scheme has two advantages. Firstly, it has a simple conceptual picture associated with the definition of spin densities, and secondly the Huckel formalism is readily accessible to experimentalists.

Some mention should be made for the particular choice of combining an ab initio treatment and a semiempirical scheme for the BHS system. Rigorously, there can be little justification for such a procedure. The approach is rationalized on the basis that while the simple π -conjugated radical systems have received considerable attention and appear to be 'theoretically well understood', the treatment of σ -radical systems has not reached the same status. Thus, it would seem worthwhile to devote effort in the direction of accurately determining the interactions between the σ -framework of BHS and the spin label and then relate this to the current treatment of a π -conjugated system.

When the expression in equation 2.61 is introduced, it alters the method of calculation slightly. For the antisymmetric case,

the c_i coefficients simply weight various matrix elements in the secular equation but for the symmetric case, simple physical insight leads us to the conclusion that the c_i 's are not simple multipliers of the appropriate matrix elements in the secular equation. The matrix elements involving configurations representing spin transfer from the spin label are not weighted while other matrix elements would be attenuated by the factor c_i . This would imply that configurations involving spin transfer from the π -molecular orbital are independent of its actual form. It should be expected that the relative importance of the spin transfer configurations would at least be dependent upon the ionization potential of the HOMO and this value is critically dependent on the eigenvalue under consideration.

Accordingly, the configuration interaction procedure has been reformulated to take account of the above mentioned factor. The total wave function is now written as

$$\Psi_T = u_1 \sum_K C_K \Psi_K + u_2 \sum_L C_L \Phi_L \quad (2.66)$$

where Ψ_K describes configurations not involving transfer from the spin label and Φ_L describes the states where an electron has been transferred from the spin label. The C_K 's and C_L 's are determined by configuration interaction within each group of configurations. The u_1 and u_2

coefficients are determined variationally, and represent the importance of each group of configurations. The c_i 's of equation 2.61 only enter the group of functions Ψ_K . This approach resembles a charge-transfer type procedure.

CHAPTER III

RESULTS

A. Geometry

The geometry of the BHS system is not known with certainty since no physical methods have yet been devised to determine the structure of molecules in dilute liquid solutions (especially radical species). One is forced to rely upon known geometrical determinations for similar systems which have dimensions determined by diffraction techniques. The geometry used here was based on the electron diffraction study of norbornane [72]. The following assignment of bond lengths and bond angles appearing in Figure 3.1 has been made.

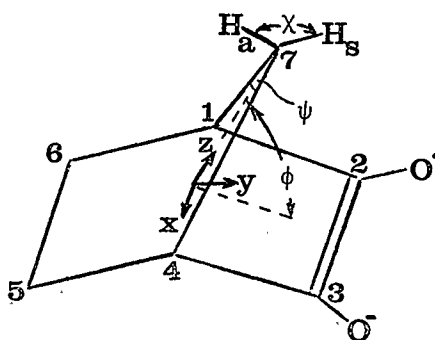


Figure 3.1 Relevant Angular Variables for Bicyclo [2.2.1] heptane semidione radical anion.

Quantity	Value
C-C all bonds except C ₂ -C ₃	1.555Å
C ₂ =C ₃	1.40Å
C-H all bonds	1.115Å
Angle ψ	96°
Angle ϕ	120°
Angle χ	109°28'

Table 3.1 Geometric Parameters.

Atom	Co-ordinates (a. u.)		
	x	y	z
H _S	0.0	1.720386	3.182901
H _A	0.0	-1.720386	3.182901
C ₇	0.0	0.0	1.966302
C ₃	1.322838	2.433210	-1.404819

Table 3.2 Geometrical Co-ordinates

The co-ordinates of the various atoms of concern here are given in atomic units in Table 3.2. The number of significant figures for the co-ordinates is not an indication of accuracy, but simply for convenience in identification in the computer input and for subsequent reference. Most calculations have been carried out in the more convenient axis system oriented with the z-axis along the π -orbital and origin at C_3 . For this particular choice, the co-ordinates are as shown in Table 3.3. This cartesian framework offers the optimum advantage when 2p type orbitals are resolved into x, y and z components. Insofar as the calculations are concerned only this model system has been considered and no attempt has been made to study the changes in hyperfine coupling which occur when the co-ordinates are changed from those in Table 3.3.

All calculations were carried out with the orbital exponents (see equation (2.58)) assigned the following values:

$$\zeta_c = 1.625 \quad \text{for carbon } 2s, 2p_x, 2p_y \text{ and } 2p_z \text{ orbitals}$$

$$\text{and } \zeta_h = 1.000 \quad \text{for the hydrogen } 1s \text{ orbitals.}$$

These orbital exponents were considered as fixed quantities and were not optimized to minimize the energy of the system.

One further simplification has been made in that

Atom	Co-ordinates (a.u.)		
	x	y	z
H _A	-5.864322	1.322838	2.085924
H _S	-2.842199	1.322838	3.730819
C ₇	-3.748752	1.322838	1.797726
C ₃	0.0	0.0	0.0

Table 3.3 Co-ordinates for transformed axis system.

Internuclear Separation (in a.u.)	$\frac{8}{3} \pi g_N \beta_N \langle \pi \delta(r_H) \pi \rangle$ (in gauss)
2.0	11.1
3.0	1.69
4.0	0.26
4.5	0.10
5.0	0.039
6.0	0.006
7.0	0.0009

Table 3.4 Values of the integral $\frac{8}{3} \pi g_N \beta_N \langle \pi | \delta(r_H) | \pi \rangle$

matrix elements containing the operator $\sum_{\mu < \lambda}^N \frac{Z_{\mu} Z_{\lambda}}{r_{\mu\lambda}}$ have been neglected.

This has no effect on the calculation of the eigenvectors in the configuration interaction procedure; only the eigenvalues are changed, due to the fact that terms such as $\langle \psi_K | \sum_{\mu < \lambda}^N \frac{Z_{\mu} Z_{\lambda}}{r_{\mu\lambda}} | \psi_L \rangle$ can be partitioned into a separate diagonal matrix (when an orthonormal basis is used).

In chapter two it was pointed out that nonlocal-direct contributions can be neglected. This assumption is frequently

employed in the literature. The integral $\frac{8\pi}{3} g_N \beta_N \langle \pi | \delta(r_H) | \pi \rangle$ has been examined for several values of the internuclear distance. The integral is evaluated with the π -orbital aligned along the internuclear separation and no angular factor is considered. The results appear in Table 3.4. The Hartree-Fock functions of Jucys [62] were employed. As can be seen, the integral is negligible for carbon-hydrogen internuclear separations greater than 5 bohr and will be neglected for distances of interest here, i.e. $r_s = 4.87$ bohr and $r_a = 6.36$ bohr.

B. Results for Model I

In order to facilitate discussion of the importance of various terms to the hyperfine coupling, the contributions arising from the different configurations have been reproduced in tabular form. Table 3.5 presents the results for the anti-proton coupling and Table 3.6 contains the results for the syn-proton coupling. The first two entries of each table denote the particular configurations whose interaction is being considered, eg. K and L, where the numbering corresponds to the wave functions given in equations (2.12) to (2.17). Columns three, four and five denote respectively the values of $\langle \Psi_K | \sum_k \sigma_{zk} \delta(r_H) | \Psi_L \rangle [1s(0)]^2^{-1}$, C_K and C_L (see equation (2.33)). The final entry represents the contribution to the hyperfine coupling for the particular configurations under consideration. These latter entries must be multiplied by 507.1 to convert them to gauss. The final coupling constants obtained are:

$$A_H \text{ (anti)} = 7.99 \text{ gauss}$$

$$A_H \text{ (syn)} = 2.62 \text{ gauss}$$

Although the bicyclo [2.2.1] heptane semidione system is

K	L	Hyperfine Factor	C _K	C _L	Contribution
1	1	.322598E-02	.899138E 00	.899138E 00	.260804E-02
1	2	0.	.899138E 00	.419209E 00	0.
1	3	.503585E 00	.899138E 00	.379813E-02	.171976E-02
1	4	-.623799E-01	.899138E 00	.125673E 00	-.704876E-02
1	5	.318959E-01	.899138E 00	.148359E-02	.425476E-04
1	6	0.	.899138E 00	.181322E-02	0.
2	1	0.	.419209E 00	.899138E 00	0.
2	2	.322598E-02	.419209E 00	.419209E 00	.566921E-03
2	3	.514341E 00	.419209E 00	.379813E-02	.818939E-03
2	4	.225538E-01	.419209E 00	.125673E 00	.118821E-02
2	5	.441093E-01	.419209E 00	.148359E-02	.274331E-04
2	6	.225538E-01	.419209E 00	.181322E-02	.171436E-04
3	1	.503585E 00	.379813E-02	.899138E 00	.171976E-02
3	2	.514341E 00	.379813E-02	.419209E 00	.818939E-03
3	3	.101332E 01	.379813E-02	.379813E-02	.146179E-04
3	4	-.130215E-01	.379813E-02	.125673E 00	-.621545E-05
3	5	.254665E-01	.379813E-02	.148359E-02	.143500E-06
3	6	-.130215E-01	.379813E-02	.181322E-02	-.896771E-07
4	1	-.623799E-01	.125673E 00	.899138E 00	-.704876E-02
4	2	.225538E-01	.125673E 00	.419209E 00	.118821E-02
4	3	-.130215E-01	.125673E 00	.379813E-02	-.621545E-05

..../Cont'd

K	L	Hyperfine Factor	C _K	C _L	Contribution
4	4	.120623E 01	.125673E 00	.125673E 00	.190508E-01
4	5	0.	.125673E 00	.148359E-02	0.
4	6	0.	.125673E 00	.181322E-02	0.
5	1	.318959E-01	.148359E-02	.899138E 00	.425476E-04
5	2	.441093E-01	.148359E-02	.419209E 00	.274331E-04
5	3	.254665E-01	.148359E-02	.379813E-02	.143500E-06
5	4	0.	.148359E-02	.125-73E 00	0.
5	5	.315361E 00	.148359E-02	.148359E-02	.694122E-06
5	6	.616763E 00	.148359E-02	.181322E-02	.165914E-05
6	1	0.	.181322E-02	.899138E 00	0.
6	2	.225538E-01	.181322E-02	.419209E 00	.171436E-04
6	3	-.130215E-01	.181322E-02	.379813E-02	-.896771E-07
6	4	0.	.181322E-02	.125673E 00	0.
6	5	.616763E 00	.181322E-02	.148359E-02	.165914E-05
6	6	.120623E 01	.181322E-02	.181322E-02	.396579E-05

Table 3.5 Contributions to hyperfine coupling for the anti-proton
for model I.

K	L	Hyperfine Factor	C_K	C_L	Contribution
1	1	.451816E-02	.905972E 00	.905972E 00	.370844E-02
1	2	0.	.905972E 00	.423266E 00	0.
1	3	.503585E 00	.905972E 00	-.440672E-03	-.201050E-03
1	4	-.738236E-01	.905972E 00	-.365150E-02	.244220E-03
1	5	.377472E-01	.905972E 00	.636948E-02	.217823E-03
1	6	0.	.905972E 00	.249249E-02	0.
2	1	0.	.423266E 00	.905972E 00	0.
2	2	.451816E-02	.423266E 00	.423266E 00	.809447E-03
2	3	.514341E 00	.423266E 00	.440672E-03	-.959356E-04
2	4	.266913E-01	.423266E 00	-.365150E-02	-.412529E-04
2	5	.522011E-01	.423266E 00	.636948E-02	.140733E-03
2	6	.266913E-01	.423266E 00	.249249E-02	.281590E-04
3	1	.503585E 00	-.440672E-03	.905972E 00	-.201050E-03
3	2	.514341E 00	-.440672E-03	.423266E 00	-.959356E-04
3	3	.101288E 01	-.440672E-03	-.440672E-03	.196694E-06
3	4	-.154102E-01	-.440672E-03	-.365150E-02	-.247968E-07
3	5	.301383E-01	-.440672E 03	.636948E-02	-.845937E-07
3	6	-.154102E-01	-.440672E-03	.249249E-02	.169261E-07
4	1	-.738236E-01	-.365150E-02	.905972E 00	.244220E-03
4	2	.266913E-01	-.365150E-02	.423266E 00	-.412529E-04
4	3	-.154102E-01	-.365150E-02	-.440672E-03	-.247968E-07

..../Cont'd.

K	L	Hyperfine Factor	C _K	C _L	Contribution
4	4	.120623E 01	-.365150E-02	-.365150E-02	.160831E-04
4	5	0.	-.365150E-02	.636948E-02	0.
4	6	0.	-.365150E-02	.249249E-02	0.
5	1	.377472E-01	.636948E-02	.905972E 00	.217823E-03
5	2	.522011E-01	.636948E-02	.423266E 00	.140733E-03
5	3	.301383E-01	.636948E-02	-.440672E-03	-.845937E-07
5	4	0.	.636948E-02	-.365150E-02	0.
5	5	.315361E 00	.636948E-02	.636948E-02	.127943E-04
5	6	.616763E 00	.636948E-02	.249249E-02	.979165E-05
6	1	0.	.249249E-02	.905972E 00	0.
6	2	.266913E-01	.249249E-02	.423266E 00	.281590E-04
6	3	-.154102E-01	.249249E-02	-.440672E-03	.169261E-07
6	4	0.	.249249E-02	-.365150E-02	0.
6	5	.616763E 00	.249249E-02	.636948E-02	.979165E-05
6	6	.120623E 01	.249249E-02	.249249E-02	.749368E-05

Table 3.6 Contributions to hyperfine coupling for the syn-proton
for model I.

of primary concern, the case of the bicyclo [2.2.1] heptyl system attached to a spin label which is antisymmetric to the plane of symmetry of the molecule has also been investigated. Such a case would be the bicyclo [2.2.1] heptane semiquinone radical anion shown in Figure 3.2. In this case, the unpaired electron in the spin label is in an M.O. which is antisymmetric to reflection in the plane containing the syn- and anti-protons (7), and bisecting the 2, 3 and 5, 6 bonds.

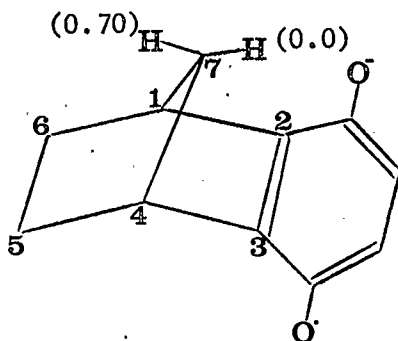


Figure 3.2 Bicyclo [2.2.1] heptane semiquinone radical anion.

The assumption made is that the geometry of the saturated part of the model system is unaltered by interchange of the spin labels. The uncertainties in the geometry of the fragment initially chosen are probably larger than any changes of geometry due to change of the spin label.

Since Whiffen's simple model is not in full accord with experimental results we have calculated all of the cross terms explicitly. The results for the anti- and syn-proton couplings are given in Table 3.7 and Table 3.8. The various column entries have similar meanings to those of Tables 3.5 and 3.6. The smaller number of entries in each of Tables 3.7 and 3.8 is due to the fact that matrix elements between exchange polarization configurations and those configurations describing electron transfer vanish because of the particular antisymmetric case under consideration.

The values of the hyperfine couplings for the case when the highest occupied M.O. is antisymmetric to the plane of symmetry of the molecule are found to be:

$$A_H (\text{anti}) = 1.53 \text{ gauss.}$$

$$A_H (\text{syn}) = 1.98 \text{ gauss.}$$

C. Results for Model II

Since a non-orthogonal basis set was employed for this model, a finite contribution to the coupling is obtained from the ground state configuration. The hyperfine coupling arising from the

K	L	Hyperfine Factor	C _K	C _L	Contribution
1	1	.322598E-02	.907090E 00	.907090E 00	.265438E-02
1	2	0.	.907090E 00	.420936E 00	0.
1	3	.503585E 00	.907090E 00	-.150885E-03	-.689238E-04
2	1	0.	.420936E 00	.907090E 00	0.
2	2	.322598E-02	.420936E 00	.420936E 00	.571602E-03
2	3	.514341E 00	.420936E 00	-.150885E-03	-.326673E-04
3	1	.503585E 00	-.150885E-03	.907090E 00	-.689238E-04
3	2	.514341E 00	-.150885E-03	.420936E 00	-.326673E-04
3	3	.101332E 01	-.150885E-03	-.150885E-03	.230694E-07

Table 3.7 Contributions to hyperfine coupling for the
anti-proton for the antisymmetric case.

K	L	Hyperfine Factor	C _K	C _L	Contribution
1	1	.451816E-02	.906756E 00	.906756E 00	.371486E-02
1	2	0.	.906756E 00	.421656E 00	0.
1	3	.503585E 00	.906756E 00	-.463128E-03	-.211478E-03
2	1	0.	.421656E 00	.906756E 00	0.
2	2	.451816E-02	.421656E 00	.421656E 00	.803301E-03
2	3	.514341E 00	.421656E 00	-.463128E-03	-.100441E-03
3	1	.503585E 00	-.463128E-03	.906756E 00	-.211478E-03
3	2	.514341E 00	-.463128E-03	.421656E 00	-.100441E-03
3	3	.101288E 01	-.463128E-03	-.463128E-03	.217251E-06

Table 3.8 Contribution to hyperfine coupling for the syn-proton
for the antisymmetric case.

ground state configuration has been calculated to be:[†]

$$A_H(\text{sum})g = 0.49 \text{ gauss}$$

Now based on equation (2.41), the hyperfine coupling can be represented by:

$$A_H(\text{sum}) \approx A_H(\text{sum})g + 1014.2 \sum_k \langle \Psi_k | H_P | \Psi_g \rangle \langle \Psi_g | H_F | \Psi_k \rangle / \Delta_E \quad (3.1)$$

$$\Delta_E = E_g - E_k \quad (3.2)$$

This simplification results since the deviations from orthogonality are not large. The various terms necessary for the evaluation of equation (2.41) are summarized in Table 3.9. The hyperfine factors in Table 3.9 must be multiplied by 507.1 to convert them to gauss. With larger overlap factors the other terms in equation (2.40) will become progressively more important. The values contributed by each configuration to the main term of equation 3.1 are:

[†] Recall that this model will only allow the sum of the hyperfine constants and not their individual values to be calculated,

E_k	$\langle \psi_k H_p \psi_g \rangle$	Hyperfine Factor	$\langle \psi_k \psi_g \rangle$
k=g -2.42635			
2 -1.51935	-0.105388	0.157191×10^{-2}	0.862631×10^{-3}
3 -1.53390	0.127569×10^{-2}	0.352843	0.149412×10^{-2}
4 -2.62511	0.627364×10^{-2}	0.290941×10^{-1}	0.180736×10^{-1}
5 -1.33290	-0.637540×10^{-1}	-0.143413×10^{-1}	0.486361×10^{-2}
6 -0.427210	0.550055×10^{-2}	-0.290941×10^{-1}	-0.823447×10^{-4}

Table 3.9 Matrix Elements for Model II.

$$A_{H_2} = +0.19 \text{ gauss}$$

$$A_{H_3} = -0.51 \text{ gauss}$$

$$A_{H_4} = +0.93 \text{ gauss}$$

$$A_{H_5} = -0.85 \text{ gauss}$$

$$A_{H_6} = +0.081 \text{ gauss}$$

The contributions from other terms in equation (2.41) are small. For example, the first four terms within the first summation of equation (2.41) give rise to the following contributions:

$$\text{First term (principal contribution)} = -0.16 \text{ gauss}$$

$$\text{Second term (secondary contribution)} = -0.94 \times 10^{-3} \text{ gauss}$$

$$\text{Third term (secondary contribution)} = -0.21 \times 10^{-2} \text{ gauss}$$

$$\text{Fourth term (secondary contribution)} = -0.39 \times 10^{-2} \text{ gauss}$$

The value for the sum of the syn-and anti-coupling constants based on equation (3.1) is:

$$A_H (\text{sum}) = 0.32 \text{ gauss}$$

D. Extended Model

(a) Symmetric Case

This section outlines how model I may be extended by relating the hyperfine coupling to the spin density on the nearest centre of the spin label. It might be argued that since model I as it presently stands is independent of the spin density on the spin label, then the results obtained do not have any validity. This conclusion can be reached by the erroneous procedure of weighting each of the matrix elements of configurations which depend on spin exchange polarization and leaving all of the electron transfer configurations unaltered. The weighting factors will be $(c_1+c_2)^{2n}$ where c_1 and c_2 refer to LCAO coefficients of the HOMO of the adjacent centres of the spin label. The spin transfer configurations, in which an electron has been removed from the spin label have no π -M.O. term appearing in the configuration and hence no $(c_1+c_2)^{2n}$ factor results. Simply weighting each configuration in this manner expresses the belief that the importance of the spin transfer configurations are independent of the π -M.O. This is clearly not so, and the only justification needed to demonstrate that model I is a sound approximation is that the changes in the various exchange polarization matrix elements (due to the weighting factors) are countered by the changes in the spin transfer terms due to changes in

the LCAO coefficients of the π -M.O. This can be done if the situation regarding the interaction between the spin label and the σ -framework is viewed as resembling the interaction in a weakly bound molecular complex.

In order to simplify the procedure somewhat, the configurations $\parallel \pi b \bar{\pi} \parallel$ and $\parallel \pi a \bar{\pi} \parallel$ were neglected. This is justified on the basis of their contribution to the hyperfine coupling in model I (see Table 3.5 and 3.6). Two principal groups were constructed. The exchange polarization configurations are placed into one group, denoted Φ_E , and the spin transfer configuration in the other group denoted Φ_T . The total wave function of the system is then given by:

$$\Psi_{\text{TOTAL}} = u_1 \Phi_E + u_2 \Phi_T \quad (3.3)$$

$$\text{where } \Phi_E = \sum_K C_K \Psi'_K \quad (3.4)$$

$$\Phi_T = \Psi_4 \quad (3.5)$$

$$\Psi'_K = (c_1 + c_2)^n \Psi_K \quad (3.6)$$

u_1 and u_2 are coefficients to be determined by the variation method subject to the normalization constraint $u_1^2 + u_2^2 = 1$. The coefficients

are determined as:

$$u_1 = [1+4\rho R^2]^{-1/2} \quad (3.7)$$

$$u_2 = 2R\rho^{1/2}[1+4\rho R^2]^{-1/2} \quad (3.8)$$

where we have substituted $\rho = c_1^2$. R is given by:

$$R = -W_{ET}[W_{TT}-E_L]^{-1} \quad (3.9)$$

where the W 's are defined by the following notation:

$$W_{XY} = \langle \Phi_X | H | \Phi_Y \rangle \quad (3.10)$$

and E_L is the lowest eigenvalue of the appropriate secular equation and is given by:

$$E_L = \frac{1}{2}[W_{EE}+W_{TT}] - [\frac{1}{4}(W_{EE}-W_{TT})^2 + W_{ET}^2]^{1/2} \quad (3.11)$$

The hyperfine coupling is then obtained from equation (2.3). The result is:

$$A_H = [g_e \beta_e \langle S_z \rangle \langle I_z \rangle]^{-1} \{ \langle \Phi_E | H_F | \Phi_E \rangle u_1^2 + \langle \Phi_T | H_F | \Phi_T \rangle u_2^2 + 2 \langle \Phi_E | H_F | \Phi_T \rangle u_1 u_2 \} \quad (3.12)$$

Equation (3.12) can be written in the form:

$$A_H = 4\rho [1+4\rho R^2]^{-1} [Q_E + RQ_C + R^2 Q_T] \quad (3.13)$$

where Q_E , Q_T and Q_C represent the contributions to the hyperfine coupling arising from exchange polarization, spin transfer interactions and cross terms between exchange polarization and spin transfer configurations respectively. These terms have the following form:

$$Q_E = \left[\frac{8\pi}{3} g_N \beta_N |1s(0)|^2 \right] \sum_K \sum_L C_K C_L \Omega_{KL} \quad (3.14)$$

$$Q_T = \left[\frac{8\pi}{3} g_N \beta_N |1s(0)|^2 \right] \Omega_{44} \quad (3.15)$$

$$Q_C = \left[\frac{16\pi}{3} g_N \beta_N |1s(0)|^2 \right] \sum_K C_K \Omega_{4K} \quad (3.16)$$

where

$$\Omega_{KL} = \langle \Psi_K | \sum_k \sigma_{zk} \delta(r_{Hk}) | \Psi_L \rangle [|1s(0)|^2]^{-1} \quad (3.17)$$

The ratio u_2/u_1 is given by:

$$u_2/u_1 = 2R\rho^{\frac{1}{2}} \quad (3.18)$$

It is found to be of the appropriate range to counterbalance the weighting factors $(c_1 + c_2)^{2n}$. This allows us to place semiquantitative importance on the unaltered form of model I.

Equation (3.13) now provides a means of studying the variation of hyperfine coupling with the spin density ρ on the adjacent centres of the spin label. Figure 3.3 shows the variation of A_H according to equation (3.13). It is implicit from the appearance of the limiting behaviour of equation (3.13); i.e. $A_H \rightarrow 0$ as $\rho \rightarrow 0$, that we have neglected interactions with more distant orbitals on the spin label.

(b) Antisymmetric case

For the antisymmetric case the configurations are partitioned into (a) the ground state, and (b) the singly excited configurations. Following the same approach as outlined in the previous section, the following result for the dependence of the hyperfine coupling on the spin density is obtained.

$$A_H = \rho \{ [1 + R_A]^{-1} [Q_G + R_A Q_{GE} + R_A^2 Q_E] \} \quad (3.19)$$

The various symbols have meanings similar to those outlined for

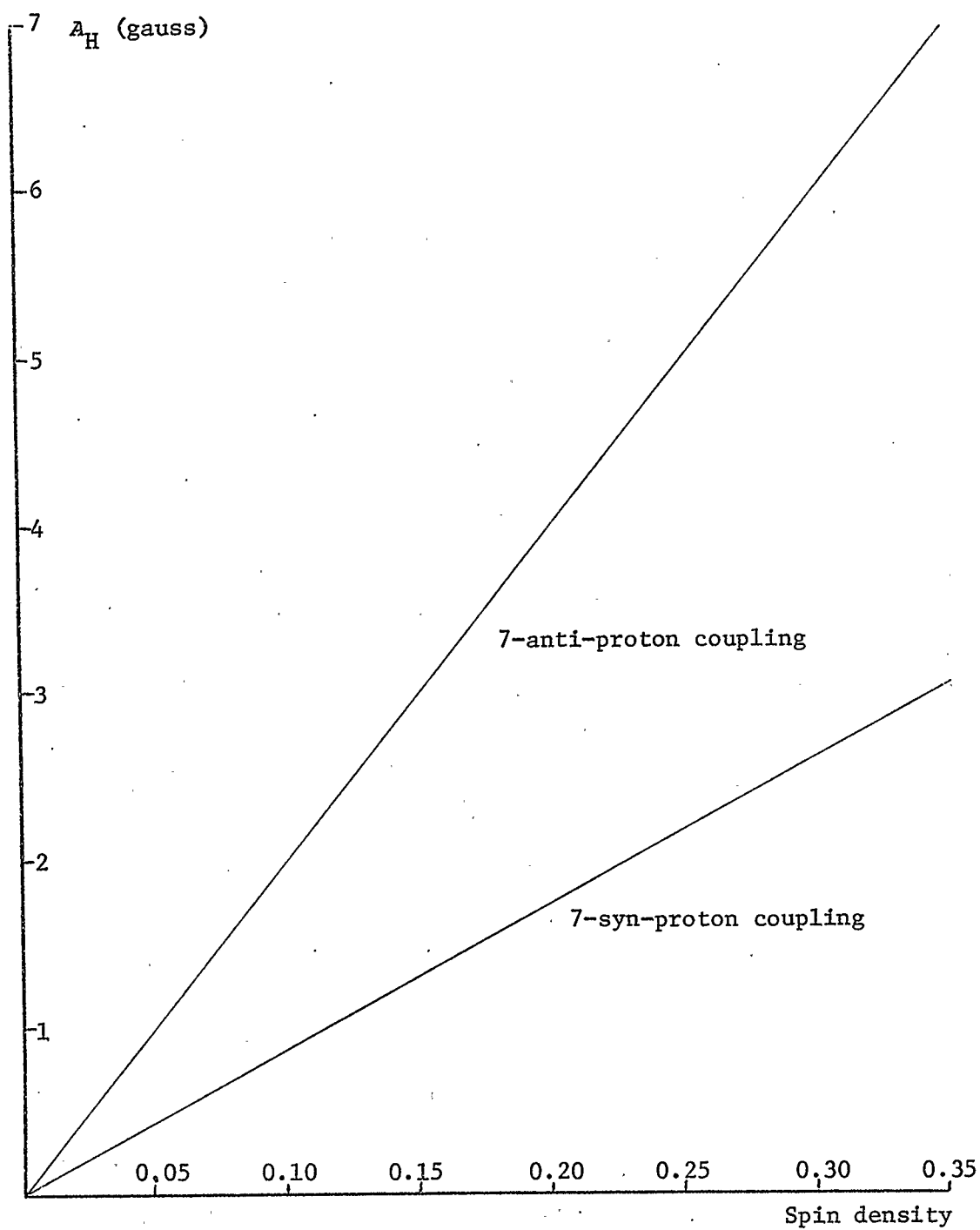


Figure 3.3 Variation of A_H with spin density for the symmetric case.

equation (3.13). They are:

$$\rho_G = \left[\frac{8\pi}{3} g_N \beta_N |1s(0)|^2 \right] \Omega_{GG} \quad (3.20)$$

$$\rho_{GE} = \left[\frac{16\pi}{3} g_N \beta_N |1s(0)|^2 \right] \sum_K C_K \Omega_{KG} \quad (3.21)$$

$$\rho_E = \left[\frac{8\pi}{3} g_N \beta_N |1s(0)|^2 \right] \sum_K \sum_L C_K C_L \Omega_{KL} \quad (3.22)$$

$$R_A = -W_{EG} [W_{EE} - E_{LA}]^{-1}$$

Figure (3.4) illustrates the variation of the hyperfine coupling as a function of the spin density for the antisymmetric case based on equation (3.19).

Equations (3.13) and (3.19) require the spin density on the spin label to be determined. Treating the various spin labels as isolated π -conjugated systems the spin densities shown in Figure 3.5 have been obtained. The necessary semiempirical parameters have been taken from Streitwieser [63].

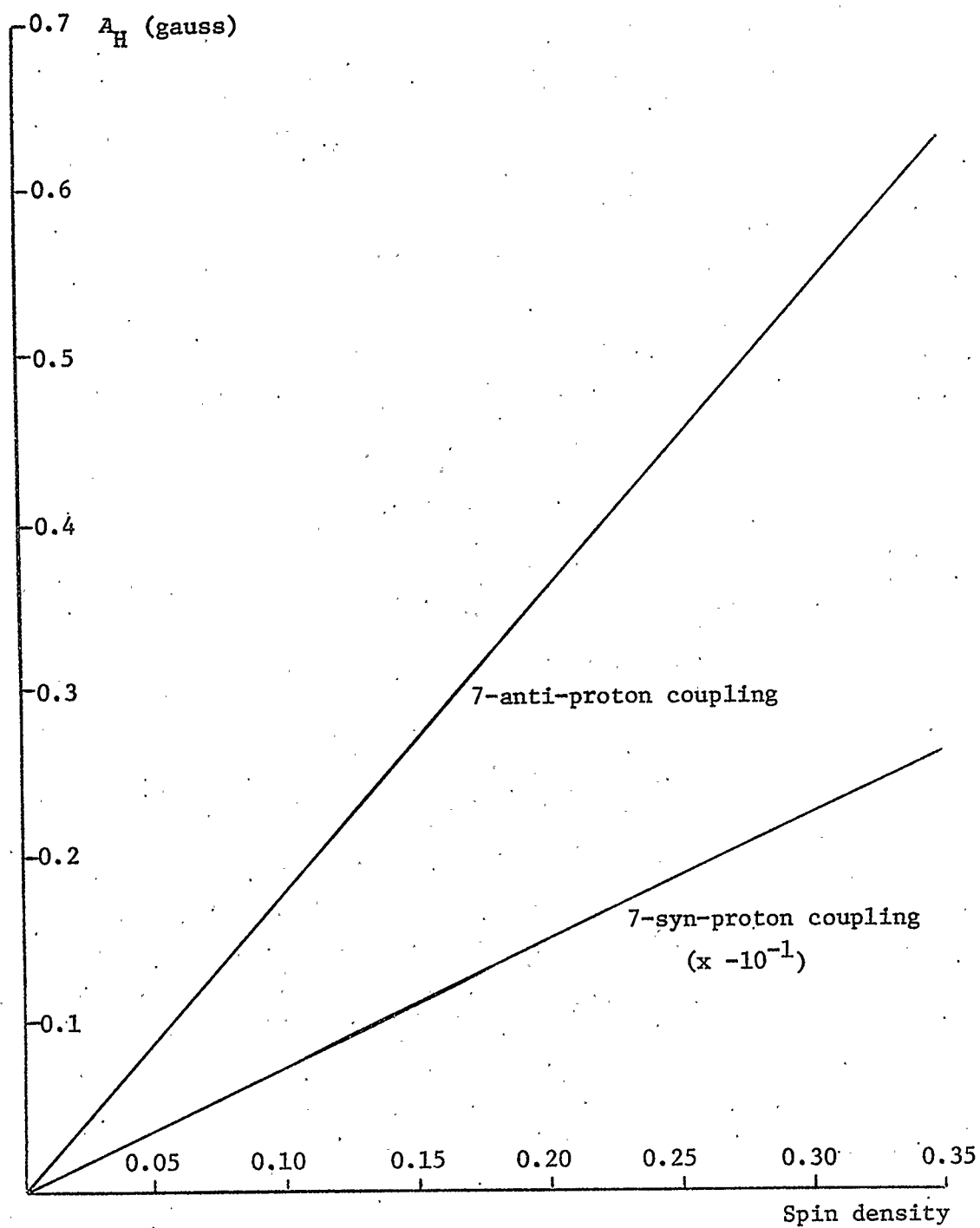


Figure 3.4 Variation of A_H with spin density for the antisymmetric case.

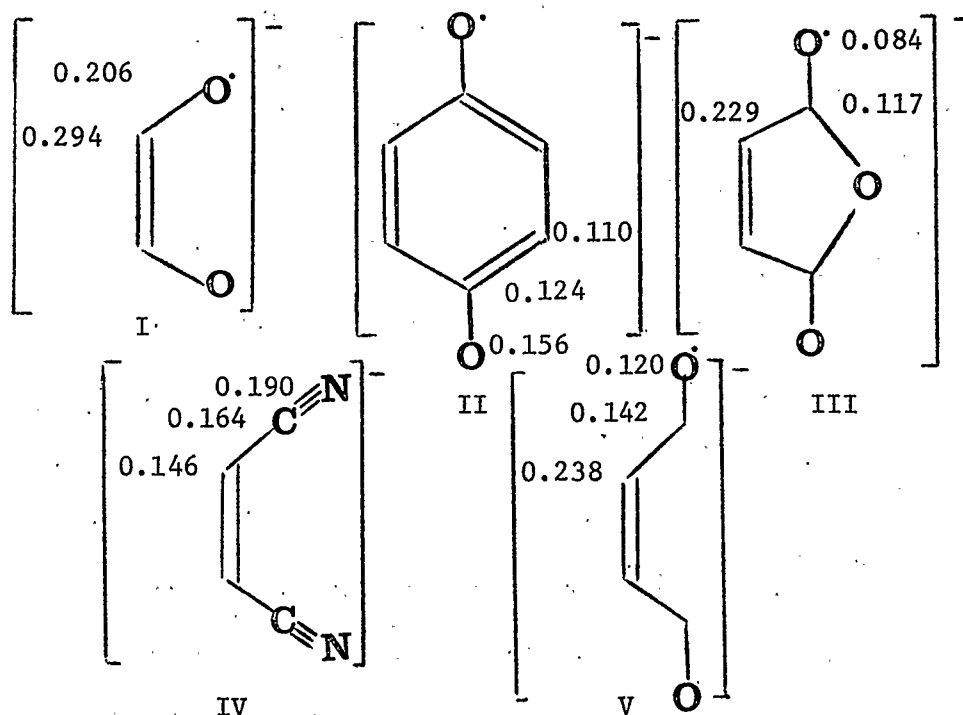


Figure 3.5 Spin Densities for various spin label systems.

There is a considerable shortage of experimental data for hyperfine couplings with different spin labels. The only available data pertinent to the present work is presented in Table 3.10.

Since preparing new spin labels is not a trivial assignment, it would seem wise to more fully investigate the spin labels that are presently available. An investigation of the positive ions of the spin labels shown in Figure 3.5 would be of considerable interest. The following predictions for the positive ions

Radical Anion	Spin Density at Adjacent Site	Calculated Anti Coupling	Calculated Syn Coupling	Observed	
				Anti	Syn
I	0.294	5.8	2.5	6.54	0.41
II	0.110	.20	$-.8 \times 10^{-2}$	0.66	0.0
III	0.299	.54	$-.2 \times 10^{-1}$	1.03	0.47
IV	0.146	.26	$-.1 \times 10^{-1}$	-	-
V	0.238	.43	$-.2 \times 10^{-1}$	-	-

Table 3.10 Calculated syn-and anti-proton couplings for
radical anions.

have been made and results are presented in Table 3.11.

Radical Cation	Spin Density at Adjacent Site	Calculated Anti-Coupling	Calculated Syn-coupling
I	0.088	0.16	-0.7×10^{-2}
II	0.250	5.0	2.2
III	0.384	7.6	3.3
IV	0.212	4.2	1.8
V	0.373	7.3	3.2

Table 3.11 Calculated Syn- and Anti-proton Couplings for radical cations.

CHAPTER IV

DISCUSSION OF RESULTS

A. Model I

(a) Symmetric case

The prohibitive limitation of making generalizations for the systems exhibiting long-range proton hyperfine couplings is primarily one of uncertainty in knowledge of the stereochemistry. In view of this, it is impossible to generalize from the σ -fragment of the bicyclo [2.2.1] heptyl system to other σ -systems in any fashion other than a qualitative manner. The general results that are obtained for the bicyclo [2.2.1] heptyl framework should apply to some extent to similar systems as for example, the bicyclo [2.2.2] octyl semidione. To obtain semiquantitative predictions for other such systems, detailed calculations are required.

The result for the anti-proton coupling obtained for model I is in good agreement with the experimental results. The largest anti-proton coupling observed for the semidione spin label is [10] $|A_H(\text{anti})| = 6.97$ gauss, and the value calculated for model I is 7.99 gauss. The model is somewhat tarnished by the results for the

syn-proton coupling. The experimental value is [10] $|A_H(\text{syn})| \approx 0.4$ gauss and the calculated value is 2.62 gauss. To calculate by presently available computational procedures a hyperfine coupling of such a small magnitude must be considered an extremely difficult, if not impossible task for a molecule of the size of BHS.

It is of considerable value to know the sign of the hyperfine coupling, in order to make a comparison with the calculated result. The only experimental work along this line has been an investigation of the N.M.R. spectra of the system illustrated in Figure 4.1 [26].

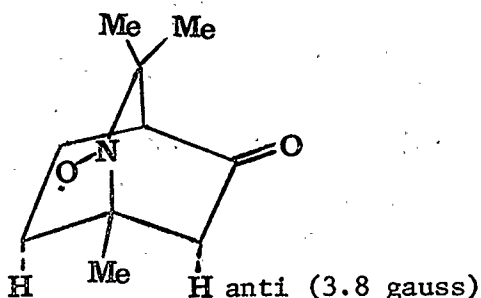


Figure 4.1 1,3,3 - trimethyl 2-azabicyclo [2.2.2]
octane-5-one 2-oxide radical.

A number of peaks corresponding to small couplings in the range $+ 0.13 \text{ gauss} > A_H > - 0.57 \text{ gauss}$, and a major peak at very low field corresponding to the anti-protons shown in Figure 4.1 were observed. It can be shown [64] that $\Delta H/H$ (ΔH is the shift; H the magnetic field

strength) is proportional to $-\rho(r_N)$, the unpaired spin density at the nucleus N whose nuclear magnetic resonance is being observed.

A down field shift requires that $\rho(r_N)$ be positive and hence the hyperfine coupling is positive. It is probably possible to generalize this experimental work to hyperfine couplings for anti-protons in the closely related BHS system. If this generalization is correct, then the experimental and calculated values for the anti-coupling constant for BHS both have a positive sign.

The case of the syn-coupling constant presents more difficulty in the allocation of sign. The experimental work on the above molecule, Figure 4.1, is not sufficiently complete to identify the sign of the syn-coupling constant. With some of the very small syn-couplings observed experimentally, it is not at all unlikely that the sign is both negative and positive depending on the exact stereochemical arrangement of such protons.

(i) Mechanistic contribution to proton coupling

In Table 3.5 the breakdown of the hyperfine coupling was presented for the anti-proton, into the contributions from the various configurations. It is clear that states involving electron donation from the σ -fragment to the spin label make a negligible

contribution to hyperfine coupling (ψ_5, ψ_6). The major contribution arises from the electron transfer configuration $\psi_4 = \parallel ab\bar{b} \parallel$. The next most important contribution arises from the cross terms between the aforementioned electron transfer configuration and the ground state configuration. These contributions are of opposite sign and reduce the calculated hyperfine coupling quite considerably. It should be noted that a calculation based only on exchange polarization, i.e. the inclusion of configurations ψ_1, ψ_2 and ψ_3 leads to a hyperfine coupling that is somewhat small.

Comparison of Tables 3.5 and 3.6 shows the striking dependence of the hyperfine coupling on geometry. From Table 3.6 it is observed that the major contribution to the syn-coupling constant arises from the ground state configuration, i.e. a local direct contribution. Once again, configurations involving electron transfer to the spin label are insignificant. For the syn-coupling constant, the configuration $\parallel ab\bar{b} \parallel$ is now of minor significance compared with its contribution to the anti-proton coupling. Most other contributions are small and of variable sign, and collectively they contribute roughly one-quarter of the calculated syn-coupling constant.

The most important point which becomes apparent is that the cross terms between configurations representing different mechanisms are not negligible. This fact makes any discussion about

individual mechanisms meaningless, since the contribution from one particular mechanism now depends in part on the existence of other mechanisms operating simultaneously. The separation that has been made for the purpose of discussion was to partition the cross terms into one group, contributions arising solely from a particular mechanism into a second group, and so on. For the purposes of general discussion it will be assumed that in the somewhat loose sense, each mechanism has its own particular identity.

(b) Antisymmetric case

The calculated values for the antisymmetric case are A_H (anti) = 1.53 gauss and A_H (syn) = 1.98 gauss[†]. Experimental results for the bicyclo [2.2.1] heptene semifuraquinone radical anion, which has an antisymmetric HOMO associated with the spin label are $[24]|A_H$ (anti)| = 1.41 gauss and $|A_H$ (syn)| = 0.79 gauss. As for the symmetric case the agreement for A_H (anti) is quite good, but A_H (syn) is still predicted to be too large. Most other systems exhibit smaller couplings, but the ratio A_H (anti)/ A_H (syn) usually remains around the value 2 except when A_H (syn) is unobserved.

[†] These results are based on the important condition that the geometry remains unaltered on changing spin labels.

(i) Mechanistic contribution to proton coupling

For both the syn- and anti-coupling constants, the major contribution arises from the ground state configuration $\Psi_1 = \|\pi b \bar{b}\|$. The admixture of singly excited configurations makes only a minor overall correction to the calculated hyperfine couplings. This is completely the reverse situation to that which is found in the simplest possible limiting case of the fragment being studied in model I, namely the aromatic C-H system. The difference is due to the non-orthogonal nature of the π - and σ -systems of the BHS molecule.

B. Model II

Although model II is not treated to the same degree of approximation, the results compare satisfactorily with model I. Unfortunately the individual couplings cannot be determined. This fact of course, does not dismiss the possibility that the sum of the two couplings is fortuitously in the correct range, which could occur if the splitting constants were of opposite sign. The only case in which the proton couplings will be individually determined is when they occupy equivalent sites, in which case they will naturally have equal values.

In general the attenuation of hyperfine couplings along the chain of the simple alkyl radicals may be taken as evidence for the use of a localized bond description for such systems. The merit of such a description is no longer easy to assess in view of the experimental results obtained from long-range systems. Since model II explicitly considers the use of nonlocalized orbitals, the viewpoint has been taken, based on the results of both models I and II, that the actual description of bonding in a semiquantitative manner is independent of the particular character of the orbitals. Such a viewpoint is only held when stereochemical features are present which allow for long-range π - π and π - σ interactions.

C. Extended Model

(a) Symmetric case

The agreement of predicted couplings based on equation (3.13) with those obtained experimentally (see Table 3.10) is fairly good for the anti-coupling. The syn-coupling is still predicted to be too large. It is impossible to make any generalization in view of the lack of sufficient experimental data. It may prove possible to obtain a better fit for the syn-couplings when the

appropriate experimental data becomes available by making a single empirical correction to equation (3.13).

There are two points which require some attention at this point. The first is that the equation (3.13) is obtained on the basis of the naive definition, equation (2.5), which provides a straightforward route for a simple calculation of ρ . Russell and co-workers [65,66] have made estimates of the spin density at the carbonyl carbon $2p\pi$ orbital from some simple semidione systems. Their results are essentially the same as those reported in Figure 3.5. More sophisticated calculations [43] indicate that the carbonyl carbon $2p\pi$ spin density is fairly small, most of the unpaired electron resides in the $2p\pi$ orbitals of the oxygen atoms. The spin densities appear to be positive in the cases studied, using the procedure outlined in reference [43]. The problem of the discrepancy between the calculated ρ values could be avoided completely by leaving the LCAO coefficients of the HOMO of the spin label in the final form for calculating hyperfine couplings. The problem would then resolve to the determination of such coefficients in a non-empirical calculation.

The disparity between Russell's estimate and the more sophisticated calculation is evidence for our lack of information regarding the precise distribution of unpaired spin density in small conjugated systems. In view of this difficulty, the simple approach

employed seems to recommend itself, although there may well be limitations in certain instances.

The second point concerns the conditions under which equation (3.13) is useful. It should prove satisfactory for a group of different spin labels where changes in ρ are sufficient to give a reasonable clear effect and where geometric changes are at a minimum. For the symmetric case there is insufficient data to assess the merit of equation (3.13).

Small changes are often observed due to substituent effects. Such effects are most striking for the syn-couplings due to their relatively small magnitude. Equation (3.13) is not designed for the study of such effects unless the substituent is on the spin label, and primarily alters the computed hyperfine coupling by changing ρ .

Equation (3.13) could be modified by choosing R as an empirical parameter transferable from system to system and obtained by fitting the calculated values to the experimental results of some reference system,[†] for example the BHS molecule.

[†] There is ample precedent for a procedure of this kind in almost all branches concerning quantum mechanical predictions on molecules.

For such a procedure, the calculated R and the empirical R would be quite close for the anti-protons, but for the syn-coupling, R would need to be chosen in such a way as to cause a reduction in the calculated coupling constant. The other quantities appearing in equation (3.13) need to be calculated for each principal σ -geometry. Relating the Q 's in terms of various geometrical parameters is possible, but such expressions may be useless in view of their extreme complexity and highly specific nature.

(b) Antisymmetric case

The results for the anti-couplings are predicted in the correct order, i.e. A_H (anti)(semifuraquinone) $>$ A_H (anti)(semiquinone). The predicted splittings are slightly small. The syn-couplings based on equation (3.19) are calculated to be very small. This is essentially the experimental finding, however, some relatively large deviations are observed, for only small changes in the spin density on changing from the semiquinone to the semifuraquinone spin label. This indicates the need for increasing the factor in the curly brackets of equation (3.19). The general comments made for the symmetric case are also relevant at this point.

Two observations may be made for the syn-coupling.

Firstly, the appearance of a negative hyperfine coupling is noted.

Secondly, the R_A dependence of equation (3.19) (which is proportional to minus the sum of the cross terms between the ground and excited states) is reasonably critical in determining the sign.

R_A is negative for the syn-proton, so a negative coupling arises whenever $R_A Q_{GE} > Q_E R_A^2 + Q_G^2$ (all Q 's are positive, and vary only slightly on changing from the anti- to the syn-orientation). R_A however, is of opposite sign for the syn- and anti-protons. An increase in R_A by approximately 20% for the syn-coupling produces an increase in the coupling by a factor of approximately eight. The best recourse seems to be to apply equation (3.19) with an empirical R_A parameter as discussed in the same context for the symmetric case.

D. General Comments

There has been considerable discussion in the experimental papers as to which is the correct mechanism leading to long-range coupling. Some remarks on these various proposals can now be made. Various suggestions put forward concern more complicated systems exhibiting long-range couplings. These systems will be discussed in view of the possibility that such systems may exhibit coupling mechanisms other than those already discussed.

The first observation that can be made is the general absence of hyperfine coupling from the bridgehead protons. The Heller-McConnell equation [67], takes the form

$$A_H = (B_0 + B \cos^2 \theta) \rho_{C-C-H} \quad (4.1)$$

where B_0 (associated with contribution from spin polarization) and B are constants, and θ is the angle between the direction of the $2p\pi$ orbital and the plane passing through C-C-H. If this equation can be applied to the calculation of the bridgehead proton coupling constants ($\theta \approx 90^\circ$ for these protons), then the contribution from spin polarization (B_0) is approximately 0. to 0.2 gauss at maximum for the general case. This would imply that any indirect spin polarization through the σ -bond system would in general give rise to a negligible contribution at the more distant anti-and syn-protons.

Russell and Chang [5, 6] and Kosman and Stock [22] were the first to observe systems in which there was an additional π -electron system involved. Kosman and Stock suggested that either an electron transfer process or a direct overlap effect might give rise to the large vinyl proton couplings in, for example, the molecule in Figure 4.2.

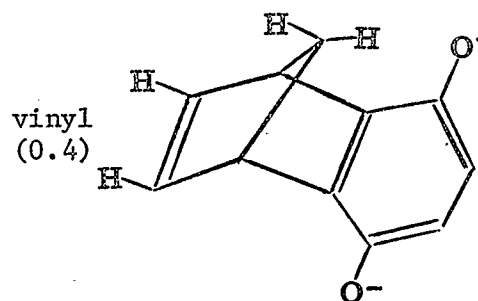


Figure 4.2 Bicyclo [2.2.1] heptene
semiquinone radical anion.

Direct overlap contributions (distant-direct effect) have been calculated to be generally small (see chapter three), which dismisses the possibility that the vinyl couplings arise from this effect. Nelson and Trost [18] pointed out that rear lobe interaction of the π -orbitals of the double bond and orbitals of the C-H bond of interest may account for the size of the anti-coupling.

From an investigation of a considerable number of unsaturated analogues of BHS, it has become apparent that larger anti-proton couplings are usually associated with the introduction of unsaturated character in the σ -framework (see for example Figure 4.2). In view of this observation one might be tempted to assign the observed increase in anti-coupling to the back- π -interaction mechanism. Whether this observation in fact supports Nelsen and Trost's proposal is not

at all clear in view of the results obtained for the syn-coupling constants. The syn-coupling constants are also found to be larger in the more unsaturated systems. For these protons no suitable back-sided interaction can be proposed. It may well be that the observed changes are associated with changes in stereochemistry. In view of the calculated results and the lack of any firm substantiating evidence for the proposal of Nelsen and Trost, the major cause of coupling is assigned to the previously stated mechanisms. Further evidence appears from the fact that large couplings for long-range protons have been observed when additional unsaturated character is absent. This would seem to indicate that the back- π lobe interaction pathway is of secondary importance.

One of the simple empirical observations to be made [7] is the so-called 'W plan' arrangement. The idea is that a sizeable coupling is only observed when the bonding between the $2p\pi$ atomic orbital and the proton in question fits a W pattern. The idea is illustrated in Figure 4.3.

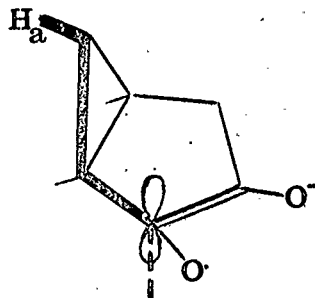


Figure 4.3 'W plan' for anti-coupling.

The *W* plan essentially imposes considerable geometrical restriction by requiring a particular fixed stereochemistry. Note that the *W* plan does not imply an interaction through the bond system, but merely the overall interaction direct or otherwise, gives the largest coupling when the arrangement is as shown in Figure 4.3. The syn-protons do not give this arrangement.

Qualitatively the *W* plan formulation is substantiated to a degree by the present calculations. Although a variable geometry has not been employed, the decisive difference in the results for the anti- and syn-protons in the symmetric case seems to provide some validity for the idea of particularly favourable stereochemical orientations. The calculations for the antisymmetric case are not found to be so critically dependent on the change from syn- to anti-configurations. It may be that the *W* plan is only an important guide to long-range

coupling when a certain mechanism is operating. From the calculations it would be tentatively concluded that the particular mechanism is the electron transfer process from the spin label.

Lemaire, Rassat and Rey [26] have disputed the validity of the *W* plan based on two arguments. Firstly they pointed out that strong coupling is observed in cases when the *W* arrangement is not satisfied. However, the radical shown in Figure 4.4 (a) was examined [26] and the anti-proton coupling which would be expected on the basis of the *W* plan was not observed.

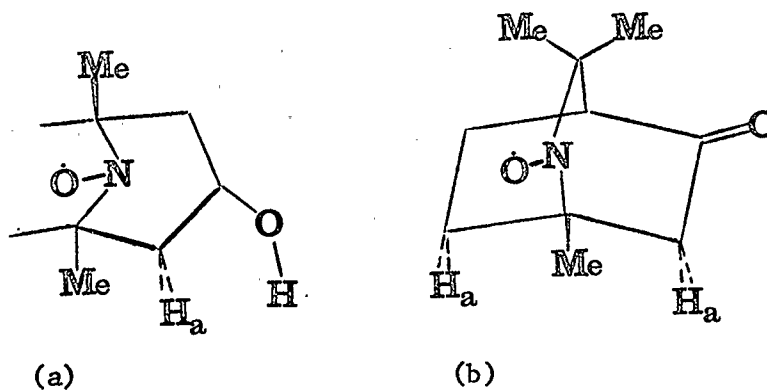


Figure 4.4 Nitroxide radicals examined.

This radical should be compared with Figure 4.4 (b) in which a sizeable anti-coupling is observed. With respect to the first argument above, if strong coupling is confined to less than approximately one gauss,

then the argument is correct. All major couplings in excess of about 1.5 gauss seem to fit the *W* plan approximately. The second remark rests on the rather critical assumption that the anti-protons of the radicals (Figure 4.4 (a) and 4.4 (b)) occupy similar stereochemical positions. This seems to be unconvincing evidence for discarding the simple concept of the *W* plan. If the experimental evidence for the molecule in 4.4 (a) is correct, then the proposal of assigning a particular mechanism in conjunction with the *W* plan may avoid this present difficulty.

The possibility of nonclassical interactions has not gone unnoticed [10,18,22]. Structures of the form represented in Figure 4.5 have been invoked to rationalize 'rear-lobe' interactions. There is no experimental evidence that structures similar to that shown in Figure 4.5 (b) have actual existence.

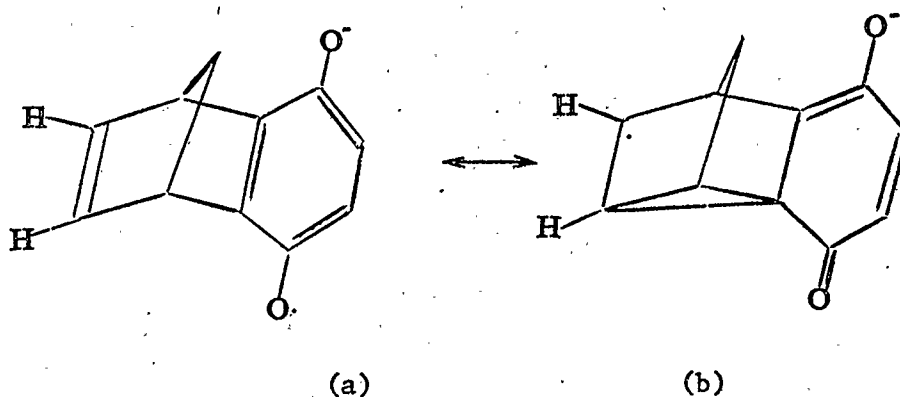


Figure 4.5 Nonclassical structure for the bicyclo [2.2.1]heptene semiquinone.

Structures such as Figure 4.5 (b) need only be viewed as one of the hybrid representations contributing to the overall picture of the molecule. The corresponding question of the existence of nonclassical character in the nonbornyl cation has brought forth some interesting experimental evidence in support of the nonclassical structures [61].

Kosman and Stock [15] argue on the basis of results from methylated derivatives of the 'vinyl bridge', that because the ratio A_{Me}/A_H is very small, no electron density is transferred to the vinyl carbon atoms (via nonclassical structures). This evidence is not convincing in view of the uncertainty in determining the applicability of the Heller-McConnell equation to such systems.

The direct (nonbonded) interactions treated in this thesis could be interpreted as nonclassical contributions. If this interpretation is employed; then nonclassical contributions must be considered to be important.

Other mechanisms which have been suggested, although not substantiated by any satisfactory evidence [14,15,24] are mechanisms based on electron transfer by a non-localized orbital scheme, direct (through space) and indirect (through bond) spin polarization. With the exception of the indirect spin polarization route, the other proposed mechanisms are the ones that have been explored in this study.

Kosman and Stock have made one particularly interesting

observation [15]. This concerns the equivalence of all anti-coupling constants for bicyclo [2.2.1] heptyl semiquinone radical anion. This has been suggested as evidence to show that there is no basic difference in the coupling mechanism for the anti-protons of the semiquinone, whether the protons are in or out of the node of the molecular symmetry plane. This observation is apparently limited to the semiquinone spin label.

Kosman and Stock have also pointed out that since the syn- and anti-protons of the heptyl semiquinones are in the nodal plane of the HOMO of the spin label, then all direct interactions are excluded. They then incorrectly assume that such couplings are produced by indirect spin polarization. As we have already shown, direct interactions cannot be excluded.

There is one further class of radicals for which model I must be considered as a highly suitable description. These are the rigid radicals produced during the irradiation process. The simplest possible system investigated is the cyclopropylcarbinyl radical [29], Figure 4.6.

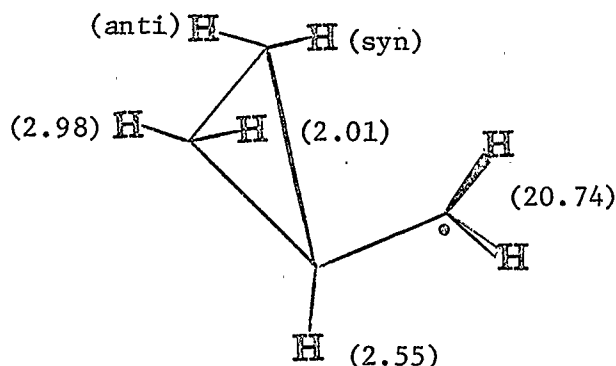


Figure 4.6 Cyclopropylcarbiny radical.

The major point to be noted, is the reasonably large syn-couplings, which are comparable to the results calculated for model I. However the changes in geometry are no doubt too large to make any firm conclusion regarding this agreement. Further derivatives of the cyclopropylcarbiny radical have been investigated and the general results are similar to those of the parent system [30].

The radicals illustrated in Figure 4.7 (a,b) give results which are not inconsistent with data for the other radicals. The assignment for system 4.7 (c) is marked by the absence of a 7-anti-proton coupling. In view of the other experimental results and the fact that a poorly resolved spectrum is reported, the assignment would appear to be incorrect.

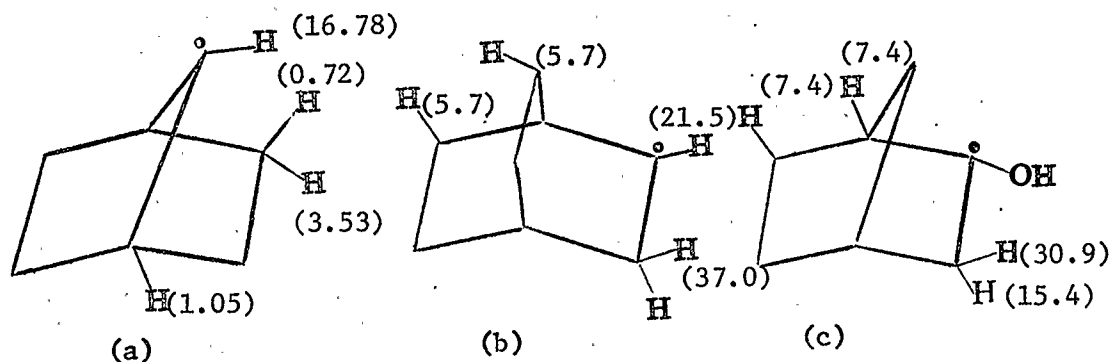


Figure 4.7 Some radicals exhibiting long-range couplings produced by irradiation processes.

E. Other Theoretical Work

Underwood and Givens [68] have carried out extended Huckel calculations for some of the semidiones. In some cases the agreement is satisfactory, in other cases quite unsatisfactory. Some of their calculated results are given in Figure 4.8. The calculated results are in brackets, and where a change in geometry has been made, a second estimate is also reported.

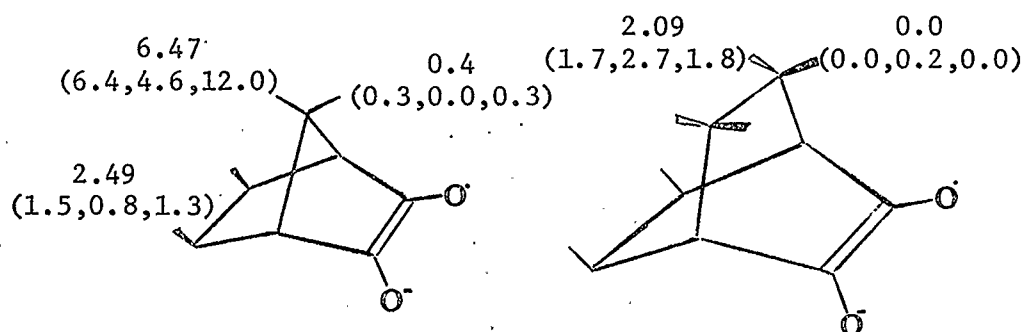


Figure 4.8 Extended Huckel calculations for some semidiones.

Such results must not be considered very seriously if one is attempting to explain the mechanism of long-range coupling. All integrals in this scheme are calculated by semiempirical procedures. As previously mentioned in chapter two, the Huckel formalism as applied by Underwood et al. essentially emphasizes the electron delocalization process and neglects the electron polarization process. From the calculations reported in chapter three, it was found that spin polarization was of some importance due to the large contributions to hyperfine coupling from certain cross terms. It further appears that Underwood and Givens have based part of their calculations on one set of orbital exponents and completed the calculations with a different set of exponents.

Several INDO[†] calculations [28,69] have been reported on the bicyclic systems. The work of Bakuzis et al. [28] , showed that the coupling was fairly sensitive to the geometry. Underwood et al., [69] found reasonably good agreement with observed values for BHS. The results were again found to be sensitive to geometrical changes. The main problem in such calculations is that agreement is no doubt fortuitous in view of (a) the dependence on semiempirical parameterization, and (b) the neglect of many important integrals, especially those describing the direct mechanism of coupling. This computational scheme does have the advantage that it can be applied to the molecule as a whole. The INDO scheme retains more integrals than most other approximate empirical molecular orbital procedures.

Three calculations on couplings in aliphatic fragments have been reported. The first two [50, 70] concluded the possibility of negative coupling constants for distant protons. Both calculations depend on the assumption that spin polarization is the only contributing mechanism. The calculations were based on the neglect of any direct

[†] Briefly stated, the INDO scheme is an SCF procedure for solution of the Hartree-Fock equations in which both π - and σ -bonding systems may be treated. The name INDO emerges from the particular procedure by which the necessary integrals are approximated.

interaction between the $2p\pi$ orbital and the long-range protons. This is a debatable approximation. Its only merit lies in the fact that the calculations are reported for a randomly orientated chain. The actual results are satisfactory [50] until the δ proton is encountered, in which case the sign and order of magnitude of the splitting appear to be predicted incorrectly.

Barfield [71] has calculated γ -couplings from a polynomial in angular variables of the propyl fragment. The polynomial was obtained on the basis of expanding the contributing integrals in angular variables. Barfield obtained integrals from various sources, some being based on semiempirical estimates, others were based on more rigorous calculations. All direct integrals however, were neglected. This seems unsatisfactory in view of the attempt to calculate couplings in the rigid cyclohexane radical. The calculated results for this latter system are fairly satisfactory (if the experimental sign is positive). The agreement could well be altered by the inclusion of direct interactions. An important point which Barfield has demonstrated is that the sign of the γ -coupling constant may be positive or negative depending on the conformation. This result is also obtained in the present work for the extended model as applied to the antisymmetric case.

Barfield makes the following observation about his

calculations; " γ -hyperfine couplings have been observed in strained bicyclic molecules, but it would not be reasonable to compare these with the calculated values, as the exchange integral parameters are based on the unstrained hydrocarbons". In view of this remark it would appear more satisfactory to proceed from systems of fixed geometry, i.e., the bicyclic systems, and then calculate all the necessary integrals. It would then be possible to determine the major mechanisms for each principal geometry. This procedure is obviously preferred over Barfield's approach of retaining only a minimum of integrals with their associated angular dependence.

CHAPTER V

SUMMARY AND CONCLUSION

The results of this work may be summarized as follows:

(1) The predicted couplings for bicyclo [2.2.1] heptane semidione radical anion (case 1) according to model I are:

$$A_H (\text{anti}) = 7.99 \text{ gauss}$$

$$A_H (\text{syn}) = 2.62 \text{ gauss}$$

(2) When the highest occupied molecular orbital of the spin label is antisymmetric (case 2) then:

$$A_H (\text{anti}) = 1.53 \text{ gauss}$$

$$A_H (\text{syn}) = 1.98 \text{ gauss}$$

(3) The dependence of the hyperfine coupling on the spin density at the adjacent site of the spin label for case 1 is:

$$A_H = 4\rho [1 + 4\rho R]^{-1} [Q_E + RQ_C + R^2 Q_T]$$

(4) For case 2 the dependence is:

$$A_H = \rho \{ [1 + R_A]^{-1} [Q_G + R_A Q_{GE} + R_A^2 Q_E] \}$$

(5) For model II the predicted coupling is:

$$A_H (\text{syn} + \text{anti}) = 0.32 \text{ gauss}$$

(6) The hyperfine couplings are found to depend critically on the stereochemistry. The dominant mechanism for the anti-coupling for case 1 is found to arise from a direct electron transfer process. For the syn-coupling, direct exchange polarization is dominant. For case 2, only direct exchange polarization is important.

(7) Predictions for the hyperfine coupling have been made for some cation radicals.

The calculations reported are the first to include direct interactions for long-range hyperfine couplings. The reason for the neglect of such interactions in the existing papers on this subject may be attributed to the inadequacy of semiempirical criteria for estimating the integral parameters. The method employed here could also be applied to systems other than those containing long-range couplings. The systems which may be studied are those

shown in Figure 5.1, where the semiempirical procedures do not

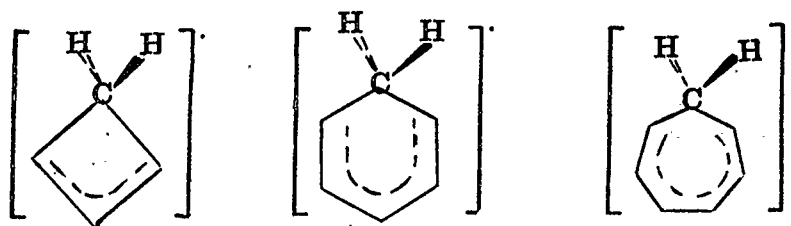


Figure 5.1 Possible systems for future investigation.

predict satisfactorily the coupling constants for the protons shown in the figure.

At the present stage of the work a few points still remain unsettled. The primary questions are: What is the effect of using a minimal basis set? In what way do substituents alter the observed hyperfine coupling?

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APPENDIX I

The derivation of equation 2.40 is outlined here. In the usual notation,

$$H\Psi_n = E_n\Psi_n \quad (A.1)$$

$$H = H^0 + \lambda H^1 \quad (A.2)$$

$$\Psi_n = \Psi^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots \quad (A.3)$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (A.4)$$

$$\Psi_n^1 = c_{11} \Psi^0 + c_{22} \Psi^0 + \dots c_m \Psi_m^0 + \dots \quad (A.5)$$

Substitution of equations A.5 to A.2 in equation A.1 leads to the well known result:

$$(H^0 - E_n^0) c_m \Psi_m^0 = E_n^1 \Psi_n^0 - H^1 \Psi_n^0 \quad (A.6)$$

The coefficients c_m are determined from equation A.6 as

$$c_m = \{ \langle \Psi_m^0 | H^1 | \Psi_n^0 \rangle - \langle \Psi_n^0 | H^1 | \Psi_n^0 \rangle \langle \Psi_m^0 | \Psi_n^0 \rangle \} \times \{ E_n^0 - E_m^0 \}^{-1} \quad (A.7)$$

Hence equation A.3 may be written to first-order,

$$\Psi_n = \Psi_n^0 + \lambda \sum_{m \neq n} c_m \Psi_m^0 + \lambda c_n \Psi_n^0 \quad (A.8)$$

The coefficient c_n may be determined by the constraint that

$$\langle \Psi_n | \Psi_n \rangle = 1 \quad (A.9)$$

ψ_n may however be approximated in first-order, in which case

$$c_n \approx - \sum_{m \neq n}^{\infty} c_m \langle \psi_m^0 | \psi_n^0 \rangle \quad (\text{A.10})$$

Therefore equation A.8 may be rewritten (setting $\lambda = 1$) as

$$\begin{aligned} \psi_n &\approx \psi_n^0 + \sum_{m \neq n} \{ \langle \psi_m^0 | H' | \psi_n^0 \rangle - \langle \psi_n^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | \psi_n^0 \rangle \} \\ &\quad \times \{ \psi_m^0 - \langle \psi_m^0 | \psi_n^0 \rangle \psi_n^0 \} \{ E_n^0 - E_m^0 \}^{-1} \end{aligned} \quad (\text{A.11})$$

which is the expression given in equation 2.40.