SYNTHETIC MODIFICATION OF SPIN DENSITY IN PHENANTHRENESEMIQUINONES, ZN(II)-PHENANTHRENESEMIQUINONE AND NI(II)-PHENANTHRENESEMIQUINONE COMPLEXES

By

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ABSTRACT

SYNTHETIC MODIFICATION OF SPIN DENSITY IN PHENANTHRENESEMIQUINONES, ZN(II)-PHENANTHRENESEMIQUINONE AND NI(II)-PHENANTHRENESEMIQUINONE COMPLEXES

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Contained within this body of work is a study that aims to quantify spin density delocalization in 3,6-R₂-phenanthrenesemiquinone (3,6-R₂-PSQ, where R = OMe and H) radicals and their metal complexes (where metals= Zn^{II} , Ga^{III} and Ni^{II}), of the form [M(tren)(PSQ)](BPh₄)_n, where M is a metal that is listed above, tren = tris(2-aminoethyl)amine, PSQ = phenanthrenesemiquinone and BPh₄ = tetraphenylborate. Spin delocalization will be scrutinized by analyzing carbonyl carbon hyperfine coupling constants by continuous wave electron paramagnetic resonance (CW-EPR) spectroscopy, electron spin echo envelope modulation (ESEEM) spectroscopy, and hyperfine sublevel correlation (HYSCORE) spectroscopy. These examinations will reveal the influence molecular structure has on the hyperfine coupling at the carbonyl carbon nuclei. Spin delocalization has been quantified by isotopically labeling the carbonyl carbon nuclei with carbon-13 nuclei. ¹³C-labelled quinones were synthesized from a sequence of reactions, beginning with 13 C- α -N,N'-dimethylformamide and 2,2'-dibromobiphenyl to form a diformyl-biphenyl. The carbonyl carbons were then coupled with hydrazine via a reductive cyclisation reaction, followed by oxidation with CrO₃ to afford the quinone. CW-EPR of the ¹²C isotopologues revealed ¹H fine structure in the organic radicals and the Zn^{II}-PSQ complex. Inspection of the ¹³C-labeled compounds provided isotropic hyperfine coupling constants for all compounds studied except for Ni^{II} complexes; any fine structure from Ni^{II} CW-EPR spectra was unable to be resolved. The magnitude of all isotropic coupling constants fell within the range of 0 - 3 MHz. ESEEM and

HYSCORE spectroscopies allowed for scrupulous investigation of the dipolar coupling. Carbonyl carbon dipolar couplings varied across the spectrum of compounds examined. This study shows promise for the use of ESEEM and especially HYSCORE spectroscopies for examining the spin properties of molecules in the field of molecular magnetic materials.

Copyright by LARRY D. MORRIS III 2017 This dissertation is dedicated to my wife, Melissa, my daughter Arlyn Mae, and my son, Ronan.

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Chapter 1. Introduction to Spin Exchange and ¹³C-Labelling of Phenanthrenequinones

1.1 Background of Research

The very cornerstone of the research presented within this dissertation is based on results from DFT (Density Functional Theory) calculations on [Ni(tren)(3,6-R₂-PSQ)]⁺ (where R is 17 various substituents varying in electron-withdrawing/-donating character) complexes¹. These complexes exhibit a particular intramolecular property known as exchange coupling. Exchange coupling is a physical phenomenon in which two or more unpaired electrons on separate nuclei communicate electronically. This is a stabilization effect and can be as large as hundreds of wavenumbers (cm⁻¹). This communication can occur by various methods: 1. "direct exchange", in which two spin centers are directly bonded to each other; 2. "super exchange", communication between the spin centers occurs through a diamagnetic mediator; 3. "double exchange", which is a complicated "hopping" type mechanism between paramagnetic centers and a diamagnetic bridge. Only direct exchange will be addressed in the context of the compounds studied in this dissertation.

In a direct exchange mechanism, two different forms of exchange coupling can occur, depending on the nature of the magnetic orbitals involved in the exchange. If the magnetic orbitals are aligned parallel to each other, then the coupling is said to be antiferromagnetic. If the magnetic orbitals are orthogonal (in other words, no orbital overlap) then the interaction is ferromagnetic. To describe this physical interaction mathematically, a Hamiltonian of the form

$$\widehat{H} = J\widehat{S}_1 \cdot \widehat{S}_2 \tag{1.1}$$

is employed. Specifically, the Heisenberg Dirac van Vleck (HDvV) Hamiltonian above is one expression of the exchange interactions and will be the only expression used in this dissertation.

J is the exchange coupling constant and is directly related to the magnitude of the interaction. The sign of *J* is also sensitive to the kind of interaction; when J > 0, antiferromagnetic coupling is the mechanism and when J < 0, ferromagnetic coupling is present. This is represented pictorially in Figure 1.



Figure 1-1. Left: Interaction between two $S = \frac{1}{2}$ centers where the ground state is the singlet. Right: Interaction where the triplet is the ground state.

The exchange coupling constant, J, is directly proportional to the product of the spin densities of the spin centers $J^{2,3}$, (see equation 2 below). Thus, the spin density is the progenitor of the magnitude of the exchange coupling.

$$J \approx \rho(S_1)\rho(S_2) \tag{1.2}$$

The energy splitting separating the singlet (S = 0) and triplet (S = 1) states in Figure 1 can be calculated with respect to *J*. Using the Kambe approximation⁴, which assumes $\mathbf{S}_{T} = \mathbf{S}_{1} + \mathbf{S}_{2}$, and squaring both sides of the equation and solving for $\mathbf{S}_{1} \cdot \mathbf{S}_{2}$, one can obtain the following relationship

$$\boldsymbol{S_1} \cdot \boldsymbol{S_2} = \frac{\boldsymbol{S_T^2} - \boldsymbol{S_1^2} - \boldsymbol{S_2^2}}{2} \tag{1.3}$$

This can then be inserted into equation 1, to afford the following equation

$$\mathbf{H} = \frac{1}{2} \cdot J_{12} \cdot (\mathbf{S}_{\rm T}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2)$$
(1.4)

It is also known from quantum mechanics that when a squared operator operates on a particular wave function, the eigenvalue can be obtained from the following equation:

$$\mathbf{S}_{\mathbf{T}}^{2} \mathbf{\Psi} = \mathbf{S}(\mathbf{S}+1) \mathbf{\Psi} \tag{1.5}$$

When this relationship is combined with the operator equivalent form of (1.3), the following equation is the result:

$$E = \frac{1}{2} \cdot J_{12} \cdot [S_T(S_T + 1) + S_1(S_1 + 1) + S_2(S_2 + 1)]$$
(1.6)

From this equation, one can calculate the relative energies of the individual spin states of a given system, and thus the energy difference(s) that separate them. For example, if there was a two spin system where $S_1 = 1$ for a high spin Ni^{II} ion in an octahedral environment and $S_2 = \frac{1}{2}$ for an organic radical that was directly bound to the Ni^{II} nucleus, then the following relative energies and energy splittings could be calculated for the two spin states:

$$E_{S=\frac{3}{2}} = \frac{1}{2} \cdot J_{12} \cdot \left[\frac{15}{4} - \frac{8}{4} - \frac{3}{4}\right] = \frac{J_{12}}{2}$$
$$E_{S=\frac{1}{2}} = \frac{1}{2} \cdot J_{12} \cdot \left[\frac{3}{4} - \frac{8}{4} - \frac{3}{4}\right] = -J_{12}$$

$$\left| \mathbf{E}_{\mathbf{S}=\frac{3}{2}} - \mathbf{E}_{\mathbf{S}=\frac{1}{2}} \right| = \frac{3}{2} J_{12}$$

Figure 2 depicts a splitting diagram of this interaction. Now, if $J >> k_BT$, then there will be little probability of populating the doublet state and only an isolated, quartet ground state will exist at room temperature. This is the exact situation that has been observed experimentally, both by variable temperature magnetic susceptibility, as well as variable temperature CW-EPR measurements.



Figure 1-2. Energy diagram for the interaction of a Ni^{II} ion and semiquinone.

As it is depicted in Figure 2, the exchange interaction is ferromagnetic for these Ni-SQ complexes and as it was stated earlier, this is a result of the orthogonality of the magnetic orbitals. The unpaired electrons reside in e_g orbitals on nickel, specifically the $d_{x^2-y^2}^2$ and $d_{z^2}^2$ orbitals. The unpaired electron on the semiquinone resides in a p – orbital. These electrons are exchangeable and obey Hund's rule of maximum multiplicity, therefore the ground state is a quartet.

The calculations mentioned in the beginning of this chapter were carried out to assess how the exchange coupling constant and average oxygen spin density varies with choice of substituent⁵, and are pictured in Figure 3. These calculations were a part of an effort to uncover the mechanism of spin polarization by choice of substituent. The mechanism was not uncovered,



but many consequences of spin polarization in exchange coupled molecules were observed.

Carbonyl-O (p)

Figure 1-3. Average oxygen atom spin density versus *J* in $[Ni(tren)(3,6-R_2-PSQ)]^+$ complexes.

The calculations clearly show a linear trend in choice of substituent when comparing exchange coupling constant, J, and average oxygen spin density. This linear trend was also observed in Cr^{III} analogues, where the coupling was antiferromagnetic, due to the overlap of the π -type orbitals of the t_{2g} orbitals and the semiquinone π radical. The inherent observation in these results is that when R is an electron withdrawing group, J is large and when R is electron donating J is small, relative to R = H. These calculations, that examine several substituents based on exchange coupling, are unparalleled in the literature. Venegas-Yazigi and coworkers produced a study on bis-phenoxo bridged dicopper(II) complexes where they examined the

effects of several structural parameters on exchange coupling⁵. In particular, *J* versus the Hammett σ parameter where the Cu-O-Cu angle is 105° and the Cu-O-C (phenoxo) angle is 0° (in plane) and 50° (out of plane). In both instances of Cu-O-C angle, a linear dependence on *J* and σ was observed. A similar trend in electronegativity was also observed, only for a small series of substituents (R = CH₃, H, CONH₂, CO₂H, CN, NO₂). These complexes, however, have an inherent problem in that the exchange coupling is too large to be measured by variable temperature magnetic susceptibility. Therefore, this work examines spin density fluctuations near the exchange coupling site.

The system of study is [Ni(tren)(PSQ)]⁺ The design of this system is not our own, but is rather based on a molecule synthesized by Andrea Dei and Alessandro Bencini⁶. The system has modified been slightly in the *dl*-5,7,7,12,14,14hexamethyl-1,4,8,11that tetraazacyclotetradecane (CTH) ancillary ligand has been replaced by tris(2-aminoethyl)amine (tren). The reason for this switch is because CTH is chiral and has the ability to form isomers, whereas tren does not form isomers. A secondary purpose of tren is to ensure an octahedral geometry for Ni^{II} by occupying coordination sites, not occupied by the semiquinone ligand. A monosemiquinone complex was chosen to study one exchange interaction. Again, specifically a direct exchange interaction was desired to examine the effects of spin density at the exchange center on spin density.



Figure 1-4. Molecular structure of [Ni(tren)(PSQ)]⁺.

A quinone was chosen because of its redox active nature and wealth of known information. The three oxidation states of quinones allow for them to be manipulated synthetically, which is advantageous for synthesizing metal complexes. Quinones are the fully oxidized version of the molecule and are not very strong Lewis bases/nucleophiles; however, quinone-transition metal complexes are known⁷. The one-electron reduced form, the semiquinone, is a radical containing molecule where most of the spin density of the ligand resides on the oxygen atom. These radicals are generally not air-stable and therefore must be handled in air-free atmospheres. Although these radicals are not air-stable, when bound to a metal ion, as a solid the compounds can be stable from days months. In air, solutions of to



Figure 1-5. Oxidation states of phenanthrenequinone.

semiquinone-metal complexes can easily be oxidized, so care must be taken when handling these types of compounds. The semiquinone form, although having an extra electron compared to the quinone form, is still a relatively poor nucleophile. The two-electron reduced form, the catecholate, is a strong nucleophile/Lewis base and is desirable for complexation reactions to metals. Complexes within this body of research were prepared by reducing a quinone to the catecholate, followed by addition of the catecholate solution to a metal precursor complex, and finally oxidizing the metal-catecholate complex with a chemical oxidant to produce the desired metal-semiquinone. Lastly, phenanthrenequinone was chosen so as to delocalize the spin density to a greater extent than benzosemiquinones, and create a greater likelihood for exchange coupling constants to be directly measured by variable temperature magnetic susceptibility measurements. Unfortunately, this was not realized when three Ni^{II} complexes were made (where $R = NH_2$, H and NO₂), and their magnetic susceptibilities showed no temperature dependence. This being the case, it was decided to examine spin density at, or near, the exchange site directly.

In order to examine spin density fluctuations a few items must be taken into consideration. If our intent is to gain knowledge about spin density then we must examine a property that is directly tied to spin density, so we will be examining hyperfine coupling constants. Specifically, a hyperfine interaction is the coupling of the radical's spin (*S*) to the spin of a nucleus (*I*). Thus hyperfine coupling necessitates both an open shell molecule and a nucleus with spin. Since we are dealing in the nature of radical containing compounds our method of detection is electron paramagnetic resonance (EPR).

Due to our interest in the magnetic exchange, it would be desirable to know the magnitude of spin density at the center of the exchange interaction, since it is near-impossible to measure J in

 Ni^{II} -PSQ⁺ complexes in a typical manner (other methods to measure exchange coupling constants exist but are costly and cumbersome). However, there are some obstacles to overcome when considering measuring hyperfine coupling constants at oxygen atoms. First, ¹⁶O has no nuclear spin and therefore an isotope must be used in its place, ¹⁷O, which implies isotopic labeling. Fortunately for quinones it is quite simple to exchange oxygen atoms with ¹⁷OH₂, and a mild acid in a non-aqueous environment⁸. The cost of ¹⁷OH₂ is high (~ \$2,000/gram at the outset of this research project), however, and enrichment methods are effective but not a scale that is feasible for synthesizing an amount for physical characterization, synthesizing metal complexes and EPR experiments⁹.

1.2 Introduction to spin delocalization and ¹³C as an isotopic label for measuring spin delocalization

Seeing as there are certain obstacles to overcome with ¹⁷O labeling, we chose to use ¹³C as a spin label. By measuring the hyperfine coupling at the carbonyl carbon in free radicals, d¹⁰-semiquinone complexes and Ni^{II}-semiquinone complexes, a single study has come about that tracks spin density (via hyperfine coupling) fluctuations in molecules in a manner not previously studied. ¹³C-labelling of the carbonyl carbon nuclei will also provide some ease in interpretation due to the I = $\frac{1}{2}$ nucleus; however, this does not come without obstacles to overcome. Thus, the effect of spin density delocalization on semiquinones, M^{II}-semiquinone complexes, as well as Ni^{II}-semiquinone complexes, has been examined.

Spin density delocalization and spin polarization are terms that may be difficult to understand in terms of their context. In the context of this work spin density delocalization is a manifestation of where the radical wave function has been dispersed, and spin polarization is the perturbation of the wave function by some stimulus. Within this context, one can refer to substituent effects, from complex to complex, as a means of polarizing spin density, as in the computational study mentioned at the beginning of this chapter. The bulk of the material in this dissertation will focus on the delocalization of the unpaired spin density on the PSQ moiety.

Room temperature, CW-EPR experiments have the resolution necessary to detect the spin density at the nucleus. This is often referred to as the scalar coupling, isotropic coupling or the Fermi isotropic coupling. Specifically, this is the amount of spin density in the s-orbitals. In aromatic compounds this is on the order of 0 - 20 MHz¹⁰, given that aromatic radicals generally reside in p-orbitals. The spacing between lines in the EPR signal are due to the isotropic hyperfine coupling, which is tied directly to the sigma bonding environment of the nucleus. Isotropic hyperfine coupling constants, or a_{iso} , are also directly observable from ENDOR spectra and can be extrapolated from ESEEM spectra.

Electron Spin Echo Envelope Modulation, ESEEM, is a pulsed technique performed at fixed magnetic field values that measures the decay of the amplitude of a spin echo as a function of time. This time trace is then background corrected and Fourier transformed and results in a frequency spectrum. The frequency spectrum is an expression of the unpaired spin density and the nuclei on which it resides. The frequency at which a resonance occurs coincides with the Larmor frequency of a specified nucleus. The Larmor frequency is the frequency at which a particular nucleus precesses in a given magnetic field and is represented mathematically in the equation below,

$$\omega = -\gamma\beta \tag{1.7}$$

where ω is the Larmor frequency, γ is the gyromagnetic ratio of the nucleus in a magnetic field and β is the magnetic field. In a typical ESEEM experiment there is a preparatory pulse followed by a second pulse at a specified time length, τ , after the first, and finally a third pulse creates a stimulated echo and this third pulse is applied at varying times after the second pulse to record echo amplitude as a function of time. ESEEM can also be a two pulse experiment, but only three pulse experiments were used in the assessment of the molecules studied in this dissertation.

HYSCORE is a two-dimensional EPR technique that teases apart the strong and weak hyperfine couplings, relative to the Larmor frequencies of the nuclei involved. A twodimensional technique necessitates a second observable, to obtain this a fourth pulse is placed between the second and third pulses of the ESEEM pulse sequence. This allows for two dimensions of time to be monitored. The data is worked-up similarly to that of a onedimensional experiment, but the main difference is that a two dimensional Fourier transform is applied to the background corrected spectrum and the data is presented as a two-dimensional contour plot, separated into quadrants. Only quadrants one and two are displayed; quadrant one displays weak hyperfine couplings (A < 2v) and strong couplings (A > 2v) are found in quadrant two. As in two-dimensional NMR experiments (like COSY), the on-diagonal elements are a consequence of the one dimensional spectral features mapping onto each other and the offdiagonal elements are due to the so-called hyperfine sublevel correlations.

The details and necessities of the experiments and analysis thereof will be explained in the forthcoming chapters.

1.3 Contents of Dissertation

The information, data, results and analysis in this dissertation can be grouped into three sections: (1) spin density delocalization in PSQ radical anions; (2) the effect of Lewis acidity on

spin density delocalization, utilizing $[Zn(tren)({}^{13}C_2PSQ)](BPh_4)$ and $[Cd(tren)(PSQ)](BPh_4)$ complexes; (3) and finally the effect of exchange coupling on spin density delocalization in $[Ni(tren)({}^{13}C_2PSQ)](BPh_4)$ and $[Ni(tren)(3,6-(OMe)2-{}^{13}C_2PSQ)](BPh_4)$.

Chapter 2 examines spin density distribution in PSQ and 3,6-(OMe)₂-PSQ radicals. The study begins with a DFT analysis of the carbonyl carbon and oxygen spin density distribution. It was found that the majority of the alpha spin density is contained within the carbonyl units of the ligands and is split, symmetrically between the two units. Average spin densities are presented due to the symmetry of the molecules. No linear trend was found in comparing carbon and oxygen spin density. The chapter then switches to mainly experimental results and analysis, beginning with synthesis of the ¹³C-labeled phenanthrenequinones and their physical characterization. Proceeding synthesis are CW-EPR, ESEEM and HYSCORE results from the four radical compounds, paired with simulation results and DFT predictions of hyperfine coupling constants.

Moving forward, Chapter 3 discusses spin polarization dependence on Lewis acidity. Specifically, PSQ was bound to transition metals with full d shells, Zn^{II} and Ga^{III}. The choice of metals is based on the Ni^{II} complexes. Zn^{II} was chosen because its charge to size ratio is similar to that of Ni^{II}'s, and it is diamagnetic and thus limits our study to focus on the semiquinone ligand. To restate, the purpose of using ¹³C-labeling was to measure hyperfine coupling constants near the exchange center in the Ni^{II} complexes, thus we desire to know the spin density near the exchange center in the absence of unpaired electrons at the metal center. This system, therefore, is absent of exchangeable electrons and becomes an excellent background for the exchange coupled complexes. Ga^{III} was originally chosen as a backdrop for Ni^{II} and Cr^{III}-PSQ complexes because the synthesis was more straight-forward and a crystal structure of the

catecholate complex was known. Additionally, it was desired to know if any hyperfine coupling was present at the metal center, and Ga allows such measurements due to the I = 3/2 nuclei of ⁶⁹Ga and ⁷¹Ga. This chapter is analogous to Chapter 2 in that DFT results of spin density fluctuations in the ligand carbonyl unit are examined, synthesis of the complexes is explained and a full EPR treatment is presented.

Following Chapter 3 adds the final layer of spin distortion based on the physical surrounding of the PSQ radical. The effect of exchange coupling on spin density is examined by studying [Ni(tren)(¹³C₂PSQ)](BPh₄) and its ¹²C isotopologue. As in the previous chapters, the hyperfine coupling of the ¹³C atoms is examined with CW and pulsed techniques. The CW-EPR line shape is completely dominated by isotropic exchange coupling and zero-field splitting. Only a small line shape change is observed between the ¹²C and ¹³C spectra in the g-2 region; unfortunately, this difference in line shape could not be resolved by simulations. ESEEM and HYSCORE were employed to study the hyperfine coupling at various magnetic field values, based on the CW-EPR spectrum, so as to fully characterize the EPR line shape. It was found that in going from high field to low field, the effect of the ¹³C hyperfine disappears. This is most likely an effect of moving from g-2 to g-4, because the radical wave function is mostly associated with the PSQ ligand. Also presented in Chapter 4 is a comparison of the DFT results with the experimental hyperfine coupling constants.

The finale of this dissertation culminates all the conclusions and short-comings of this study and lays out the landscape of the future of the project in light of the short computational study completed for this closing chapter. First, Chapter 5 compares exchange coupling constants in [Ni(tren)(SQ)]+ complexes. Various semiquinone and α -diimine ligands are examined to assess the following postulate: is it possible to construct a Ni^{II}-SQ based system in which the exchange coupling constant is small enough, in magnitude, and the spin density at the exchange center can be monitored by EPR techniques, whether it be by CW-EPR, ENDOR, ESEEM and/or HYSCORE? It is noted that, this research group may be the only research group attempting to decrease the amount of exchange coupling. Groups are typically interested with increasing J so as to increase the likelihood that the molecule/material will exhibit magnetic properties that would be amenable to making usable molecular magnetic materials, such as single molecule magnets¹¹. Regardless of the progress of other groups, we aspire to gain knowledge of the spin density at the exchange center concomitantly whilst knowing J in a series of derivatives with symmetrically placed substituents on the SQ backbone; this study would produce the knowledge necessary to construct molecular magnetic materials with a bottom-up type approach. In order to reach such goals, the results in Chapter 5 point towards using ¹⁷O as a spin label. The results also show that for each SQ ligand, there is a dependence of J based on choice of substituent.

Additionally, this final chapter brings together the results of this dissertation and places them all under a single light. The final chapter explains that it was the hope of this study, as a whole, to assess if there would be appreciable differences in ¹³C hyperfine coupling constants to determine an experimental substituent effect. This would then be correlated with theoretical results of hyperfine coupling constants and *J* values. And if there was a correlation between hyperfine interactions and *J* what would that perpetuate for constructing molecular magnetic materials? That would be the full realization of this project, creating molecular magnetic materials base on a "bottom up" approach.

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Chapter 2. Quantifying Spin Density Delocalization in Phenanthrenesemiquinones

2.1 Introduction

The scope of this research is to theoretically and experimentally determine if unpaired electron density can be displaced, delocalized or polarized by means of a substituent effect. To an extent, this is the most rudimentary form of experiment for the chemist; create a molecule, take a measurement, modify the molecule, take a measurement, etc. It is a simple means of altering the physical properties and/or reactivity of molecules. Increasing the nucleophilicity of an organic molecule in substitution reactions, changing the steric bulk on a ligand system to prevent unwanted excited state geometries, these are a couple of examples where modifying chemical structure changes both the physical properties and/or the chemical reactivity of a molecule. In the interest of this type of study, the goal of this project is to learn how to better construct molecular magnetic materials. The method for this goal is taking a simple redox active ligand and attempting to manipulate its unpaired electron distribution by modifying the molecular structure.

The system for studying spin properties affected by substituent choice are semiquinones. Semiquinones have been vastly studied for several decades. The richness of their redox chemistry lends them to several fields of study including, but not limited to, valence tautomerism^{1–4}, electron transfer processes^{5–7}, synthetic oxidants^{8,9} and molecular magnetic materials^{10–13}. The eventuality of this project points towards studying the magnetic properties of exchange coupled, semiquinone-paramagnetic transition metal complexes (Chapter 4). Prior to studying said exchange coupled molecules, we wish to learn more about spin density
delocalization within the ligand. In order to assess this inquiry, a combined computational and experimental study has been undertaken concerning 3,6-R₂-phenanthrenesemiquinones (3,6-R₂-PSQs).



Figure 2-1. Structure of 3,6-R₂-PSQ radical anions with proton numbering scheme.

Another facet of this study is to elucidate spin density parameters from hyperfine coupling constants and compare these findings to Zn^{II} -PSQ, Ga^{III} -PSQ and Ni^{II} -PSQ complexes. As of recently, there has not been such a study undertaken in the literature. Labeling semiquinones to extract spin density information through EPR techniques is not a new experimental method. There have been limited examples in the literature that study the carbonyl oxygen spin density by substituting ¹⁷O for ¹⁶O in *para*-semiquinones to measure the hyperfine coupling at the oxygen atoms¹⁴. Time-resolved EPR¹⁵ experiments as well as simple continuous wave-electron paramagnetic resonance (CW-EPR) experiments have been undertaken to measure hyperfine coupling constants in complex biological environments and simple organic molecules, respectively. Time resolved studies of 1,4-naphthoquinone in Photosystem II revealed that oxygen atoms were non-equivalent due to strong hydrogen bonding; and as a consequence to the hydrogen bonding, the anisotropic coupling (*T*) was unable to be determined. In other studies, typical CW-EPR experiments were conducted on mostly *para*-semiquionones^{16,17,18}. The oxygen hyperfine coupling was found to be of similar magnitude (7-10 G, 19-29 MHz) in each case of

the organic molecules; however, in molecules containing more oxygen atoms than the two semiquinone groups, the hyperfine coupling was smaller. Attempts to measure anisotropic contributions to the hyperfine coupling in chloranil radical anion were successful, but showed variance in the hyperfine coupling in using various methods to produce the semiquinone from the parent quinone¹⁷. This is an important note from the literature because it is similar to the findings of this work. The method of reduction has an influence on the spin density map of the molecule, due to the physical nature of the method used; e.g. using sodium versus potassium to reduce the Q to the SQ. To generalize this statement, the method by which the radical is produced has an influence on the spin density.

As it was stated in the introductory chapter, the method for measuring differences in hyperfine coupling amongst semiquinones is isotopic labeling. Specifically, the carbonyl carbons will be exchanged for ¹³C nuclei. There have been experimental studies using ¹³C to study spin density distribution in semiquinones. Recently, ¹³C-labeling in quinones has been most prominent in biological chemistry. Labeling carbonyl carbons¹⁹ as well as ring²⁰ and substituent carbons²¹ in ubisemiquinone-10 (a *para*-quinone) has proved to be a powerful technique in uncovering structural information regarding the chemical environment; specifically hydrogen bonding networks and the effect of the hydrogen bonding on the hyperfine coupling at the carbonyl carbons. It was found that the carbonyl carbons were non-equivalent due to strong hydrogen-bonding at one of the oxygen atoms.

In addition to magnetic resonance, density functional theory (DFT) calculations provide for a theoretical basis of where the unpaired spin density resides in the open shell molecules. There have been numerous DFT studies of semiquinones^{22–25}. DFT results allow for a deep comparison of structural parameters, electronic structure, magnetic properties and other

quantities not easily obtained from experiment. It should be noted that although experimental spin density values are compared to theoretical results, the series of molecules studied by DFT were intended to uncover trends and not calculate the absolute magnitudes of the values.

Experimentally, there is a wealth of knowledge to be learned from conventional EPR. Fine structure in CW spectra can be used to measure isotropic hyperfine, a_{iso} , couplings. This can be powerful information for determining wave function contribution across a molecule, electronic structure, or even structural parameters. Indeed, the difference in line shape alone can indicate qualitatively if a substituent effect is operative. The semiquinones and their ¹³C isotopologues studied in this chapter have been designed to determine, quantitatively, the effect of substituent on spin delocalization/polarization in phenanthrenesemiquinones. Therefore, a combination of CW-EPR, ESEEM and HYSCORE spectroscopic techniques have been undertaken to determine both isotropic, a_{iso} , and anisotropic, or dipolar, *T*, carbonyl carbon hyperfine splitting constants.

As detailed below, in the CW-EPR section, the ${}^{13}C$ - a_{iso} only accounts for the spin density at the nucleus, and does not include the spin density residing in *p*-orbitals. The spin density residing in *p*-orbitals is called the anisotropic hyperfine coupling. So, along these lines, ESEEM and HYSCORE experiments have been carried out to determine the anisotropic portion of the ${}^{13}C$ -hyperfine coupling. ESEEM has been largely successful for our system due to the large anisotropic portion of the hyperfine coupling. To add a second dimension to this study we have also included HYSCORE results, which directly reveal frequency correlations arising from the same hyperfine coupling. Although there may be small portions of anisotropy on the protons from spin polarization of the radical, for the purpose of this study, the focus has been placed on the ${}^{13}C$ nuclei and the anisotropy on the protons have been ignored.

2.2 Experimental

General Methods. Reagents were purchased from commercially available sources and used without further purification unless otherwise stated. [Carbonyl-¹³C]N,N'-dimethylformamide was purchased from Cambridge Isotope Labs with 99% ¹³C enrichment in 1 mL ampoules and used as received. Stabilizer-free tetrahydrofuran was purchased from Fisher Scientific and either distilled over sodium metal and benzophenone and freeze, pump, thawed to remove O₂, or taken from a dry still with a solvent bomb. Elemental analyses and electro-spray ionization ESI mass spectra were obtained through the analytical facilities at Michigan State University. GC mass spectra were obtained on a Hewlett Packard G1800D GCD system equipped with an electron ionization detector or acquired by the analytical facilities at Michigan State University. NMR spectra were collected on Agilent DDR2 500 MHz Spectrometers equipped with 7600A autosamplers at the Max T. Rogers NMR Facility at Michigan State University.

Synthesis. 2,2'-Diformylbiphenyl (1). The procedure for the preparation of this molecule is based on a literature procedure for a similar molecule²⁶. 624 mg (2.0 mmol) g of 2,2'- dibromobiphenyl was placed in a round bottom flask, evacuated with nitrogen and equipped with a gas-flow adapter and dry still adapter. A minimal amount of dry THF was added to the flask from a dry still and the flask was placed in a 0°C bath. 5.0 mL (8.0 mmol) n-BuLi was added drop wise, via syringe, over the course of five minutes; this changed the reaction mixture from clear/colorless to cloudy/light yellow. After the addition the solution was stirred for 20 minutes at 0°C. 0.93 mL (12.0 mmol) of Anhydrous DMF was then added drop wise, by syringe; this changed the reaction mixture clear/colorless. This was then removed from the ice bath and stirred for one hour. The reaction was then quenched with 30 mL of 1 M HCl (aq). The product was extracted with dichloromethane (3 x 50 mL) and the combined organic layers were washed

with water and dried over MgSO₄. The MgSO₄ was filtered off and the CH₂Cl₂ was evaporated to dryness to produce a yellow oil. This product was used without further purification. Yield: (>100%). MS [GC m/z (rel. int.)]: C₁₄H₁₀O₂⁺ 210.1 (10). ¹H-NMR (500 MHz, CDCl₃, δ): 9.82 (d, 2H, CHO), 8.05 (dd, 2H, 3 and 3'), 7.65 (td, 2H, 5 and 5'), 7.58 (tt, 2H, 4 and 4'), 7.34 (dd, 2H, 6 and 6').

[1,1-Carbonyl-¹³C₂]2,2'-Diformylbiphenyl (2). Same procedure used to synthesize 2,2'diformylbiphenyl. Yield: (>100%). MS [APCI+ (TOF) m/z (rel. int.)]: (C₁₂¹³C₂H₁₀O₄+H)⁺ 213.1 (100 %). ¹H-NMR (500 MHz, CDCl₃, δ): 10.02 (s, 1H, CHO), 9.7 (s, 1H, CHO), 8.1 (m, 2H, 3 and 3'), 7.7 (td, 2H, 5 and 5'), 7.64 (tt, 2H, 4 and 4'), 7.39 (d, 2H, 6 and 6').

Phenanthrene (3). The preparation for this molecule is based on a literature procedure²⁷. 423 mg (2.01 mmol) of 2,2'-diformylbiphenyl was placed in a flask fitted with a reflux condenser and taken up in acetic acid. The reaction flask was fitted with a gas-flow adaptor and placed under N₂. The reaction flask was placed in an oil bath and heated to reflux. In a separate vial, a 0.6 M solution of N₂H₄·H₂O in Acetic acid was prepared by adding 4.1 mL AcOH to 0.123 mL (2.5 mmol) N₂H₄·H₂O. This solution was added to the refluxing mixture over the course of one hour, by pipette. The reaction turned dark red-orange as the N₂H₄ solution was added. The reaction was then refluxed for an additional two hours. The reaction vessel was then removed from the oil bath to cool down to ambient temperature and the solvent was evaporated to dryness under a stream of N₂ overnight. The light brown residue was taken up in C₆H₆ and passed through an alumina (neutral) column. The solution was evaporated to dryness and a light yellow powder was obtained. Yield: (81.4 %). MS [GC (EI) m/z (rel. int.)]; C₁₄H₁₀⁺ 178.23 (100). ¹H-NMR (500 MHz, CDCl₃, δ): 8.69 (d, 2H, 4 and 5), 7.88 (dd, 2H, 1 and 8), 7.73 (s, 2H, 9 and 10), 7.64 (td, 2H, 3 and 6), 7.58 (td, 2H, 2 and 7). [9,10-Carbonyl-¹³C₂]Phenanthrene (4). Same procedure used to synthesize phenanthrene. Yield: (64%) MS [GC (EI) m/z (rel. int.)]; $C_{12}^{13}C_2H_{10}^+$ 180.1 (100 %). ¹H-NMR (500 MHz, CDCl₃, δ): 8.68 (d, 2H, 4 and 5), 7.98 (s, H, 9), 7.88 (m, 2H, 1 and 8), 7.68-7.55 (m, 4H, 3 and 6, 2 and 7), 7.46 (s, H, 10).

9,10-Phenanthrenequinone (5). The preparation for this molecule is based on a literature procedure²⁸. 382 mg (3.802 mmol) of CrO₃ was dissolved in AcOH and the flask was placed in an ice bath. In a separate flask, 292 mg (1.6 mmol) phenanthrene was taken up in AcOH, and then added in portions over the course of 2.5 hours, at 0°C. After the addition was complete, the dark orange reaction mixture was warmed to room temperature and then stirred until a dark green reaction mixture persisted (usually 2-3 days). The reaction was quenched by pouring into ~100 mL of H₂O; this produces a yellow voluminous precipitate. The product was then extracted with EtOAc (3 x 50 mL), washed with ~10% NaHCO₃ (aq) and H₂O, and the combined organic layers were dried over MgSO₄. The MgSO₄ was filtered off and the EtOAc solution was evaporated to dryness under a stream of N₂. The yellow residue was recrystallized from hot MeOH to produce orange-yellow plates. Yield: (45%) MS [APCI+ (TOF) m/z (rel. int.)]; (C₁₄H₈O₂+H)⁺ 209.1 (100). ¹H-NMR (500 MHz, CDCl₃, δ): 8.18 (dd, 2H, 4 and 5), 8.01 (d, 2H, 1 and 8), 7.71 (td, 2H, 3 and 6), 7.46 (td, 2H, 2 and 7).

[9,10-Carbonyl-¹³C₂]9,10-Phenanthrenequinone (6). This molecule was prepared with the same procedure as 9,10-phenanthrenequinone. Yield: (43%) MS [APCI+ m/z (rel. int.)]; $(C_{12}^{13}C_2H_8O_2+H)^+$ 211.1 (100). ¹H-NMR (500 MHz, CDCl₃, δ): 8.18 (d, 2H, 4 and 5), 8.01 (d, 2H, 1 and 8), 7.71 (t, 2H, 3 and 6), 7.46 (t, 2H, 2 and 7).

2,2'-Dibromo-5,5'-dimethoxybiphenyl (7). The preparation of this molecule has been previously published²⁹. 2.5 g (11.65 mmol) 3,3'-Dimethoxybiphenyl was dissolved in AcOH

and 2.0 mL (39.02 mmol) Br₂ was added drop-wise. Almost immediately a yellow precipitate forms. The reaction was stirred at room temperature for 2 hours and then the yellow solid is filtered off and recrystallized from hot EtOH to afford colorless crystals. MS [GC m/z (rel. int.)]; (C₁₄H₄O₂)⁺ 371.9207 (100%). ¹H-NMR (500 MHz, CDCl₃, δ): 7.54 (d, 2H, 6 and 6'), 6.83 (dd, 2H, 4 and 4'), 6.80 (d, 2H, 5 and 5'), 3.82 (s, 6H, OMe).

2,2'-Diformyl-5,5'-dimethoxybiphenyl (8). The procedure for this molecule is based on a literature procedure²⁶. 2.14 g (5.5 mmol) of 2,2'-dibromo-5,5'-dimethoxybiphenyl was placed in a round bottom flask evacuated with nitrogen and equipped with a gas-flow adapter and dry still adapter. A minimal amount of dry THF was added to the flask from a dry still and the flask was placed in a -77°C bath (crushed CO₂). 17.1 mL (27.4 mmol) n-BuLi was added drop wise, via syringe, over the course of five minutes; this changed the reaction mixture from clear/colorless to cloudy/yellow. After the addition the solution stirred for 20 minutes at 0°C. 2.85 mL (37 mmol) of anhydrous DMF was then added drop wise, by syringe; this changed the reaction mixture to clear/colorless. This was then removed from the bed of crushed CO_2 and stirred for one hour. The reaction was then quenched with 30 mL of 1 M HCl (aq). The product was extracted with dichloromethane (3 x 50 mL) and the combined organic layers were washed with H₂O and dried over MgSO₄. The MgSO₄ was filtered off and the CH₂Cl₂ solution was evaporated to dryness to produce a yellow oil. This product was used without further purification. Yield: (72%). ¹H-NMR (500 MHz, CDCl₃, δ): 9.69 (s, 2H, CHO), 8.04 (d, 2H, 3 and 3'), 7.08 (dd, 2H, 4 and 4'), 6.8 (d,2H, 6 and 6'), 3.89 (s, 6H, OMe).

[2,2'-Carbonyl-¹³C₂]2,2'-Diformyl-5,5'-dimethoxybiphenyl (9). This molecule was prepared in the same way as 2,2'-Diformyl-5,5'-dimethoxybiphenyl. Yield: (>100%). ¹H-NMR

(500 MHz, CDCl₃, δ): 9.85 (s, H, CHO), 9.8 (s, H, CHO), 8.01 (m, 2H, 3 and 3'), 7.08 (dd, 2H, 4 and 4') 6.8 (d, 2H 6 and 6'), 3.89 (s, 6H, OMe).

3,6-Dimethoxyphenanthrene (10). This molecule was prepared in the same fashion as phenanthrene (**3**). Yield: (58%). MS [GC (EI) m/z (rel. int.)]: C₁₆H₁₀O₄⁺ 238 (100%). ¹H-NMR (500 MHz, CDCl₃, δ): 7.93 (d, 2H, 4 and 5), 7.78 (d, 2H, 1 and 8), 7.54 (s, 2H, 1 and 9), 7.22 (dd, 2H, 2 and 7), 4.02 (s, 6H, OMe).

[9,10-Carbonyl-¹³C₂]3,6-Dimethoxyphenanthrene (11). This molecule was prepared in the same way as phenanthrene (3). Yield: (52%). MS [GC (EI) m/z (rel. int.)]: C₁₆H₁₀O₄⁺ 240.1059 (100%). ¹H-NMR (500 MHz, CDCl₃, δ): 7.93 (d, 2H, 4 and 5), 7.78 (m, 2H, 1 and 8), 7.7-7.62 (distorted m, H, 9), 7.45-7.36 (distorted m, H, 10) 7.22 (dd, 2H, 2 and 7), 4.02 (s, 6H, OMe).

3,6-Dimethoxyphenanthrenequinone (12). This molecule was prepared in the same fashion as 9,10-phenanthrenequinone (**5**). Recrystallized Yield: (44%). MS [GC (EI) m/z (rel. int.)]: C₁₆H₁₀O₄⁺ 268 (35%). ¹H-NMR (500 MHz, CDCl₃, δ): 8.19 (dt, 2H, 2 and 7), 7.37 (d, 2H, 4 and 5), 6.96 (dd, 2H, 1 and 8), 3.75 (s, 6H, OMe).

[9,10-Carbonyl-¹³C₂]3,6-Dimethoxyphenanthrene-9,10-quinone (13). This molecule was prepared with the same procedure as 9,10-phenanthrenequinone (5). Recrystallized Yield: (59%). MS [GC (EI) m/z (rel. int.)]: C₁₆H₁₀O₄⁺ (). ¹H-NMR (500 MHz, CDCl₃, δ): 8.19 (dt, 2H, 2 and 7), 7.37 (d, 2H, 4 and 5), 6.96 (dd, 2H, 1 and 8), 3.75 (s, 6H, OMe).

Physical Measurements. X-ray Crystallography. Single crystal x-ray diffraction data was collected for compound **13** on a Bruker APEX-II CCD area detector single crystal diffractometer at the MSU Center for Crystallographic research. The crystals were irradiated with graphite-monochromatic copper K α radiation ($\lambda = 1.5418$ Å). Data were collected at 173 K with an Oxford Cryosystems low temperature device. Unit cell parameters were determined from least

squares analysis and integrated with the program SAINT v8.34A. The structures were solved using direct methods in the program Olex2 and refined with XL. Anisotropic thermal parameters were refined for all non-hydrogen atoms while hydrogen atom positions were calculated using the riding model.

EPR Spectroscopy. All EPR data were collected on a Bruker Elexsys E-680X spectrometer, operating at X-band frequency (9.42-9.71 GHz). Low temperature experiments were performed between 4-30 K using an Oxford Instruments liquid helium flow system equipped with a CF-935 cryostat and an ITC-503 temperature controller. Quinones were reduced in a glove box with excess sodium metal in THF. The resulting semiquinone solutions were then filtered through a glass frit. The filtered solutions were placed in modified Wilmad Glass SQ-706 EPR tubes with 3.8 mm diameter. Prior to sample preparation, the tubes were modified in the glass blowing lab at Michigan State University to contain a grated seal and vacuum adapter port. A vacuum was pulled on the sample tubes and then the vacuum ports were blown off at the grated seal by hydrogen torch. Prior to collecting CW-EPR data, microwave power-dependence experiments were conducted to ensure non-saturation of the EPR-signal. Continuous wave spectra were simulated using the garlic module of Easy Spin 4.5³⁰⁻³².

All pulsed experiments were conducted at X-band frequency and on the same spectrometer as stated above. ESEEM spectra were obtained using a three pulse sequence of 90° - τ - 90° -T- 90° with 90° pulse lengths of 16 ns. Tau values were chosen to suppress hyperfine contributions from weakly coupled protons. Echo amplitudes were integrated at FWHM and the T values were scanned from 40 ns to 6 µs with a 12 ns time increment. A four step phase-cycling procedure was used to eliminate unwanted 2-pulse echoes³³. Raw data were processed by phase shifting the spectra to remove the dispersion component from the time domain data. The in-phase portion of the data were normalized by dividing by a biexponential background decay function. These normalized data were then further processed by subtracting a second degree polynomial (DC-component of the signal), followed by application of a Hamming window. The data set was then zero-filled from 512 points to 1024 points and Fourier transformed. Frequency spectra are displayed as an absolute value of the transformed time domain data. ¹³C and ¹²C spectra are presented as one divided spectrum at each magnetic field value. After normalizing each time domain spectrum individually, the ¹³C spectrum was divided by the ¹²C spectrum and the same work up procedure described above was applied³⁴.

HYSCORE experiments were carried in a similar manner to the ESEEM experiments but with a four-pulse sequence of 90°- τ -90°- t_1 -180°- t_2 -90° with a 180° pulse length of 16 ns. Echo amplitudes were measured at FWHM and τ values were chosen as stated above. T₁ and t₂ values were scanned from 40 ns to 2 µs with 16 ns time increments. Data sets were 128 points in both dimensions. A 4-step phase cycling program was used to filter out unwanted 2-pulse echoes³⁵. The real, or in-phase portion of the HYSCORE data were processed, in both dimensions, by first subtracting a 2° polynomial, then tapering the data with a Hamming window and zero-filling to 256 points. A two-dimensional fast Fourier transform was applied and absolute values taken. Data are presented as a two-dimensional contour plot. Each contour plot is presented at a threshold of 5-20% of the maximum peak amplitude (z-direction).

Spectra were fit using customized MATLAB scripts where EasySpin was used to perform spectral simulations and the fminsearch function in Matlab was used to optimize the calculation parameters. Fminsearch is a function that finds the minimum of an unconstrained multivariable function using a derivative-free method³⁶. Residuals were calculated by squaring the difference

of the experimental and simulated amplitudes. Goodness of fit for each spectral fit was assessed by calculating a χ^2 value with the following equation:

$$\chi_{n}^{2} = \frac{\Sigma_{i=1}^{N} \frac{\left(y_{i}^{exp} - y_{i}^{calc}\right)^{2}}{\sigma^{2}}}{N - L}$$
(2.1)

where the sum is taken over N points, y_i^{exp} and y_i^{calc} are the experimental and calculated y-axis values, σ is the standard deviation fixed at 2% of the maximum spectral amplitude and L is the number of adjustable variables.

Calculations. Calculations were performed with the Gaussian 03^{37} computational chemistry package on the supercomputing cluster HPCC (High Performance Computing Center) at Michigan State University. Structures were drawn in GaussView 4^{38} and were optimized on phenanthrenesemiquinones (S=1/2) using the unrestricted formalism with the B3LYP³⁹⁻⁴¹ functional and 6-311g(d,p)^{42-45,46} basis set. Frequency calculations were carried out to ensure optimizations reached global minima. Single point calculations were performed at the same level of theory as geometry optimizations. In addition the "pop=(Full,NPA)" keyword command was used to calculate all molecular orbital contributions ('Full') from the atoms and spin densities computed by natural population analyses⁴⁷ (NPA) from the NBO (Natural Bond Order) package.

2.3 Results and Discussion.

Density Functional Theory. Density functional theory was employed to assess the spin density distribution based on the substituent effect of 3,6-R₂-PSQs (where $R = NH_2$, OMe, H, Br, CN, CF₃, NO₂). The unrestricted formalism was used as opposed to the restricted open shell method. The unrestricted approach polarizes all molecular orbitals into singly occupied molecular orbitals (SOMOs) for all electrons whereas restricted open shell only places the radical in a SOMO, all other electrons are paired in traditional molecular orbitals. Geometry optimizations were based on the crystal structure of phenanthrenequinone and derivatives were drawn by modifying phenanthrenequinone in GaussView4. Geometries were optimized and single point calculations were calculated at the UB3LYP/6-311g(d,p) level of theory. All derivatives were optimized to global minima and contained no imaginary frequencies. Spin density was calculated by both Mulikan and NPA analysis within the Gaussian03 software program. The NPA spin densities were calculated by subtracting the beta spin values from the alpha spin values. The spin densities presented are an average of each specific atom pair assessed; e.g. carbonyl carbons were averaged and presented as a single value.

The primary focus of this study was to compare carbonyl carbon spin density to oxygen spin density in PSQs. Although the majority of the unpaired spin density resides on the oxygen atoms, our interest is in determining whether labeling the carbonyl carbons with carbon-13 atoms is a "good" spin label for semiquinones. This method, as stated previously, has some precedence in the literature but for our interests it would be advantageous to use the carbonyl carbon as a marker for spin density variances in semiquinones with similar back bone structure. So by investigating variances in spin density through a theoretical lens, it will be apparent as to whether



or not a carbonyl carbon spin label has the potential to be effective in measuring hyperfine coupling constants effectively.

Figure 2-2. Average carbonyl carbon versus average carbonyl oxygen spin density in 3,6-R₂-PSQs.

Depicted in Figure 2 is a graph that compares the carbonyl carbon spin density to oxygen spin density. There was no linear correlation, but a general trend seems to be operative in that as average carbonyl carbon (ρ) increases, electron donating character increases. These results suggest that changes in carbonyl carbon spin density can be related to a substituent effect. The average oxygen (ρ) also increases with electron donating character, however, to a lesser extent, relative to carbon. There is somewhat of a trend from -NO₂ to -Br, however, once an actual electron donating substituent is considered, the trend devolves into clutter. Indeed, this poses

grounds for using ¹³C instead of ¹⁷O. To restate, the purpose of this exercise is to assess the ability of the carbonyl carbons to be a physical marker for tracking spin density, not necessarily to find a direct relationship between the spin density on the carbonyl carbon atoms and oxygen atoms.

The majority of the spin density, in the series of compounds resides on the oxygen atoms, holding a maximum of 83% (NO₂) of the spin density and minimum of 74% (NH₂), between the two oxygen atoms and two carbon atoms. The carbonyl carbons contribute 26% (NH₂) at the most and 17% (NO₂) at the least; figures 3 and 4 show this trend quite vividly.



Figure 2-3. Average oxygen spin density versus total carbonyl spin density.



The most notable observation here is that carbonyl carbon spin density (Figure 3) tracks with total carbonyl spin density more than oxygen spin density (Figure 4). Although there is no linear

Figure 2-4. Average carbonyl spin density versus average carbonyl carbon spin density.

correlation in Figure 4, the increasing amount of spin density on the carbonyl carbons (with respect to electronegativity of the substituent) suggests that the carbonyl carbon spin density has a greater dependence on the electronegativity of the substituent than the oxygen atoms. It is important to note that electronegativity is a property of all the electrons in the system and the spin is based solely on the electron occupying the SOMO. The carbonyl group contributes 38% to the composition of the SOMO, with 18% from oxygen and 10% from carbon (when R = H).

From this short analysis, it can be concluded that using ¹³C as a means of tracking changes in spin density could be a useful method. The changes in spin density are more drastic than 17O and even have a general trend of increasing with electron donating ability.

Synthesis. Recent EPR studies of labeled semiquinones and the synthesis of such compounds has been largely dominated by the area of bioorganic chemistry. Specifically, studying the spin density distribution of ubisemiquinone has been an area of interest due to its involvement in electron transfer chemistry in oxidases. This *para*-quinone is a six membered quinone with methyl and methoxy groups nestled between the carbonyl groups, with an additional polymeric side chain protruding from the opposite side of the ring. Similar to the study presented here, the carbonyl carbons have been replaced by ¹³C atoms in favor of tracking spin density changes^{19,48}. The labeled molecules were achieved through several synthetic steps and required several ¹³C sources. In regards to this field of study, the ring carbons²⁰ as well as the methyl and methoxy substituents²¹ have also been ¹³C-labeled and studied with EPR methods. Along the lines of isotopic labeling of quinones and investigating their spin properties, the other investigations found in the literature revolve around switching the carbonyl ¹⁶O atoms for ¹⁷O atoms¹⁵⁻¹⁷.

The syntheses of the organic molecules were based on procedures previously developed in the literature. The "total synthesis" of this model was realized through trial and error of retrosynthetic analysis. The procedure that was arrived at can be seen in Figure 5. Reducing the parent quinone and cleaving the carbon-oxygen double bonds affords phenanthrene. Phenanthrene opens up possibilities for placing carbon-13 atoms in the 9 and 10 positions of phenanthrenequinone. Splitting the 9,10 carbon-carbon double bond into two vinyl groups allows for the possibility of creating a ring closing metathesis reaction where the olefin groups of 2,2'-divinylbiphenyl would be clipped together by a first or second generation Grubbs' catalyst²⁶. However, obtaining the divinyl-biphenyl species would require a step where an aldehyde is transformed into an olefin (perhaps by a Wittig reaction). In the interest of keeping the number of reactions to a minimum, it was decided to pursue a coupling method for aldehydes, to produce a double bond from the aldehyde carbons. The final retrosynthetic step involves removing the aldehyde group and replacing it with a leaving group.



Figure 2-5. Retrosynthetic analysis for synthesizing a di-¹³C-labeled phenanthrenequinone.



Figure 2-6. General synthetic scheme for $[^{13}C_2]$ phenanthrenequinone.

The general synthetic route for the ¹³C-labeled compounds can be seen in Figure 6. The ¹³C-labeled diformyl-biphenyl compounds (both -H, compound **2**, and -OMe, compound **9**) were achieved by first adding nBuLi to 2,2'-dibromobiphenyl at low temperature, under N₂, during which lithium-bromide exchange produces a stable di-aryl-carbanion (provided the cryogenic temperature is held constant). The carbanion is then quenched by adding [¹³C]DMF to the reaction; the carbanion attacks the carbonyl carbon forming a new carbon-carbon single bond. The carbonyl oxygen is stabilized by the lithium cation until the reaction is quenched by aqueous hydrochloric acid; it has been hypothesized²⁶ that by protonating the nitrogen, the carbonyl pi bond reforms and releases dimethylamine gas to complete the formylation. Observations are consistent with this hypothesis as upon addition of acid to the reaction mixture, a colorless gas is formed. This gas was subsequently blown off with N₂.

The ¹³C-labeled diformyl biphenyl species were then subjected to a reductive homocoupling. The carbonyl groups of diformyl biphenyl were activated by dissolving the compound in AcOH. Then N_2H_4 was added to the diformyl-biphenyl compounds, at reflux, in portions over the course of two hours. After each addition, the reaction mixture became darker and more orange in color. The authors have hypothesized²⁷ that the intermediate for this reaction is an eight-membered ring



Figure 2-7. Proposed intermediate formation and expulsion of N_2 for synthesizing phenanthrene from 2,2'-diformyl biphenyl. The figure was reproduced from Reference 22.

presumably produced by a typical Schiff base reaction. The authors found that when the aldehyde proton was replaced with an alkyl or aryl group, the stable diazocine was obtained, but the reaction involving the aldehyde groups expelled N_2 and left phenanthrene as the sole product⁴⁹. After releasing N_2 , the imine carbons then clip together to produce [9,10- $^{13}C_2$]phenanthrene (Figure 7). Finally, phenanthrene was oxidized by a modified Jones oxidation with CrO₃ and AcOH to afford the [9,10-carbonyl- $^{13}C_2$]phenanthrenequinone.

The synthesis for 3,6-(OMe)2-phenanthrenequinone was performed in the same fashion as phenanthrenequinone.

Ground State Characterization. X-ray Crystallography. X-ray quality crystals of **13** were grown from slow evaporation of the CDCl₃ solvent in an NMR tube. The structure was found to be in the $P2_1/c$ space group with a residual of 0.038.



Figure 2-8. Crystal structure of $[9,10^{-13}C_2]3,6$ -(OMe)₂-PhenQ (13). The structure is displayed with thermal ellipsoids at 50% probability.

Table 1 shows the selected bond lengths and angles for **13**. The carbonyl bonds were found to be symmetrical, and of typical carbon-oxygen double bond length. The carbonyl carbon-oxygen bond lengths are similar to the carbonyl carbon-oxygen bond lengths for 9,10-phenanthrenequinone, 1.215 Å (average between 2 crystal morphologies), as well as the intradiol distance (C-C bond connecting carbonyl carbons), 1.52 Å (average between two crystal morphologies)⁵⁰. The carbon-carbon bond lengths of the central ring were found to be longer than typical aromatic carbon-carbon bond lengths, which is due to the cross-conjugated nature of the quinone group and the phenanthrene fused ring system. The C3-C8 and C9-C14 bond lengths are ~0.6-0.7 Å shorter than the C2-C3 and C14-C1 bond lengths, respectively, giving credit to the resonance structure pictured below.



Figure 2-9. Resonance structure of 3,6-(OMe)2-PhenQ.

Table 2-1. Selected bond lengths and angles for compound 13	Table 2-1.	Selected bon	d lengths	and angles	for compound	13.
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Bond Di	stances (Å)	Bond Angle	es (Degrees)
O1-C1	1.2176 (15)	O1-C1-C2	118.76 (11)
O2-C2	1.2160 (15)	O1-C1-C14	123.34 (12)
C1-C2	1.5421 (17)	C14-C1-C2	117.90 (10)
C2-C3	1.4720 (16)	O2-C2-C1	119.21 (10)
C3-C8	1.4152 (16)	O2-C2-C3	123.25 (11)
C8-C9	1.4851 (16)	C3-C2-C1	117.54 (10)
C9-C14	1.4109 (16)		
C14-C1	1.4697 (16)		

 Table 2-2. Crystal structure parameters for compound 13.

Formula	$C_{16}H_{12}O_4$
Molecular Weight	268.26
Crystal System	Monoclinic
Space Group	$P2_{l}/c$
$a/ m \AA$	6.8451 (1)

Table 2-2. (cont'd)

$b/{ m \AA}$	21.5856 (3)
c/Å	8.0850 (1)
β/°	69.4644 (7)
Volume/Å ³	1187.01 (3)
Ζ	4
Density	1.501 Mg·m ⁻³
Temperature	173 K
Reflections Measured	8695
Independent Reflections	2284
Observed Reflections with $I > 2\sigma(I)$	2137
μ (Cu K α)/mm ⁻¹	0.90
$R1[F^2>2 \sigma(F^2)]$	0.038
$wR(F^2)$	0.106

NMR Spectroscopy. ¹H-NMR spectra of the labeled and non-labeled molecules show splitting in the NMR spectra that correspond to ¹³C-labeling. Due to the $I = \frac{1}{2}$ nature of the ¹H and ¹³C nuclei, the coupling of the two nuclei should produce a splitting of the aldehyde proton in the ¹H-NMR spectrum of the labeled compound relative to the non-labeled molecule. This is precisely what is observed; the aldehyde protons correspond to one resonance at a chemical shift of 9.83 ppm in the ¹²C-diformylbiphenyl and integrate to two protons. When compared to the ¹³C-diformylbiphenyl, the single resonance splits into two separate resonances (a rather strongly coupled doublet, one at 10.0 ppm and a second at 9.65 ppm). A secondary advantage of ¹³C- labeling is proton assignment. The doublet at 8.05 in the 12 C spectrum is further split into a doublet of doublets in the 13 C spectrum, which supports the assignment of the 3 and 3' 1 H's at that resonance. The aromatic and aldehyde regions of the 1 H-NMR of (CHO)₂-Ph₂ and (13 CHO)₂-Ph₂ spectra are seen in Figure 10.



Figure 2-10. ¹H-NMR spectra of (CHO)₂-Ph₂ (bottom) and (¹³CHO)₂-Ph₂ (top). Bold numbers are relative integrals with respect to the aldehyde proton(s).

This splitting of the aldehyde protons is also observed in the ¹²C and ¹³C dimethoxy derivatives of diformyl-biphenyl (**8** and **9**). As described above, the aldehyde protons are split by the ¹³C-carbonyl carbons, and produce two singlets at 9.69 and 10.05 ppm, as well as incurring a new splitting pattern in protons 3 and 3' (8.02 ppm) by going from a doublet (¹²C spectrum) to a doublet of doublets (¹³C spectrum).



Figure 2-11. ¹H-NMR spectra of (CHO)₂-(OMe)₂-Ph₂ (bottom) and (¹³CHO)₂-(OMe)₂-Ph₂ (top). This effect can also be seen in the spectra of the labeled and non-labeled phenanthrene. The 9 and 10 protons have been assigned to the resonance at 8.03 ppm in the ¹²C-phenanthrene spectrum (Figure 11); however, in [¹³C₂]phenanthrene this single resonance also splits into two prominent resonances, 7.99 and 7.46. This spectrum is not as easily understood as the diformyl-biphenyl spectrum; the two singlets only integrate to 0.5 ¹H each, leaving the other half grouped into resonances (multiplets) at 7.6 and 7.88. The dimethoxy derivatives of diformyl-biphenyl and phenanthrene exhibit this same effect.

CW-EPR. In an EPR experiment, electron spin states are probes in the presence of an applied magnetic field. The electron Zeeman effect is the main interaction which is a

consequence of the interaction of the unpaired electron's magnetic moment and the applied magnetic field as described by:

$$\widehat{H} = -\boldsymbol{\mu} \cdot \boldsymbol{B} = \frac{g\beta_e}{\hbar} \widehat{\boldsymbol{S}} \cdot \boldsymbol{B}$$
(2.2)

where g for a free electron is 2.0023, **B** is the applied magnetic field, β is the electron Bohr magneton (9.274e-24 J·T⁻¹) and \hat{S} is the electron spin operator. Then, if the z-axis is coincident with the axis of the laboratory field, then $B_o \parallel z$, the dot product becomes

$$\widehat{H} = \frac{g\beta_e B_o}{\hbar} \widehat{S}_z \tag{2.3}$$

For an S = $\frac{1}{2}$ spin system, the stabilized microstate is $m_s = -\frac{1}{2}(\beta)$, and is aligned parallel with the applied magnetic field; the destabilized state is then $m_s = \frac{1}{2}(\alpha)$ and is aligned antiparallel with the magnetic field. These spin states are eigenfunctions of \hat{S}_z , so for spin states $|\beta\rangle$ and $|\alpha\rangle$, $\hat{S}_z|\beta\rangle = \frac{-\hbar}{2}|\beta\rangle$ and $\hat{S}_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle$. Then, the time-independent Schrödinger equation can be applied and the energies can be obtained from the energy expression below:

$$E = m_s g\beta B \tag{2.4}$$

In a conventional EPR experiment, continuous microwave radiation, of a fixed frequency, is applied to the sample and the magnetic field, *B*, is scanned to achieve resonance. The resultant EPR absorption spectrum is displayed as a first derivative, as a result of field modulation and phase-sensitive detection. Additionally, these conditions provide for accurate g-value measurement, and enhanced sensitivity. Figure 12, below, shows this effect pictorially:





The above case is for a free radical, that is not coupled to any nuclei. When the unpaired electron spin is coupled to a nuclear spin, the nuclear Zeeman and hyperfine terms are introduced to the Hamiltonian.

$$\widehat{H} = g_e \beta_e B \widehat{S}_z - g_N \beta_N B \widehat{I}_z + \widehat{S} \cdot A \cdot \widehat{I}$$
(2.5)

The second term of the Hamiltonian is the nuclear Zeeman where \hat{I} is the nuclear spin angular momentum operator. The third term is the hyperfine coupling parameter where A is the hyperfine coupling tensor, which is a 3x3 matrix that describes the coupling between the electron and nuclear magnetic moments. If the sample (paramagnetic molecule) is tumbling fast through solution, relative to the timescale of the EPR experiment, then the hyperfine coupling tensor becomes A_{iso} •1. The bold 1 is the unit matrix; with this replacement, the Hamiltonian can be written as follows:

$$\widehat{H} = \omega_S \widehat{S}_z - \omega_I \widehat{I}_z + A_{iso} \left(\widehat{I}_x \widehat{S}_x + \widehat{I}_y \widehat{S}_y + \widehat{I}_z \widehat{S}_z \right)$$
(2.6)

where $\omega_{\rm S}$ and $\omega_{\rm I}$ are simply compact ways of writing the Zeeman pre-factors (e.g., $\omega_{\rm S} = \frac{g\beta_e B_o}{\hbar}$). These are also known as the electron and nuclear Larmor frequencies in angular units. The xand y- spin operator terms can be ignored from equation 2.6 if A_{iso} << $\hbar\omega_{\rm S}$, and this yields

$$\widehat{H} = \omega_S \widehat{S}_z - \omega_I \widehat{I}_z + \frac{2\pi a_{iso}}{\hbar} \widehat{S}_z \widehat{I}_z$$
(2.7)

and a_{iso} is the isotropic hyperfine coupling with units of MHz. Using the above form of the Hamiltonian to operate on the spin product states $|m_S m_l\rangle$, yields the following energy states:

$$E_{1} = -\frac{\hbar\omega_{S}}{2} - \frac{\hbar\omega_{I}}{2} - \frac{\hbar a_{iso}}{4}$$

$$E_{2} = -\frac{\hbar\omega_{S}}{2} + \frac{\hbar\omega_{I}}{2} + \frac{\hbar a_{iso}}{4}$$

$$E_{3} = \frac{\hbar\omega_{S}}{2} - \frac{\hbar\omega_{I}}{2} + \frac{\hbar a_{iso}}{4}$$

$$E_{4} = \frac{\hbar\omega_{S}}{2} + \frac{\hbar\omega_{I}}{2} - \frac{\hbar a_{iso}}{4}$$

E₁ and E₂ correspond to the $|\beta \alpha_N\rangle$ and $|\beta \beta_N\rangle$ states, respectively, in the lower spin manifold, and E₃ and E₄ correspond to $|\alpha \alpha_N\rangle$ and $|\alpha \beta_N\rangle$ states, respectively. The allowed transitions are governed by the selection rules $\Delta m_S = \pm 1$ and $\Delta m_I = 0$; thus the transitions are E₁ \rightarrow E₃ and E₂ \rightarrow E₄. The change in energy, with respect to these transitions is then

$$\Delta E = \hbar \omega_S \pm \frac{h a_{iso}}{2} \tag{2.8}$$

and the splitting between the two nuclear states within each electron spin state are

$$\Delta E_{nuc} = \hbar \omega_I \pm \frac{h a_{iso}}{2} \tag{2.9}$$

These transitions and their associated energies are reflected below, in Figure 13.



Figure 2-13. Electronic and nuclear Zeeman effects. Allowed EPR transitions are highlighted by double-headed arrows in the M_I manifold.

Continuous Wave EPR spectra were collected at various temperatures and field modulation values. It has been documented that large field modulation values can affect lineshape, so as to cause line distortions to resemble unresolved hyperfine splitting⁵¹. In light of these observations, room temperature CW spectra were collected at 20 mG, 500 mG and 1 G modulation amplitudes. The 20 mG spectra have been simulated and fit, and are discussed in the body of this chapter while the 500 mG and 1 G spectra are located in the Chapter 2 Appendix.

The 20 mG, room temperature CW spectra were fit with the following parameters: *g*-factor, Voigtian (Gaussian + Lorentzian) peak-to-peak line-broadening (abbreviated lwpp), and isotropic hyperfine coupling parameters. The *g*-factors were taken from λ -max (inflection point) of the 1 G spectra. Initial guesses for ¹H a_{iso} values came from previous works and Gaussian03 calculations. ¹H a_{iso} values were varied until the width of the simulated spectrum matched the spectral width of the experimental spectrum. Then, line width parameters were adjusted to accommodate both Gaussian and Lorentzian parameters of the lineshape. Once a decent fit was achieved, all simulation parameters were fit with the fminsearch tool in Matlab. This was repeated until the residual value reached a minimum.



Figure 2-14. EPR spectrum of PSQ. Reproduced from Reference 52.

The EPR spectrum of PSQ has previously been recorded⁵² (Figure 14). Phenanthrenequinone was reduced with zinc metal in alkaline solution, and the spectrum was found to have five groups of five lines, which corresponds to a system where there are two groups of four equivalent protons. It was not indicated which sets of protons were considered to be equivalent and only 26 lines were observed, possibly due to overlapping lines and low resolution.

For a molecule with an equivalent pair of protons the number of lines is predicted by the formula 2nI + 1, where *I* is the nuclear spin and *n* is the number of equivalent nuclei. For example, four lines are predicted for the methyl radical and four lines are observed, in a 1:3:3:1

peak ratio^{53,54}; $I = \frac{1}{2}$ for protons and n = 3. However, for a system where there are several sets of equivalent nuclei, the equation becomes a product of the prediction for the individual sets. For PSQ with four sets of two equivalent protons each, the number of lines expected would be represented by

$$\# of Lines = [(2nI + 1)(2mI + 1)(2pI + 1)(2qI + 1)]$$
(2.10)

where n = m = p = q = 2; the result being 81 lines. As stated above, only 26 lines were observed, which leads to the conclusion that there are unresolved hyperfine couplings and/or overlapping lines.

Phenanthrenesemiquinone has also been studied by Kazuhiro in the 1960s.⁵⁵ Kazuhiro studied the EPR dependence on alkali and alkaline earth "ketyls" (semiquinone). Kazuhiro found that by reducing phenanthrenequinone into its various alkali and alkaline ketyls, the hyperfine splittings and spectral width were dependent on the reducing metal; although, Kazuhiro conceded no reason as to why this phenomenon occurred. Kazuhiro also provided hyperfine splittings for a free radical phenanthrenequinone, reduced with potassium in liquid ammonia. The main difference between Kazuhiro's work and that of Sands', aside from the reduction methods, is that the protons are grouped differently. Sands shows two sets of hyperfine splittings, 4.65 MHz and 1.07 MHz, for two sets of four protons, while Kazuhiro has three groups of protons for the free radical, 4.37 MHz (four equivalent protons), 1.23 MHz (two protons) and 1.01 MHz (two protons).



Figure 2-15. Room temperature EPR spectrum (black) and simulation (red) of PSQ radical anion at 20 mG modulation amplitude. Simulation parameters: g = 2.00754, lwpp = 0.0005 mT, 0.0191 mT, a_{iso} values: ²³Na = 1.32 MHz, ¹H_{4,5} = 0.77 MHz, ¹H_{2,7} = 1.19 MHz, ¹H_{1,8} = -4.06 MHz and ¹H_{3,6} = -4.75 MHz. Experimental parameters: 9.85 GHz μ W frequency, 0.50 mW power, 3508 G center field, 20 G sweep width, 20 mG modulation amplitude, 1024 points. $\chi^2 = 0.39$.

The room temperature, CW spectrum of the PSQ radical anion at 20 mG modulation amplitude is shown in Figure 15 (see above). These values correlate well with what has been found in the literature for PSQ (in MHz): 4.68, 3.78, 1.18, 0.56⁵⁶. The number of lines present in the spectrum is approximately 38, which does not agree with the theoretical number of lines. The approach to fit this spectrum was to include only the protons; however, this path produced a simulation that required one set of two protons to be inequivalent. After further investigation, it

was found that in order to properly model the spectra above, a sodium ion was needed in the simulation. With a sodium ion included, the total expected number of lines is 324. It is perhaps the case that all the lines are not visible due to the limits of the spectrometer.

Figure 16 depicts a cartoon that includes a sodium ion as part of the model system. Initially it was not our impression that sodium was participating in the hyperfine coupling; again, upon analyzing the spectrum, it became clear that the four groups of two protons were not the only active nuclei. Using only four groups of two protons produced line shapes that were not consistent with the experimental spectrum. As previously stated, making one set of protons inequivalent allowed for a proper line shape; however, this approach was not logical as the molecule has C_{2v} symmetry and the proton hyperfine coupling constants will be the same for corresponding protons across the vertical mirror plane. Thus, a single sodium ion was added to the simulation, in addition to the four groups of two protons; this addition produced a line shape similar to that of the experimental spectrum. It is not known that the sodium ion is interacting with the oxygen atoms directly, because there is no crystal structure of this species, but due to the electrostatic nature of the two components, this was the most logical place for the Na⁺. In the literature, this is referred to as ion pairing and is consistent with Kazuhiro's analysis.⁵⁷ Upon addition of the Na⁺, the spectrum was able to be fit with a respectable χ^2 value of 0.39.



Figure 2-16. Possible Na⁺ coordination to PSQ⁻⁻.



Figure 2-17. PSQ (black) and [¹³C₂]PSQ (red) overlaid CW spectra.

Figure 17 shows the spectra of PSQ (black) versus [${}^{13}C_{2}$]PSQ (red). ${}^{13}C_{1}$ abelling appears to have an overall line-broadening effect, relative to the ${}^{1}H_{-}$ coupling in PSQ. Figure 18 depicts the ${}^{13}C_{2}$ PSQ spectrum (black) and simulated spectrum (red). The [${}^{13}C_{2}$]PSQ CW data was simulated by first holding the PSQ ${}^{1}H_{-}a_{iso}$ constant, as well as the linewidth parameters and *g*-factor. Then, ${}^{13}C_{-}a_{iso}$ values were added and varied until a minimal residual value was obtained; the linewidth parameters and *g*-factor were adjusted for an optimal χ^{2} value. The data were found to be fit with ${}^{13}C_{-}a_{iso}$ values in the range of 1.5 – 2.2 MHz (absolute values). These values were obtained by varying carbonyl carbon hyperfine coupling and linewidth parameters. It will become more clear in the ESEEM section as to why the spectrum was fit with multiple ${}^{13}C_{-}a_{iso}$ values, but to summarize shortly, ESEEM data suggest the presence of multiple species. Figure 18 shows the [${}^{13}C_{2}$]PSQ spectrum and spectral fit with ${}^{13}C_{-}a_{iso} = 1.57$ MHz. CW simulations were not dependent on the sign of the hyperfine coupling.



Figure 2-18. Room temperature EPR spectrum (black) and simulation (red) of ¹³C₂PSQ radical anion at 20 mG modulation amplitude. Simulation parameters: g = 2.00755, lwpp = 0.0001 mT, 0.0222 mT, ¹³C- a_{iso} values: 1.57 MHz. Experimental parameters: 9.85 GHz μ W frequency, 0.50 mW power, 3508 G center field, 20 G sweep width, 20 mG modulation amplitude, 1024 points. $\chi^2 = 0.85$.



Figure 2-19. Room temperature EPR spectrum (black) and simulation (red) of ${}^{13}C_2PSQ$ radical anion at 20 mG modulation amplitude. Simulation parameters: g = 2.00755, lwpp = 0.0001 mT, 0.0255 mT, ${}^{13}C$ - a_{iso} values: 2.17 MHz. Experimental parameters: 9.85 GHz μ W frequency, 0.50 mW power, 3508 G center field, 20 G sweep width, 20 mG modulation amplitude, 1024 points. $\chi^2 = 1.02$.

Table 3 summarizes the results from the simulations/fits and DFT calculations found for PSQ and [$^{13}C_2$]PSQ a_{iso} values. The first row contains the results from simulating the experimental spectrum of the NaPSQ complex, the second row contains the Fermi analysis from PSQ⁻⁻ and the third row contains the Fermi analysis from NaPSQ. After analyzing the CW data, further calculations were undertaken to properly compare to the NaPSQ complex. The DFT module used for calculating isotropic hyperfine coupling constants is the Fermi contact integral. With respect to 1 H- a_{iso} values, the predicted values resemble the calculated values quite well. Most importantly, the order of ascending/descending magnitude of hyperfine coupling agrees between
the fits and DFT results. These values do resemble what has been seen in the literature for PSQ. In all cases the H_{3,6} values are in agreement. There is some discrepancy between the remaining ¹H values; the NaPSQ DFT model seems to model the ¹H- a_{iso} values to a greater degree while the PSQ model accurately predicts the H_{2,7} and H_{4,5} values. Two other reports have found two sets of four equivalent protons with $a_{iso} = 4.65$ and 1.065 MHz⁵⁷, and three sets of protons (one group of four protons and 2 groups of 2 protons each) with $a_{iso} = 4.372$, 1.233 and 1.01 MHz⁵², respectively.

Table 2-3. ¹H, ¹³C and ²³Na a_{iso} and DFT calculated values (Fermi contact integral). All values in MHz.

	H _{3,6}	H _{1,8}	H _{2,7}	H4,5	²³ Na	¹³ C _{C=0}
Data - a _{iso}	4.75	4.06	0.77	1.19	1.32	1.57,2.17
PSQ - Fermi	-4.59	-2.38	0.43	1.33	-	-10.25
NaPSQ - Fermi	-4.69	-4.41	1.14	1.37	-7.06	-1.84



Figure 2-20. Visual representation of Table 3. The a_{iso} values listed are located at each of their respective nuclear positions.

The greatest disagreement in values concerns the carbonyl carbon and ²³Na a_{iso} values. Undeniably, the ²³Na- a_{iso} value found by the simulation completely disagrees with the calculated value. Previously, the sodium ion contribution to the hyperfine coupling was unrecorded and/or, not measured⁵⁷. Hyperfine coupling constants for metals in a series of compounds of Group III metal halides chelated to PSQs were measured by Klimov, et al. In the closest comparison, aluminum was found to have a $a_{iso} = 5.88$ MHz in [Al(PSQ)Cl₂]. Though, no other studies were found to quantitatively accommodate Group I or Group II metal contribution to the hyperfine. The first of these studies have begun here, with sodium.

Including Na⁺ in the experiment was both favorable and detrimental to the experiment. In favor of using Na as a reductant, it showed that a significant portion of spin delocalization is possible, across the carbonyl bridge. As a detriment to the experiment, the Na⁺ adds to the complexity of the spectrum, as will also be evidenced in the ESEEM section below. Ideally, an isolated picture of PSQ's spin distribution would have been advantageous, rather than a NaPSQ complex. An unobstructed view of the hyperfine interaction could be achieved by reducing phenanthrenequinone by electrical ionization, or even using a different reducing metal. For example, ³⁹K has an I = 3/2 nucleus, but the Larmor frequency would be quite small, approximately 0.7 MHz at 3500 G (g 2). In addition, the hyperfine coupling to ³⁹K would be reduced by a factor of 5.6, relative to ²³Na; this factor comes is a result of comparing the nuclear g-values.

The carbonyl carbon values were correctly predicted by the NaPSQ model calculation, rather than PSQ⁻, which does not include sodium contribution. Figure 16 depicts the Na⁺ ion coordinated between the two carbonyl oxygen atoms, which is supported by the difference in calculated hyperfine coupling of the PSQ and NaPSQ carbonyl carbons. Comparatively, there have not been other studies where carbon-13 was used as an isotopic label at the carbonyl carbon in phenanthrenequinone; there have been some accounts in other *ortho*-semiquinones, however. The carbonyl carbons of *ortho*-benzosemiquinone have been found to have an $a_{iso} = 5.66$ MHz⁵⁸,

which is several times than what was found for carbonyl carbons in this work. This could be attributed to the greater degree of delocalization in PSQ, due to the extended aromatic network.

The sign of the hyperfine is not usually obtainable from conventional CW experiments, but rather a culmination of several techniques. One of which includes a double ENDOR technique that probes the ENDOR transition of one type of nuclei followed by a second ENDOR excitation of another type of nucleus. The sign of the hyperfine is then determined by the change of intensity from the first ENDOR signal to second ENDOR signal^{59,60}.

The isotropic hyperfine coupling can be related to the spin density through the following equation:

$$a_{iso}(N) = \frac{4\pi}{3} g_e g_N \beta_e \beta_N \langle S_z \rangle^{-1} \rho(N)$$
(2.11)

where g_e is the electron g-factor, g_n is the nuclear g-factor, β_e is the electron Bohr magneton, β_N is the nuclear Bohr magneton, S_z is the spin operator and $\rho(N)$ is the Fermi contact integral at nucleus N, or the spin density at nucleus N. Nguyen and coworkers have summarized the collection of physical constants for individual nuclei with the following singular constants; a_{iso} in MHz and spin density is therefore unitless⁶¹:

$$a_{iso}({}^{1}H) = 4469.7\rho({}^{1}H)$$
 (2.12a)

$$a_{iso}(^{13}C) = 1124.1\rho(^{13}C)$$
 (2.12b)

If then, these equations are applied to the a_{iso} values obtained in Table 1, the following spin densities are obtained for PSQ, in Table 4.

	H _{3,6}	H _{1,8}	H _{2,7}	H4,5	²³ Na	¹³ C _{C=0}
$\rho(N)_{\text{Data}}(x10^{-3})$	1.06	0.91	0.17	0.26	-	1.39,1.93
$\rho(N)_{\text{Fermi}}(x10^{-3})$	1.05	0.99	0.25	0.30	-	1.6

Table 2-4. Calculated spin density values from equations 2.8a and 2.8b for NaPSQ complex (data and from Fermi analysis). Spin density values are unit-less.

The second radical system studied was 3,6-(OMe)₂-PSQ radical anion. Unlike the PSQ system, this radical anion has not been investigated previously by EPR. The addition of methoxy groups introduces π - donating effects to the phenanthrene ring system, as well as σ - accepting. In the DFT study it was found that, relative to PSQ, the methoxy substituents polarized spin away from the oxygen atoms; the decrease in oxygen spin density is ~2.5%, relative to PSQ. However, this EPR study is concerned with difference in carbonyl carbon hyperfine coupling between the two compounds, which is related to spin density, but is not the same as spin density. Regardless of the differences of the two quantities, the hyperfine interaction will be used to calculate the isotropic contribution to the spin density, just as with PSQ.

The CW EPR spectrum of Na(3,6-(OMe)₂-PSQ) can be seen in Figure 26. The number of lines present is approximately 32, which like NaPSQ, does not agree with the number of theoretical lines. The number of lines that should be present, according to equation 2.5, is 1,620, which is inconsistent with the number of lines present. This is consistent, however, with the NaPSQ complex.



Figure 2-21. Room temperature EPR spectrum (black) and simulation (red) of Na(3,6-(OMe)₂-PSQ) radical anion at 20 mG modulation amplitude. Simulation parameters: g = 2.00746, *lwpp* = 0.0015 mT, 0.0135 mT, a_{iso} values: ²³Na = 1.17 MHz, ¹H_{Me-a} = 0.56, ¹H_{Me-b} = 0.41 ¹H_{4,5} = 0.96 MHz, ¹H_{2,7} = 1.01 MHz and ¹H_{1,8} = 3.84, MHz. Experimental parameters: 9.85 GHz μ W frequency, 0.5 mW power, 3508 G center field, 20 G sweep width, 20 mG modulation amplitude, 1024 points. $\chi^2 = 0.52$.

Similarly, to NaPSQ, the final values of the simulation were found by holding the gfactor and linewidth parameters constant, and varying the hyperfine parameters until the width of the simulation matched the spectral width of the experimental spectrum. The linewidth parameters were adjusted to account for the Gaussian and Lorentzian lineshape and finally all the parameters were then minimized with fminsearch in Matlab, until a global minimum was reached. Methoxy protons were not originally considered in the simulations but were added to account for the high degree of splitting in the spectrum. The hyperfine coupling constants are comparatively less than the hyperfine couplings from NaPSQ (see Table 5 below). By replacing the 3,6-protons with methoxy groups, the hyperfine coupling is now spread to the methoxy groups as well. In addition to being a π -donating group, methoxy substituents also double as sigma-acceptors, so it is sensible that the proton couplings are smaller in magnitude, relative to NaPSQ, because the isotropic contribution to the hyperfine is directly related to the *s* – electron density. Additionally, the majority of the DFT predicted ¹H a_{iso} values agree with the experimental results. The one discrepancy being that DFT predicted that methoxy protons have a larger coupling than the 4,5-protons on the ring.



Figure 2-22. [¹³C₂]3,6-(OMe)₂-PSQ (red) versus 3,6-(OMe)₂-PSQ (black) spectra.

The room temperature, CW spectrum of $[{}^{13}C_2]3,6-(OMe)_2$ -PSQ versus 3,6-(OMe)_2-PSQ can be seen above in Figure 22. The effect of ${}^{13}C$ addition is apparently rather small and the resulting EPR spectrum resembles the ${}^{12}C$ spectrum almost perfectly. The spectrum (black) and fit (red) of $[{}^{13}C_2]3,6-(OMe)_2$ -PSQ is shown in Figure 23. The spectrum was fit with ${}^{13}C a_{iso} =$ 0.41. This spectrum was fit with multiple ${}^{13}C a_{iso}$ values, similarly to $[{}^{13}C_2]$ PSQ; the additional ${}^{13}C a_{iso}$ values are 0.98 MHz and 0.16 MHz. The reason for multiple ${}^{13}C a_{iso}$ values is due to ESEEM data confirming multiple species in solution. The other spectral fits are shown in the Chapter 2 Appendix.



Figure 2-23. Room temperature EPR spectrum (black) and simulation (red) of Na[${}^{13}C_2$]3,6-(OMe)₂-PSQ at 20 mG modulation amplitude. Simulation parameters: g = 2.007443, lwpp = 0.0015 mT, 0.0145 mT, ${}^{13}C$ - a_{iso} value: 0.41 MHz. Experimental parameters: 9.85 GHz μ W frequency, 0.5 mW power, 3508 G center field, 20 G sweep width, 20 mG modulation amplitude, 1024 points. $\chi^2 = 0.50$.

In terms of a substituent effect, there does seem to be a difference between PSQ and 3,6-(OMe)₂-PSQ. Considering ¹H a_{iso} values alone, ¹H_{1,8} and ¹H_{2,7} decrease from PSQ to 3,6-(OMe)₂-PSQ. Moving to carbonyl carbons, a much more dramatic effect is operative. [¹³C₂]PSQ has a_{iso} values in the range of 1.5 – 2.2 MHz while [¹³C₂]3,6-(OMe)₂-PSQ was found to have a_{iso} values 0.15 - 1 MHz. Table 5 tabulates the isotropic coupling pathways for Na(3,6-(OMe)₂-PSQ).

	H _{1,8}	H _{2,7}	H4,5	H _{Me-a}	H _{Me-b}	²³ Na	¹³ C _{C=0}
_							
Data - a_{iso}	3.84	1.01	0.96	0.56	0.41	1.17	0.41,0.16,0.98
OMePSQ-	-1.40	-0.54	0.43	0.23	-0.17	-	-9.85
Fermi							
NaOMePSQ -	-3.71	1.41	0.42	0.71	-0.14	-6.98	-1.25
Fermi							

Table 2-5. ¹H, ¹³C and ²³Na *a*i_{so} coupling constants, in MHz, for Na(3,6-(OMe)₂-PSQ).



OMePSQ-DFT/Fermi Contact Integral

0.23

0.23

-0.17

Figure 2-24. Visual representation of Table 4. The a_{iso} values listed are located at each of their respective nuclear positions.

Table 2-6.	Calculated	spin dens	ity values	from equat	ions 2.8a an	d 2.8b for Na	a(3,6-(OMe) ₂ -
PSQ).							

	H _{1,8}	H _{2,7}	H _{4,5}	H _{Me-a}	H _{Me-b}	¹³ C _{C=0}
$ ho(N)_{\text{Data}}(x10^{-4})$	8.59	2.26	2.14	1.25	0.91	3.66,1.42,8.72
ρ(N) _{Fermi} (x10 ⁻⁴)	8.30	3.15	0.94	1.59	0.31	11.1

Table 6 compares the calculated spin density at the nucleus to the observed (fit) values from the Nguyen constants. The spin density reflects the same trend as the hyperfine coupling constants, and in most cases is comparable to the spin density calculated from the Fermi contact integrals. The spin density is largest for H_{1,8} and the largest carbonyl carbon value (8.59 and 8.72, respectively), while unquestionably the carbonyl carbon has the largest spin density from the Fermi analysis. Although these values seem large, they are an order of magnitude smaller than the NaPSQ values. With the addition of a Na⁺, it appears that the experimental model is not in agreement with the theoretical model discussed earlier in this chapter. The carbonyl carbon spin density value calculated from the Fermi contact integral for NaPSQ (1.6) falls within the range of spin density values obtained from fitting the experimental data (1.39-1.93); however, this is not true for Na(3,6-(OMe)₂-PSQ). The spin density of the carbonyl carbons obtained from conversion of the Fermi contact integral from DFT calculations (11.1) exceeds the range of values obtained for the experimental set of data (1.42-8.72).

This is an interesting result, as it was also observed in the $[Ni(tren)(3,6-R_2-PSQ)]^+$ DFT calculations. The OMe derivative had similar, but less spin density at the carbonyl carbon atoms, relative to the proteo complex. It is interesting that amongst the additional layers of complexity, covalent bonding to a metal (in this case experimentally observed by x-ray diffraction), electron spin exchange, spin polarization effects from unpaired electrons on the metal, etc., there remains a common thread between the radical compounds and Ni^{II} complexes.

ESEEM Spectroscopy. ESEEM (Electron Spin Echo Envelope Modulation) spectroscopy was employed to further understand the complexities of the NaPSQ and Na(3,6-(OMe)2-PSQ) CW-EPR spectra. CW-EPR was performed under ambient conditions and the tumbling of the molecules in solution nulls any anisotropic, or dipolar (T), contribution to the hyperfine coupling.

ESEEM spectroscopy indirectly measures anisotropic contributions to the hyperfine coupling by measuring interferences between the different EPR transition frequencies (refer to Figure 13 above) that are involved in creating an electron spin echo. This technique will be quite useful in unraveling the complications that arose in the CW spectra, by shedding a light on the dipolar coupling. The spin echo is a physical observable that occurs as a result of spins refocusing from a pulse of [microwave] radiation.

To move forward, however, the energy splitting diagram in Figure 13 must be amended to include nuclear effects. The spin Hamiltonian for an $S = \frac{1}{2}I = \frac{1}{2}$ system is now of the form:

$$\frac{\hat{H}}{\hbar} = \frac{g_e \beta_e B}{\hbar} \hat{S}_Z + A_{ZZ} \hat{S}_Z \hat{I}_Z + A_{XZ} \hat{S}_Z \hat{I}_X - \frac{g_N \beta_N B}{\hbar} \hat{I}_Z$$
(2.13)

Where the first and last terms are the electronic and nuclear Zeeman interactions, and the middle terms are the electron-nuclear hyperfine coupling terms as described previously in the CW section. $A_{ZZ} = A = A_{\parallel}cos^2\theta + A_{\perp}sin^2\theta$ and $A_{XZ} = B = (A_{\parallel} - A_{\perp})cos\theta sin\theta$ where A_{\perp} and A_{\parallel} are the principal values in an axially symmetric hyperfine coupling tensor:

$$\begin{bmatrix} A_{iso} - T & \cdots & \cdots \\ \cdots & A_{iso} - T & \cdots \\ \cdots & \cdots & A_{iso} + 2T \end{bmatrix}$$

The angle θ describes the angle between the principal axis of the hyperfine coupling tensor and the applied magnetic field, B₀ and $T = \frac{g_e g_N \beta_e \beta_N}{r^3}$. Using a basis set of $|m_S, m_I\rangle$, the Hamiltonian matrix can be diagonalized resulting in eigenvalues of the four energy levels produced by an $S = \frac{1}{2}I = \frac{1}{2}$ system, as seen in Figure 25 below.





Figure 25 shows the splitting of the β and α electron spin manifolds due to an $I = \frac{1}{2}$ nucleus. The ordering of the states is the same as that of Figure 13, where $|4\rangle = |\beta \alpha_N\rangle$, $|3\rangle = |\beta \beta_N\rangle$, $|2\rangle = |\alpha \beta_N\rangle$ and $|1\rangle = |\alpha \alpha_N\rangle$. The angles ϕ_β and ϕ_α determine the direction of the nuclear spin frequency, and ω_β and ω_α are the angular hyperfine frequencies and are defined by the equations:

$$\omega_{\alpha} = \sqrt{\left(\omega_{I} - \frac{A}{2}\right)^{2} + \frac{B^{2}}{4}}$$
(2.14)

$$\omega_{\beta} = \sqrt{\left(\omega_{I} + \frac{A}{2}\right)^{2} + \frac{B^{2}}{4}}$$
(2.15)

In measuring EPR spectra under ambient conditions, only the isotropic portion of the hyperfine coupling is measurable; any anisotropic effects are canceled-out due to tumbling in solution. Freezing the sample removes any tumbling motion and anisotropic effects can arise. The nuclear states are now mixed in each electron spin manifold, as in Figure 25, and therefore the spin states, $|1\rangle$, $|2\rangle$, $|3\rangle$ and $|4\rangle$ are mixed and all transitions are allowed. The EPR transitions in Figure 25 marked |u| and |v| are the normalized probability amplitudes and correspond to former (in CW-EPR) allowed and forbidden EPR transitions, respectively. Application of a pulse of microwave radiation excites all four transitions simultaneously. Multiple pulses can cause molecules to branch from one transition to another during the pulse sequence.

Branching establishes interferences on the echo amplitude that occur at frequency differences between the transitions. For example, the result of taking the difference between the frequency of $|1\rangle \rightarrow |3\rangle$ and $|1\rangle \rightarrow |4\rangle$ is a frequency corresponding to $\frac{|4\rangle-|3\rangle}{h}$. Keeping in mind that the sample is frozen, that frequency has both isotropic and anisotropic hyperfine components. Determining isotropic hyperfine coupling from CW-EPR is important for untangling these dipolar hyperfine components observed by ESEEM.

Figures 26 and 27 show a vector picture and timing diagram, respectively, for a two-pulse ESEEM experiment. Initially, the bulk magnetization, \vec{M} , is aligned with the external, fixed, magnetic field along the *z* axis. A 90° pulse is applied and this places the magnetization perpendicular to B_0 , in the *xy* plane. The magnetization then begins to fan out in the *xy* plane into spin packets during a duration of time period τ . Some spin packets experience stronger local magnetic field effects than others and develop a positive phase while the spin packets that experience weaker local magnetic field effects have a negative phase. After the time period τ , a 180° microwave pulse is applied that turns the spins about the *x* axis; the spin packets then begin to rephase and an echo is observed after a time period of 2τ . The amplitude of the echo decay is then measured as a function of τ .⁶²



Figure 2-26. Vector model of a two pulse ESEEM experiment.





In two-pulse ESEEM, modulation occur at the fundamental hyperfine frequencies, as well as at sum and difference combination frequencies. The resolution is also poor due to fast spin-spin relaxation times. Inclusion of a third microwave pulse increases sensitivity by eliminating the sum and combination frequencies and only detecting the hyperfine frequencies. The echo amplitude decay is now monitored with respect to a τ + T time period and allows for a much longer decay, resulting in higher hyperfine frequency resolution. Additionally, the time period τ can be varied and is most often set at integer values of a particular Larmor frequency. This allows for the suppression of modulations from weakly coupled nuclei; this is known as the tau suppression effect. For the purpose of this study, τ was set at various proton Larmor frequencies, in order to enhance the hyperfine frequencies from the ¹³C-labelled carbonyl carbons.



Figure 2-28. Timing diagram of a three pulse ESEEM sequence.

ESEEM spectra were collected at a magnetic field value of 3455 Gauss (g 2), at 4 K or 10 K. Tau (τ) values were chosen to suppress modulations from weakly coupled protons. Time domain spectra were normalized by division of a background decay function, then application of a Hamming window, followed by a zero filling to double the data set length and Fourier transformation. Spectra are displayed as absolute values of the Fourier transform. For analysis of ¹³C couplings the time domain data for ¹²C and ¹³C isotopologues were normalized and then ¹³C spectra were divided by ¹²C spectra to isolate the effect of the ¹³C hyperfine interaction. Divided time domain data were then worked up as stated above.

Time and frequency domain data were simulated by the Saffron module within Easyspin. The spectra were fit with the fminsearch function in Matlab. The best fits were obtained from simulating the time domain data and their Fourier transforms, separately; it should be noted that this process of simulating both the time and frequency domain spectra is essential for obtaining all information from the modulation decay of the time trace, and the resonances of the frequency spectra. Initially, the carbonyl carbons were treated as an equivalent set and the a_{iso} values were fixed to the values obtained from the CW fits and only the dipolar couplings were varied. It became quite apparent, while attempting to fit the data, that a single set of values obtained would

not be ideal for fitting the data. The time and frequency domain spectra were then simulated and fit to accommodate for multicomponent systems. The proton hyperfine couplings were left out of the simulations because the labeled spectra were divided by the ¹²C spectra and thus the ¹H a_{iso} values have been divided out. Hyperfine coupling parameters were simulated by taking the anisotropic hyperfine coupling tensor from the DFT results and transforming them to their spherical hyperfine components, *a* (isotropic), *T* (dipolar), and ρ (rhombicity), as seen in equation 2.13.

$$\boldsymbol{A}_{diag} = a_{iso}\boldsymbol{I} + \boldsymbol{T} = \begin{pmatrix} a_{iso} & 0 & 0\\ 0 & a_{iso} & 0\\ 0 & 0 & a_{iso} \end{pmatrix} + \boldsymbol{T} \begin{pmatrix} -(1-\rho) & 0 & 0\\ 0 & -(1+\rho) & 0\\ 0 & 0 & 2 \end{pmatrix}$$
(2.16)

These parameters were used as initial guesses and were subjected to simulations and fits until values were achieved that gave minimum χ^2 values. Only time domain fits were able to be achieved with residual values of 10 % or less; further work is being done to optimize the frequency domain parameters and reach an agreement between time and frequency domain spectra.

Figure 28 shows the frequency domain ESEEM ${}^{13}C/{}^{12}C$ spectrum and fit, and Figure 29 shows the normalized time domain ${}^{13}C/{}^{12}C$ spectrum and fit. Peaks in the ESEEM frequency spectrum arise from Larmor frequencies of nuclei that have unpaired spin density. When a particle with a magnetic moment, and subsequently angular momentum, is placed in an external magnetic field, the magnetic field will exert a torque on the magnetic moment of the particle:

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \boldsymbol{B} = \gamma \boldsymbol{J} \times \boldsymbol{B} \tag{2.17}$$

where τ is the torque, μ is the magnetic moment, B is the external magnetic field, J is the angular momentum operator and γ is the g-factor of the electron. The Larmor frequency is the angular frequency at which the magnetic moment precesses about the external magnetic field axis

$$\omega = -\gamma B \tag{2.18}$$

where ω is the Larmor frequency. For ¹³C, $\gamma = 10.705$ MHz/T, and at a fixed field of 3455 G (0.3455 T) $\omega = 3.69$ MHz. Indeed, the first peak of the frequency spectrum occurs at 3.66 MHz, corresponding to significant spin density located on the carbonyl carbons. Initially, it was thought that the features centered at 7.8 MHz and 11.1 MHz were likely to be second and third harmonics from negative frequencies. To further drive the point that the spectrum is completely dominated by ¹³C hyperfine effects, $\gamma_{\rm H} = 42.576$ MHz·T⁻¹ and at B = 3455 G, $\omega = 14.71$ MHz. Therefore, there is no evidence of ¹H hyperfine in the divided spectrum. This can be seen in Figure 29, where the ESEEM frequency spectra of [¹³C₂]PSQ and PSQ are compared. The resonance at 14.7 MHz from the PSQ spectrum is a result of dipolar couplings from ¹H on the PSQ ring. The resonances at 3.66 MHz from both spectra are from ¹³C dipolar couplings, but the difference is that in the PSQ spectrum, the couplings are arising due to naturally occurring ¹³C and the [¹³C₂]PSQ is from enrichment of the 9 and 10 carbonyl carbons. The spectra have been normalized to show resonances from the PSQ (¹²C) sample.



Figure 2-29. $[^{13}C_2]PSQ$ (red) and PSQ (black) ESEEM frequency spectra. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value. Spectra were normalized post-Fourier transform to illustrate the differences of the



Figure 2-30. [¹³C₂]PSQ ESEEM frequency spectrum and fit for dimer. Simulation parameters: g = 2.00575, 2¹³C nuclei, $a_{iso} = 2.1713$ MHz, T = 2.7757 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value.



Figure 2-31. [¹³C₂]PSQ ESEEM time domain spectrum and fit for dimer. Simulation parameters: g = 2.00575, 2¹³C nuclei, $a_{iso} = 2.1713$ MHz, T = 2.7757 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value. $\chi^2 = 0.67$.

Initially, the data was fit with one set of two equivalent ¹³C nuclei. The peak position of the largest resonance in the frequency spectrum can be simulated with a single pair of ¹³C nuclei where $a_{iso} = 2.17$ MHz, T = 2.78 MHz. Clearly, though, this model of a single NaPSQ ion-pair cannot be the most accurate portrayal of the unpaired spin density. The shape may be reminiscent of the resonance at 3.66 MHz, but the intensity is not reproduced by this simple model. The corresponding fit for the time trace does bare some semblance to the data; however, after ~ 1.8 us the beating is no longer in accord with the data and the simulation does not track with the data. This data can also be modeled with four equivalent carbon nuclei, as a dimer, with the same isotropic and dipolar values. This is some evidence that this peak at 3.66 MHz is from a dimer or similar species in solution. This model does not account for the entire data set, though. The humps at 8.0 and 11.8 MHz are unaccounted for in this model.



Figure 2-32. [¹³C₂]PSQ ESEEM frequency spectrum and fit for multicomponent system. Simulation parameters: g = 2.00575, Dimer: 4 ¹³C nuclei, $a_{iso} = 2.1713$ MHz, T = 2.7757 MHz, $\rho = 0$ MHz; ion-pair: 2 ¹³C nuclei, $a_{iso} = 1.5741$ MHz, T = 13.5674 MHz, $\rho = 0.44$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value.



Figure 2-33. [¹³C₂]PSQ ESEEM time domain spectrum and fit for multicomponent system. Simulation parameters: g = 2.00575, Dimer: 4 ¹³C nuclei, $a_{iso} = 2.1713$ MHz, T = 2.7757 MHz, $\rho = 0$ MHz; ion-pair: 2 ¹³C nuclei, $a_{iso} = 1.5741$ MHz, T = 13.5674 MHz, $\rho = 0.44$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value. $\chi^2 = 0.22$.

The total frequency spectrum (see above) can be modeled by a multiple component system. The system contains a dimer of two phenanthrenequinone moieties bridged by one sodium cation, and a single NaPSQ ion-pair. The dimer has four equivalent ¹³C nuclei with $a_{iso} = 2.17$ MHz, T = 2.78 MHz and $\rho = 0$ MHz. The second species in this system consists of two equivalent ¹³C nuclei with $a_{iso} = 1.57$ MHz, T = 13.56 MHz and $\rho = 0.44$ MHz. Inclusion of a second species improves the fit for both the time domain and the Fourier transform. The biggest improvement being that the second and third humps at 8 MHz and 11 MHz, respectively, have been fit. Therefore, it can be concluded that since the peak at 3.66 MHz can be fit with two pairs of equivalent carbons, that the resonances at 8 MHz and 11 MHz are either solely due to the ion-

pair or from the combination of the two species. It is noted that these humps cannot be fit by only the ion-pair, in the absence of the dimer.



Figure 2-34. Cartoon depiction of the ion-pair and dimer of the NaPSQ multicomponent system. **Table 2-7.** Hyperfine coupling parameters for NaPSQ dimer and molecule. All values in MHz.

	aiso	Т	ρ
NaPSQ Dimer	2.17	2.77	0
NaPSQ Ion-Pair	-1.57	13.57	0.44

Pictured above are cartoons of the proposed structures of the dimer and molecule that make up the multicomponent system of the NaPSQ complex. It is a bit easier to see how the unpaired electron density can be delocalized, to a greater extant, in the dimer system. Simply, the dipolar coupling is smaller in the dimer, relative to the NaPSQ molecule, due to spin delocalization across the Na⁺ bridge, to a second set of carbonyl units. The dimer has been drawn with a single radical, as opposed to two radicals on each quinone moiety. It has been drawn as such because the system has been modeled with Na a_{iso} coupling and there is, therefore, potential communication between the two quinones. Additionally, CW measurements did not indicate any triplet state formation. The rhombicity component has been introduced because without it, the intensity of the resonances at 8 MHz and 11.8 MHz would be quite large. The inclusion of rhombicity for the molecule decreases the intensity of the simulated peak at 11.8 MHz and leaves all other peaks unaltered. In terms of physical effects, an $S = \frac{1}{2}$ system that exhibits rhombicity is more of a second order effect. As indicated by equation 2.9, the rhombicity is a perturbation on *T*, the dipolar coupling.

Pictured below is the ESEEM spectrum and fit of $[^{13}C_2]_{3,6}$ -(OMe)₂-PSQ (Figures 35 and 36). This particular fit, though, is only of the first peak. Similar to $[^{13}C_2]_{PSQ}$, the first peak (3.66 MHz) can be fit with a single set of parameters. In contrast to $[^{13}C_2]_{PSQ}$, the first peak is not modeled by four carbons, but six; in other words, not a dimer, but a possible homoleptic complex, with a single sodium ion bonded to three quinone ligands with $a_{iso} = 0.98$ MHz and T = 1.15 MHz. Three pairs of carbon atoms were used in order to accurately model the intensity of the peak at 3.66 MHz.



Figure 2-35. [¹³C₂]3,6-(OMe)₂-PSQ ESEEM frequency spectrum and fit for the homoleptic complex. Simulation parameters: g = 2.00507, 6¹³C nuclei, $a_{iso} = 0.9758$ MHz, T = 1.15 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value.



Figure 2-36. [¹³C₂]3,6-(OMe)₂-PSQ ESEEM time domain spectrum and fit for the homoleptic complex. Simulation parameters: g = 2.00507, 6 ¹³C nuclei, $a_{iso} = 0.9758$ MHz, T = 1.15 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value. $\chi^2 = 0.94$.

The process of fitting this spectrum was much more difficult than that of $[^{13}C_2]PSQ$. This was also a multicomponent system, but not two components were needed to properly simulate the spectrum, but rather three: a homoleptic complex, a dimer and an ion-pair. Also differentiating from the analysis of $[^{13}C_2]PSQ$, the components are not 1:1, but rather 4:1:1, homoleptic complex : dimer : ion-pair, respectively (Figures 37, frequency, and 38, time domain).



Figure 2-37. [¹³C₂] 3,6-(OMe)₂-PSQ ESEEM frequency spectrum and fit for multicomponent system. Simulation parameters: g = 2.00507, homoleptic complex: 6 ¹³C nuclei, $a_{iso} = 0.9758$ MHz, T = 1.15 MHz, $\rho = 0$ MHz (4 of these); dimer: 4 ¹³C nuclei, $a_{iso} = 0.3849$ MHz, T = 7.9563 MHz, $\rho = 0$ MHz; ion-pair: 2 ¹³C nuclei, $a_{iso} = -0.4155$ MHz, T = 16.1325 MHz, $\rho = 0.63$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value.



Figure 2-38. [¹³C₂] 3,6-(OMe)₂-PSQ ESEEM time domain spectrum and fit for multicomponent system. Simulation parameters: g = 2.00507, homoleptic complex: 6 ¹³C nuclei, $a_{iso} = 0.9758$ MHz, T = 1.15 MHz, $\rho = 0$ MHz (4 of these); dimer: 4 ¹³C nuclei, $a_{iso} = 0.3849$ MHz, T = 7.9563 MHz, $\rho = 0$ MHz; ion-pair: 2 ¹³C nuclei, $a_{iso} = -0.4155$ MHz, T = 16.1325 MHz, $\rho = 0.63$ MHz. Experimental conditions: 345.5 mT magnetic field, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns tau, 40 ns starting T value. $\chi^2 = 0.35$.

After fitting the peak at 3.66 MHz with a single, homoleptic complex, a dimer and ion-pair were added to the simulation to account for the remaining resonances in the ESEEM spectrum. The structures that were added after several attempts with varying a_{iso} values; indeed, even after fitting the resonance at 3.66 MHz, the a_{iso} values were exchanged between homoleptic complex, dimer and ion-pair, in order to arrive at the best fit for the data. After addition of the dimer and ion-pair, the intensity of the peak at 3.66 MHz decreased; however, if the number of homoleptic complexes was increased, the intensity was restored. Thus, it was decided that multiple homoleptic complexes would be required for the fitting of this spectrum. It should be noted that upon addition of additional homoleptic complexes, no additional features were produced, only the intensity was affected.



Figure 2-39. Cartoon depiction of the Na(3,6-(OMe)₂-PSQ) multicomponent system.

Table 2-8. Hyperfine coupling parameters for Na(3,6-(OMe)₂-PSQ) homoleptic complex, dimer and molecule. All values in MHz.

	a _{iso}	Т	ρ
Na(OMe ₂ PSQ) ₃	0.98	1.30	0
NaOMe ₂ PSQ Dimer	0.38	7.96	0
NaOMe ₂ PSQ Ion-Pair	-0.41	16.13	0.63

When considering that the CW spectra can be fit with various ¹³C aiso values, and the fact that the ESEEM spectra cannot be fit with a single pair of carbonyl carbon atoms, it becomes clear that the spectra are sums of various combinations of Na⁺ and PSQ⁻/phenanthrenequinone. This is a theme within the EPR and ESEEM spectra of the molecules studied within this chapter. It is the belief of the author that when reducing the quinones with excess sodium metal, the sodium metal is a surface for reactions to occur and there could be numerous products from this chemistry. The outcome of such is evidenced by the findings of fitting the ESEEM spectra. Several attempts were made to understand the ESEEM data in the case of one pair of carbonyl carbon atoms, but as seen above, this was not the case. There do exist possibilities where the carbonyl carbon atoms are inequivalent, that is to say, the hyperfine coupling differs between two carbonyl carbon atoms located on the same semiquinone molecule. These possible instances have been studied by DFT and take shape of $[Na(PSQ)(THF)_n]^+$ complexes (where n = 1, 2, 3, 3) 4), where the sodium ion is bonded to a single semiquinone, while other coordination sites are occupied by various numbers of THF solvent molecules. The results of this study are not included in this work.

Lastly, when considering a substituent effect, the results of this ESEEM study are a bit chaotic. Only the dimer and ion-pair from each multicomponent system can be compared. Table 9 tabulates the isotropic, dipolar and rhombic components of the hyperfine coupling found for the dimers and ion-pairs. Considering the dimer first, the a_{iso} values follow the trend of the CW spectra, where NaPSQ has a larger value then Na(3,6-(OMe)₂-PSQ). This can be explained by the sigma-accepting nature of the methoxy groups. The oxygen atoms in the methoxy groups

have a higher electronegativity that protons; this shifts, or polarizes, the unpaired spin density away from the carbonyl carbons and results in a lower isotropic hyperfine coupling constant.

	aiso	Т	ρ
NaPSQ Dimer	2.17	2.77	0
NaOMe ₂ PSQ Dimer	0.38	7.96	0
NaPSQ Ion-Pair	-1.57	13.57	0.44
NaOMe ₂ PSQ Ion-Pair	-0.41	16.13	0.63

Table 2-9. Comparison of hyperfine coupling parameters between NaPSQ components and Na(3,6-(OMe)₂-PSQ) components.

Conversely, when comparing dipolar values, the situation is reversed; dipolar coupling values are larger for Na(3,6-(OMe)2-PSQ) than for NaPSQ. This can be accounted for by considering the pi-donating ability of the oxygen atoms of the methoxy groups. The radical allows for the methoxy oxygen atoms to participate in the resonance of the fused ring system through the pi electrons, specifically the unshared electrons on the oxygen atoms. An illustration of this resonance effect is seen in Figure 40 below.



Figure 2-40. Resonance structures of 3,6-(OMe)₂-PSQ⁻⁻ illustrating the pi-donating character of the methoxy group.

While this finding is interesting and agrees with the DFT study, these results are due to a mixture of species produced by reaction with sodium metal. So it would be advantageous to synthesize a single ion pair, a dimer and perhaps a homoleptic complex and compare their

spectra, as well as mixtures to assess the validity of the analysis of this study. These experiments will be performed elsewhere as they aren't the focus of this study.

HYSCORE

HYSCORE (Hyperfine Sublevel CORrElation) spectra were taken at the same magnetic field value as ESEEM spectra, 3455 G (345.5 mT), with the same tau value, $\tau = 136$ ns, and the same temperature, 4 K. HYSCORE spectra were not fit, but only simulated. The simulations presented are simply overlaid onto the spectra themselves. Before diving any further into the actual results, a qualitative description of HYSCORE spectroscopy is presented.

Concisely, HYSCORE can be described as a modified, two-dimensional, four-pulse ESEEM experiment. Two-dimensional, three pulse ESEEM experiments do exist, however they are usually foregone for the HYSCORE experiment, due to low resolution and other complications⁶³. The pulse sequence for HYSCORE can be seen below; the experiment is a modified form of three pulse ESEEM with the addition of a π -pulse in between the second and third $\pi/2$ pulses. This additional pulse not only bisects the *T* dimension into *t1* and *t2* but creates nuclear coherence transfer echoes. The second π pulse creates a nuclear coherence evolution, then the π pulse flips these nuclear coherences between the α and β spin manifolds. This creation of two, individual nuclear coherence evolution times, allows for Fourier transform in two dimensions and production of cross peaks at (ω_{12}, ω_{34}) and (ω_{34}, ω_{12}) that correlate to the nuclear transitions in the α and β electron spin manifolds. Additionally, due to the nuclear coherence transfer, the two dimensional patterns produced are not the same in every quadrant; when ω_{12} and ω_{34} have the same sign and the coupling is weak ($A/2 < \omega_0$) the peaks appear in the first and

third quadrant while for the strong coupling case $(A/2 > \omega_I) \omega_{12}$ and ω_{34} have different signs and the peaks are in the second and fourth quadrants⁶³.





The time domain data are worked up similarly to ESEEM time domain data, the greatest difference being that each time domain is worked up separately until a two-dimensional Fourier transform is applied. Following FT work-up, the data is presented as a contour plot. In this section the ¹³C data have not been divided by their ¹²C counterparts, as in the previous ESEEM section.

Pictured in Figure 42 is the contour plot of $[^{13}C_2]PSQ$. The most noticeable features of this spectrum is that there are on-diagonal peaks in both the first (weak coupling) and second quadrant (strong coupling) centered at the ^{13}C Larmor frequency (3.7 MHz). To compare these two features, the more intense peak is located in the first quadrant, indicating that there is a component that has dipolar coupling less than the Larmor frequency, and there exists a less intense component that has dipolar coupling that is larger than the Larmor frequency. This notion is supported by the ESEEM analysis. It should also be noted that these on-diagonal peaks are possibly due to non-ideal pulses and/or superimposed echoes on the HYSCORE modulations.

Cross peaks are observed in the first quadrant at (11.23,3.74) and (3.74,11.23) and in the second quadrant at (-11.23,3.74) and (-3.74,11.23). These peaks are centered about the ¹³C Larmor frequency, 3.70 MHz, and thus are the result of ¹³C hyperfine coupling. The shapes of the peaks in the first quadrant follow that peaks perpendicular to the diagonal are a feature of weakly coupled nuclei. This is evidence for $T < 2v_I$; a dipolar coupling corresponding to the proposed dimer structure. In quadrant two, the shapes of the peaks run parallel to the diagonal, indicating strong coupling of the magnitude $T > 2v_I$. These peaks would then correspond to the carbonyl carbons from the ion-pair.



Figure 2-42. HYSCORE spectrum of $[{}^{13}C_2]$ PSQ. Experimental settings: 345.5 mT Field, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 time.

The $[^{13}C_2]PSQ$ HYSCORE spectrum has been simulated in three various fashions: dimer only, ion-pair only, and one simulation containing both the dimer and the ion-pair. It was done this way in order to identify the strong and weak components, separately, and then compare them to the simulation of the entire spectrum (quadrants one and two).


Figure 2-43. HYSCORE spectrum (black) and simulation (red) of the [$^{13}C_2$]PSQ dimer. Simulation parameters: g = 2.00575, 4 ^{13}C nuclei, $a_{iso} = 2.1713$ MHz, T = 2.7757 MHz, $\rho = 0$ MHz. Experimental conditions: 346 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t₁ and t₂ values.

The HYSCORE simulation of the dimer, is pictured above in Figure 43. The same parameters for the ESEEM simulation of the dimer were used here, except for some experimental parameters. The position of the peak has been accurately modeled, even though the shape has not. The cross peaks produced by the simulation are merely shy of the observed cross peaks of the experimental spectrum, and are indicative that the dimer is the source of the weakly coupled carbonyl carbons. The second quadrant shows no resonances produced by this simulation and thus indicates no strong coupling from this species.

In contrast to the dimer simulation, the ion-pair simulation (Figure 44, below) has produced resonances in the first and second quadrants, as well as cross peaks. The ends of the cross peaks in the second quadrant nearly correspond to the positions of the observed cross peaks. This shows more evidence that it is possible for a second, strongly coupled component to be present in solution.



Figure 2-44. HYSCORE spectrum (black) and simulation (red) of the [$^{13}C_2$]PSQ ion-pair. Simulation parameters: g = 2.00575, 2 ^{13}C nuclei, $a_{iso} = 1.5741$ MHz, T = 13.5674 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t₁ and t₂ values.

Lastly, the combined simulation of the ion-pair and dimer produces a simulation that is reminiscent of the simulation of the dimer (Figure 45). It is possible that the intensity of the dimer is much greater than that of the ion-pair and therefore only the dimer is visible. Similarly, to constructing two dimensional spectra of HYSCORE data, the simulations also have a Zthreshold that must be varied. This threshold is typically varied until only the resonances are visible and the noise (baseline) has been eliminated from the spectrum. That being said, no other resonances were found in the first or second quadrants by varying the Z-threshold parameters. Conclusively though, the presence of cross peaks and the ability of the simulations to produce cross peaks in the first and second quadrants is more evidence to the conclusions of the ESEEM section.



Figure 2-45. HYSCORE spectrum (black) and simulation (red) of the [$^{13}C_2$]PSQ multicomponent system. Simulation parameters: System 1, g = 2.00575, 4 ^{13}C nuclei, $a_{iso} = 2.1713$ MHz, T = 2.7757 MHz, $\rho = 0$ MHz; System 2, 2 ^{13}C nuclei, $a_{iso} = 1.5741$ MHz, T = 13.5674MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 values.

The HYSCORE spectra of $[^{13}C_2]_{3,6}$ -(OMe)₂-PSQ are presented below. The spectra and simulation results are quite analogous to those of $[^{13}C_2]_{PSQ}$, and were simulated similarly. Each species of the multi-component system was simulated separately and the final simulation includes all the components of the system. As can be seen below in the HYSCORE spectrum of $[^{13}C_2]_{3,6}$ -(OMe)₂-PSQ, resonances appear at (3.9,3.9) and (7.55,7.55) in the first quadrant and at

(-2.3,2.3) and (-6.3,6.3) in the second quadrant; the only resonance not visible from the $[{}^{13}C_2]PSQ$ HYSCORE being at (7.55,7.55). It is not a great surprise that these spectra are similar to those of $[{}^{13}C_2]PSQ$ for several reasons; however, the primary reason being that the ESEEM spectra produced by each molecule are similar in nature; each have large resonances at or near the ${}^{13}C$ – Larmor frequency, followed by two smaller humps near 8 MHz and 11 MHz.

Another similar facet of this HYSCORE are the prominent features and their respective resonances. The dominant feature in the [$^{13}C_2$]PSQ HYSCORE (and ESEEM) spectrum, at 3.66 MHz, was the result of dimer formation between two PSQ units and one bridging Na⁺ ion. This dimer was the most complex species from that reaction. Moving to [$^{13}C_2$]3,6-(OMe)₂-PSQ, the most complex species was a homoleptic complex, where Na⁺ was complexed to three PSQ moieties. Therefore, in each spectrum, the most complex species has the largest resonance at or near the $^{13}C_2$ – Larmor frequency. This observation is highly dependent on the way in which these spectra were simulated; however, the final simulations were arrived at after long and rigorous trial and error periods.



Figure 2-46. HYSCORE spectrum of $[{}^{13}C_2]3,6-(OMe)_2$ -PSQ. Experimental settings: 345.5 mT Field, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 time.



Figure 2-47. HYSCORE spectrum (black) and simulation (red) of the $[{}^{13}C_2]3,6-(OMe)_2$ -PSQ homoleptic complex. Simulation parameters: $g = 2.0057, 6 {}^{13}C$ nuclei, $a_{iso} = 0.9758$ MHz, T = 1.3064 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 values.

The next species that was examined was the dimer. The simulation produced an ondiagonal peak at (6.71, 6.71); however, the simulation also produced cross-peak arcs that radiate from the on-diagonal peak at (6.71, 6.71). They range from (4.51, 11.72) to (6.35, 7.69) and (7.69, 6.35) to (4.51, 11.72). These peaks do not appear in the experimental spectrum. In contrast to these arcs are the arc centered at (10.62, 10.62). This arc is not present in the HYSCORE, but it is close to the feature centered at 11.07 MHz in the ESEEM spectrum, and since the simulation for HYSCORE is based on the simulation for ESEEM, this is most likely showing a true. With regards to the second quadrant, cross peaks have also been produced by the simulation, indicating strong coupling being generated from the dimer. The dimer, having T = 7.96 MHz, is just over the weak coupling limit.



Figure 2-48. HYSCORE spectrum (black) and simulation (red) of the $[{}^{13}C_2]3,6-(OMe)_2$ -PSQ dimer. Simulation parameters: g = 2.0057, 4 ${}^{13}C$ nuclei, $a_{iso} = 0.3849$ MHz, T = 7.9653 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t₁ and t₂ values.



Figure 2-49. HYSCORE spectrum (black) and simulation (red) of the $[{}^{13}C_2]3,6-(OMe)_2$ -PSQ ion-pair in Quadrant II. Simulation parameters: g = 2.0057, 2 ${}^{13}C$ nuclei, $a_{iso} = -0.4155$ MHz, T = 16.1325 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 values.

Lastly, the simulations for the ion-pair and the entire multiple components system. The simulation for the ion-pair produced features only present in the second quadrant, indicating coupling larger than twice the Larmor frequency; this is upheld by T = 16.13 MHz for the molecule. Compare this to the simulation of the entire system and everything becomes irrelevant except for the homoleptic complex, in Quadrant I. This is analogous to [¹³C₂]PSQ, as the HYSCORE simulation for the entire system resembled only the dimer system, rather than both

components. Again, this could be for a variety of reasons but it seems most likely that the homoleptic complex may be the most prominent component of the mixture. Additionally, though, an on-diagonal peak is produced in Quadrant II, precisely at the ^{13}C – Larmor frequency and frequency of the most intense resonance. It nearly maps onto the existing diagonal peak from the spectrum.



Figure 2-50. HYSCORE spectrum (black) and simulation (red) of the $[{}^{13}C_2]3,6-(OMe)_2-PSQ$ multi-component system in Quadrant I. Simulation parameters: $g = 2.0057, 6 {}^{13}C$ nuclei, $a_{iso} = 0.9758$ MHz, T = 1.3064 MHz, $\rho = 0$ MHz, $4 {}^{13}C$ nuclei, $a_{iso} = 0.3849$ MHz, T = 7.9653 MHz, $\rho = 0$ MHz, and 2 ${}^{13}C$ nuclei, $a_{iso} = -0.4155$ MHz, T = 16.1325 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t₁ and t₂ values.



Figure 2-51. HYSCORE spectrum (black) and simulation (red) of the $[{}^{13}C_2]3,6-(OMe)_2-PSQ$ multi-component system in Quadrant II. Simulation parameters: $g = 2.0057, 6 {}^{13}C$ nuclei, $a_{iso} = 0.9758$ MHz, T = 1.3064 MHz, $\rho = 0$ MHz, $4 {}^{13}C$ nuclei, $a_{iso} = 0.3849$ MHz, T = 7.9653 MHz, $\rho = 0$ MHz, and 2 ${}^{13}C$ nuclei, $a_{iso} = -0.4155$ MHz, T = 16.1325 MHz, $\rho = 0$ MHz. Experimental conditions: 345.5 mT magnetic field, 4 pulse HYSCORE sequence, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 values.

To conclude the results of the HYSCORE analysis and simulations, the inclusion of these results may not be as pertinent for the analysis of this chapter, but rather Chapter 4, where HYSCORE analysis of exchange-coupled Ni-PSQ systems was valuable in characterizing the

magnetic structure. The HYSCORE analysis of this chapter would be compared to that of Chapter 4 to draw conclusions on the presence and absence of a paramagnetic Lewis acid bonded directly to the semiquinone moiety.

For the purposes of this chapter, however, the HYSCORE analysis bolstered the conclusions of the ESEEM section for $[^{13}C_2]PSQ$, but not for $[^{13}C_2](3,6-(OMe)_2-PSQ)$. The presence of cross peaks in the $[^{13}C_2]PSQ$ spectra gives credence to the hypothesis that multiple species are present in solution. However, the dipolar coupling constants for $[^{13}C_2]PSQ$ were smaller than $[^{13}C_2](3,6-(OMe)_2-PSQ)$ leading one to believe that cross peaks would be present in these HYSCORE spectra but this was not the case. Perhaps this was due to un-optimized experimental conditions; the $[^{13}C_2](3,6-(OMe)_2-PSQ)$ spectra were taken at 345.5 mT whereas the $[^{13}C_2]PSQ$ spectra were taken at 346 mT. Whatever the cause, the experimental conditions for both samples would be optimized if the various components were individually synthesized and examined.

2.4 Conclusions and Future Work

The purpose of the work of this chapter was to uncover an effect, if any, the choice of substituent has on spin density delocalization within a semiquinone. Though, there were also minor themes on display through out this investigation: the validity of ¹³C as a monitor of spin density fluctuation, the influence of counter ion on both species formation and spin density delocalization, and the limits of EPR, ESEEM and HYSCORE to study these semiquinones.

The over-arching theme to this entire work, present chapter included, is the influence a substituent has on the spin properties of phenanthrenesemiquinones. Within the molecules studied, it is evident that a substituent effect is active. It can be seen from merely comparing the

CW spectra by eye, that choice of substituent has an overall effect on line shape; which is indicative of the spin properties of the molecule. A dependence on substituent choice was also observed quantitatively, in comparing hyperfine coupling parameters obtained by EPR and ESEEM.

It was observed that ¹³C a_{iso} values were larger for PSQ than 3,6-(OMe)₂-PSQ, which was predicted by DFT, even without inclusion of Na⁺. Although DFT incorrectly predicted the ²³Na a_{iso} , this same calculation very closely predicted the isotropic hyperfine coupling constants for both ¹³C and ¹H nuclei. On the other hand, when considering the ESEEM data, dipolar values showed the opposite trend; for comparative species (i.e. molecule versus molecule and dimer versus dimer), ¹³C *T* values were slightly larger for 3,6-(OMe)₂-PSQ than PSQ. This was an interesting revelation considering DFT predicted that the total spin density for PSQ would be larger than 3,6-(OMe)₂-PSQ. This being said, using ¹³C substitution at the carbonyl carbon as a means for tracking variances in hyperfine coupling, seems to be a sound method. CW EPR and ESEEM also both proved to be powerful techniques in studying these molecules. The only shortfall in the results was from HYSCORE. At the present time it does not seem that much can be done to improve upon the lack of cross peaks in the spectra.

These results can be improved upon. The largest issue within this study lies with the method of reduction. Quinones were reduced with excess Na metal chunks in THF under anaerobic conditions. The Na metal were cut up into small cubes in order to reduce the surface chemistry; however, as witnessed by the ESEEM data and simulations, this may have been the largest road block in determining the make-up of the multi-component system. It was originally thought that only the PSQ⁻⁻ would be produced and Na would not even participate in the hyperfine interaction. This hypothesis was undercut immediately, when CW data clearly showed that the ¹H nuclei of

the PSQ moiety were not the only active nuclei present. This sodium issue also led to convoluted ESEEM and HYSCORE data as it seemed that the surface of the Na chunks had given way to various reactions, producing several different species in solution. This is also evidenced with the range of 13 C a_{iso} values obtained from CW EPR measurements. An alternative hypothesis is that during freezing (ESEEM and HYSCORE experiments conducted between 4 -10 K), small amounts of the various species precipitated out of solution, causing convoluted spectra. This sodium issue could be remedied with alternative reduction techniques.

In the following chapter, the techniques and methods used in this chapter will be applied to Ga^{III} and Zn^{II} complexes of PSQ and [¹³C₂]PSQ. These results will be directly compared to the results of this chapter to deduce the effects of Lewis acidity on spin delocalization.

APPENDIX

APPENDIX: Simulation/Fitting Scripts

CW-EPR

```
function res = PSQcwRTblc fit(hpar)
% PSQ Room Temp McCracken Re-Take and Spectral Fit
% Load the experimental spectrum
[B,y,params] = eprload('PSQcwRTblc.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = y/(max(y)-min(y)); % Normalizes the data
lmin = 185; % min point to start w/in the data set
lmax = 800; % max point to stop w/in data set
% Simulation Parameters
Sys0.S = 1/2;
Sys0.q = 2.00754;
Sys0.lwpp = [0.0005 0.0191]; %Gaussian & Lorentzian Linewidth, mT
Sys0.Nucs = '23Na,1H,1H,1H,1H'; % Treating the nuclei separately
Sys0.n = [1 2 2 2 2]; % 1 23Na, 4 classes of 2, 1H nuclei each
Sys0.A = [1.3231 0.7723 1.1914 -4.0643 -4.7515];
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000, params.A1SW*1000];
Exp.ModAmp = 0.002; %mT
Exp.nPoints = params.XPTS;
% Call the simulation program
[B,sim] = garlic(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
%offset = Edata(lmin); % corrects for baseline offset
%Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual -> value that determines difference between sim
% and spectrum.
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end;
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
return;
```

```
function res = ldm1152cwRTblc fit(hpar)
% LDM1152, [13C2]PSQ, Room Temp McCracken Re-Take and Spectral Fit
%_____
% Load the experimental spectrum
[B, spc, params] = eprload ('ldm1152cwRTblc.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = spc/(max(spc)-min(spc)); % Normalizes the data
lmin = 150; % min point to start w/in the data
lmax = 850; % max point to stop w/in data set
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.00755;
Sys0.lwpp = [0.0001 0.0222]; %mT
Sys0.Nucs = '23Na,1H,1H,1H,1H,13C'; % Treating the nuclei separately
Sys0.n = [1 2 2 2 2 2]; % 1 23Na, 4 classes of 1H, 2 13C nuclei
Sys0.A = [1.3231 0.7723 1.1914 -4.0643 -4.7515 1.57];
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000, params.A1SW*1000];
Exp.ModAmp = 0.002; % mT
Exp.nPoints = params.XPTS;
% Call the simulation program
[B,sim] = garlic(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
offset = Edata(lmin); % corrects for baseline offset
Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual -> value that determines difference between sim
% and spectrum.
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end;
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
return;
```

```
function res = ldm2140cwRTblc fit(hpar)
% LDM2140, Na(3,6-(OMe)2-PSQ), Room Temp McCracken Re-Take and Spectral Fit
8_____
% Load the experimental spectrum
[B,y,params] = eprload('ldm2140cwRTblc.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = y/(max(y)-min(y)); % Normalizes the data
lmin = 220; % min point to start
lmax = 790; % max point to stop
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.00746;
Sys0.lwpp = [0.0015 \ 0.0135];
Sys0.Nucs = '23Na,1H,1H,1H,1H,1H'; % Treating the nuclei separately
Sys0.n = [1 2 4 2 2 2]; % 1 23Na, 5 classes of 1H nuclei
Sys0.A = [-1.1677 -0.4142 0.5611 1.0046 0.9607 -3.8385];
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000, params.A1SW*1000];
Exp.ModAmp = 0.002;
Exp.nPoints = params.XPTS;
% Call the simulation program
[B,sim] = garlic(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
%offset = Edata(lmin); % corrects for baseline offset
%Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual -> value that determines difference between sim
% and spectrum.
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end;
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
return;
```

```
function res = ldm2134cwRTblc fit(hpar)
% LDM2134, [13C2] (3,6-(OMe)2-PSQ) Room Temp 20mG Sim/Fit McCracken Retake
%_____
% Load the experimental spectrum
[B, spc, params] = eprload ('ldm2134cwRTblc.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = spc/(max(spc)-min(spc)); % Normalizes the data
lmin = 220; % min point to start
lmax = 790; % max point to stop
% Simulation Parameters
Sys0.S = 1/2;
Sys0.q = 2.007443;
Sys0.lwpp = [0.0015 \ 0.0145];
Sys0.Nucs = '23Na,1H,1H,1H,1H,1H,13C'; % Treating the nuclei separately
Sys0.n = [1 2 4 2 2 2 2]; % 1 23Na, 5 classes of 1H, 2 13C nuclei
Sys0.A = [-1.1677 -0.4142 0.5611 1.0046 0.9607 -3.8385 -0.4155]; % MHz
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000,params.A1SW*1000];
Exp.ModAmp = 0.002;
Exp.nPoints = params.XPTS;
% Call the simulation program
[B,sim] = garlic(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
%offset = Edata(lmin); % corrects for baseline offset
%Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual -> value that determines difference between sim
% and spectrum.
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end;
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
```

return;

ESEEM

```
function res = LDM1152 ESEEM FFT 1peak fit(hpar)
% LDM1152, [13C2]PSQ Frequency Domain Sim/Fit
%-----
% Load the experimental spectrum
[freq,intens] = eprload('LDM1152divPSQnormSP.DTA');
freq = freq*1000; %GHz to MHz
lmin = 1;
lmax = 256;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.00575;
Sys0.Nucs = '13C, 13C';
Sys0.n = [1 1]; % 2 classes of 13C nuclei
Sys0.A = [2.1713 2.7757 0; 2.1713 2.7757 0]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.136; % Tau/microseconds
Exp.T = 0.04; % Starting T value/microseconds
Opt.nKnots = 90;
[x, y] = saffron(Sys0, Exp, Opt);
ESnormDAL; %Normalizes the simulation
res = 0;
for ipt = (lmin+1):lmax,
   res = res + (spec(ipt) - intens(ipt))^2;
end;
plot(f(lmin:lmax), spec(lmin:lmax), ' r', freq(lmin:lmax), intens(lmin:lmax), '
k');
return;
```

```
function res = LDM1152 ESEEM time 1peak fit(hpar)
% LDM1152, [13C2]PSQ Time Domain Sim/Fit
%_____
% Load the experimental spectrum
[time, amp] = eprload('LDM1152divPSQnorm.DTA');
Amp = real(amp)/max(real(amp)); % Normalizes the data
time = (time/1000)+0.136;
lmin = 1;
lmax = 512;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.00575;
Sys0.Nucs = '13C, 13C';
Sys0.n = [1 1]; % 2 classes of 13C nuclei
Sys0.A = [2.1713 2.7757 0; 2.1713 2.7757 0]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 345.5; % Magnetic Field/millitesla
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.136; % Tau/microseconds
Exp.T = 0.04; % Starting T value/microseconds
Opt.nKnots = 90;
Opt.TimeDomain = 1;
[x,y] = saffron(Sys0,Exp,Opt);
Y = real(y)/max(real(y)); % Normalizes the simulation
res = 0;
for ipt = lmin:lmax,
   res = res + (Y(ipt) - Amp(ipt))^2;
end;
plot(x(lmin:lmax),Y(lmin:lmax), ' r',time(lmin:lmax),Amp(lmin:lmax),' k');
return;
```

```
function res = LDM1152 ESEEM FFT mccracke fitC(hpar)
% LDM1152, [13C2]PSQ Multicomponent Frequency Domain Sim/Fit
<u><u><u></u></u></u>
% Load the experimental spectrum
[freq,intens] = eprload('LDM1152divPSQnormSP.DTA');
freq = freq * 1000;
lmin = 1;
lmax = 256;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.00575;
Sys0.Nucs = '13C, 13C, 13C, 13C';
Sys0.A = [2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0];
% Species 2
Sys1.S = 1/2;
Sys1.q = 2.00575;
Sys1.Nucs = '13C, 13C';
Sys1.A = [-1.5741 13.5674 0.44; -1.5741 13.5674 0.44]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 345.5; % Magnetic Field/millitesla
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.136; % Tau/microseconds
Exp.T = 0.04; % Starting T Value/microseconds
Opt.nKnots = 180;
[x0,y0] = saffron(Sys0,Exp,Opt);
[x,y1] = saffron(Sys1,Exp,Opt);
y = y0 + y1; % combine time domain traces and process
ESnormDAL; %Normalizes the simulation
res = 0;
for ipt = (lmin+1):lmax,
   res = res + (spec(ipt) - intens(ipt))^2;
end;
plot(f(lmin:lmax), spec(lmin:lmax), ' r', freq(lmin:lmax), intens(lmin:lmax), '
k');
return;
```

```
function res = LDM1152 ESEEM time fit(hpar)
% LDM1152 [13C2]PSQ Multicomponent Time Domain Sim/Fit
<u><u><u></u></u></u>
% Load the experimental spectrum
[time,amp] = eprload('LDM1152divPSQnorm.DTA');
Amp = real(amp)/max(real(amp)); % Normalizes the data
time = (time/1000) + 0.136;
lmin = 1;
lmax = 512;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.00575;
Sys0.Nucs = '13C, 13C, 13C, 13C';
Sys0.A = [2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0];
% Species 2
Sys1.S = 1/2;
Sys1.q = 2.00575;
Sys1.Nucs = '13C, 13C';
Sys1.A = [-1.5741 13.5674 0.44; -1.5741 13.5674 0.44]; % [a-iso T rhombicity]
% Experimental Parameters
Exp.Field = 345.5; % Magnetic Field/millitesla
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.136; % Tau/microseconds
Exp.T = 0.04; % Starting T Value/microseconds
Opt.nKnots = 90;
[x0,y0] = saffron(Sys0,Exp,Opt);
[x,y1] = saffron(Sys1,Exp,Opt);
y = y0 + y1;
Y = real(y)/max(real(y)); % Normalizes the simulation
res = 0;
for ipt = (lmin+2):lmax,
   res = res + (Y(ipt) - Amp(ipt))^2;
end;
plot(x(lmin:lmax),Y(lmin:lmax), ' r',time(lmin:lmax),Amp(lmin:lmax),' k');
return;
```

```
function res = LDM2134div2140ESEEM 1peak fit(hpar)
% LDM2134/LDM2140 [13C2] (3,6-(OMe)2-PSQ) Frequency Domain Sim/Fit
%_____
% Load the experimental spectrum
[freq,intens] = eprload('ldm2134div2140 136sp.DTA');
freq = freq * 1000;
lmin = 1;
lmax = 256;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.0057;
Sys0.Nucs = '13C, 13C, 13C, 13C, 13C, 13C';
Sys0.n = [1 1 1 1 1 1]; % 6 classes of 13C nuclei
Sys0.A_ = [0.9758 1.15 0;0.9758 1.15 0;0.9758 1.15 0;0.9758 1.15 0;0.9758
1.15 0;0.9758 1.15 0];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012;
Exp.tau = 0.136;
Exp.T = 0.04;
Opt.nKnots = 120;
[x,y] = saffron(Sys0,Exp,Opt);
ESnormDAL; % Normalizes the simulation
res = 0;
for ipt = (lmin):lmax,
   res = res + (spec(ipt) - intens(ipt))^2;
end;
plot(f(lmin:lmax), spec(lmin:lmax), ' r', freq(lmin:lmax), intens(lmin:lmax), '
k');
return;
```

```
function res = LDM2134div2140ESEEMtime_1peak fit(hpar)
% LDM2134/LDM2140 [13C2](3,6-(OMe)2-PSQ) Time Domain Sim/Fit
<u><u><u></u></u></u>
% Load the experimental spectrum
[time,amp] = eprload('ldm2134div2140 136.DTA');
Amp = real(amp)/max(real(amp)); % Normalizes the data
time = (time/1000) + 0.136;
lmin = 1;
lmax = 512;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.00507;
Sys0.Nucs = '13C, 13C, 13C, 13C, 13C, 13C';
Sys0.n = [1 1 1 1 1 1]; % 6 classes of 13C nuclei
Sys0.A = [0.9758 1.15 0;0.9758 1.15 0;0.9758 1.15 0;0.9758 1.15 0;0.9758
1.15 0;0.9758 1.15 0];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012;
Exp.tau = 0.136;
Exp.T = 0.04;
Opt.nKnots = 90;
[x,y] = saffron(Sys0,Exp,Opt);
Y = real(y)/max(real(y)); % Normalizes the simulation
res = 0;
for ipt = (lmin):lmax,
    res = res + (Y(ipt) - Amp(ipt))^2;
end;
plot(x(lmin:lmax),Y(lmin:lmax), ' r',time(lmin:lmax),Amp(lmin:lmax),' k');
return;
```

```
function res = LDM2134div2140 ESEEM FFT fitC(hpar)
% LDM2134/LDM2140 [13C2] (3,6-(OMe)2-PSQ) Multicomponent Frequency Domain
Sim/Fit
% Load the experimental spectrum
[freq,intens] = eprload('ldm2134div2140 136sp.DTA');
freq = freq*1000;
lmin = 1;
lmax = 256;
% Species 1
Sys1.S = 1/2;
Sysl.g = 2.0057;
Sys1.Nucs = '13C, 13C, 13C, 13C, 13C, 13C';
Sys1.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 1a
Sys1a.S = 1/2;
Sysla.g = 2.0057;
Sys1a.Nucs = '13C,13C,13C,13C,13C,13C';
Sysla.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 1b
Sys1b.S = 1/2;
Sys1b.g = 2.0057;
Sys1b.Nucs = '13C,13C,13C,13C,13C,13C';
Sys1b.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 1c
Sys1c.S = 1/2;
Sys1c.q = 2.0057;
Sys1c.Nucs = '13C,13C,13C,13C,13C,13C';
Sys1c.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 2
Sys2.S = 1/2;
Sys2.g = 2.0057;
Sys2.Nucs = '13C,13C';
Sys2.A = [-0.4155 16.1325 0.63;-0.4155 16.1325 0.63];
% Species 3
Sys3.S = 1/2;
Sys3.g = 2.0057;
Sys3.Nucs = '13C, 13C, 13C, 13C';
```

Sys3.A = [0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0];

```
% Load the experimental Parameters
```

```
Exp.Field = 345.5;
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012;
Exp.tau = 0.136;
Exp.T = 0.04;
Opt.nKnots = 180;
[x1,y1] = saffron(Sys1,Exp,Opt);
[x1a,y1a] = saffron(Sys1a,Exp,Opt);
[x1b,y1b] = saffron(Sys1b,Exp,Opt);
[x1c,y1c] = saffron(Sys1c,Exp,Opt);
[x2,y2] = saffron(Sys2,Exp,Opt);
[x,y3] = saffron(Sys3,Exp,Opt);
% combine time domain traces and process
y = y1 + y1a + y1b + y1c + y2 + y3;
ESnormDAL; %Normalizes the simulation
res = 0;
for ipt = (lmin+1):lmax,
    res = res + (spec(ipt) - intens(ipt))^2;
end;
plot(f(lmin:lmax), spec(lmin:lmax), ' r', freq(lmin:lmax), intens(lmin:lmax), '
k');
return;
```

```
function res = LDM2134div2140ESEEMtime fit(hpar)
% LDM2134/LDM2140 [13C2] (3,6-(OMe)2-PSQ) Multicomponent Time Domain Sim/Fit
% Load the experimental spectrum
[time,amp] = eprload('ldm2134div2140 136.DTA');
Amp = real(amp)/max(real(amp)); % Normalizes the data
time = (time/1000) + 0.136;
lmin = 1;
lmax = 512;
% Species 1
Sys1.S = 1/2;
Sysl.g = 2.0057;
Sys1.Nucs = '13C,13C,13C,13C,13C,13C';
Sys1.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 1a
Sys1a.S = 1/2;
Sysla.g = 2.0057;
Sys1a.Nucs = '13C,13C,13C,13C,13C,13C';
Sysla.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 1b
Sys1b.S = 1/2;
Sys1b.g = 2.0057;
Sys1b.Nucs = '13C,13C,13C,13C,13C,13C';
Sys1b.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 1c
Sys1c.S = 1/2;
Sys1c.q = 2.0057;
Sys1c.Nucs = '13C, 13C, 13C, 13C, 13C, 13C';
Sys1c.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 2
Sys2.S = 1/2;
Sys2.g = 2.0057;
Sys2.Nucs = '13C,13C';
Sys2.A = [-0.4155 16.1325 0.63;-0.4155 16.1325 0.63];
% Species 3
Sys3.S = 1/2;
Sys3.q = 2.0057;
Sys3.Nucs = '13C, 13C, 13C, 13C';
Sys3.A = [0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0];
```

```
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```

```
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012;
Exp.tau = 0.136;
Exp.T = 0.04;
Opt.nKnots = 180;
[x1,y1] = saffron(Sys1,Exp,Opt);
[x1a,y1a] = saffron(Sys1a,Exp,Opt);
[x1b,y1b] = saffron(Sys1b,Exp,Opt);
[x1c,y1c] = saffron(Sys1c,Exp,Opt);
[x2,y2] = saffron(Sys2,Exp,Opt);
[x,y3] = saffron(Sys3,Exp,Opt);
% combine time domain traces and process
y = y1 + y1a + y1b + y1c + y2 + y3;
Y = real(y)/max(real(y)); % Normalizes the simulation
res = 0;
for ipt = (lmin):lmax,
    res = res + (Y(ipt) - Amp(ipt))^2;
end;
plot(x(lmin:lmax),Y(lmin:lmax), ' r',time(lmin:lmax),Amp(lmin:lmax),' k');
return;
```

HYSCORE

```
% LDM1152 [13C2]PSQ Dimer
8-----
clear;
Sys0.S = 1/2;
Sys0.q = 2.00575;
Sys0.Nucs = '13C,13C,13C,13C'; % Treating the nuclei differently
Sys0.A = [2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1,x2,y1,p1] = saffron(Sys0,Exp,Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd));
% set threshhold for contour at 10% max amplitude
   Zthresh = 0.1*max(max(Z));
   for iy=1:512,
       for ix = 1:512,
           if Z(ix, iy) < Zthresh,
              ZR(ix, iy) = Zthresh;
           else
              ZR(ix, iy) = Z(ix, iy);
           end
       end;
   end;
8
   f1min=0.0;
   f1max=7.0;
   f2min=0.0;
   f2max=7.0;
8
   frinc=f1(2)-f1(1);
8
   xmin=floor((flmin-fl(1))/frinc)+1;
   xmax=floor((flmax-f1(1))/frinc)+1;
   ymin=floor((f2min-f2(1))/frinc)+1;
   ymax=floor((f2max-f2(1))/frinc)+1;
```

```
contour(f1(xmin:xmax), f2(ymin:ymax), ZR(ymin:ymax, xmin:xmax), 10, 'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
% LDM1152 HYSCORE Ion-Pair Simulation
<u>%______</u>
clear;
Sys0.S = 1/2;
Sys0.q = 2.00575;
Sys0.Nucs = '13C, 13C';
Sys0.A = [-1.5741 13.5674 0.44;-1.5741 13.5674 0.44];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1, x2, y1, p1] = saffron(Sys0, Exp, Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd));
\% set threshhold for contour at 10% max amplitude
    Zthresh = 0.02*max(max(Z));
    for iy=1:512,
        for ix = 1:512,
            if Z(ix,iy) < Zthresh,</pre>
              ZR(ix, iy) = Zthresh;
            else
              ZR(ix, iy) = Z(ix, iy);
            end
        end;
    end;
00
    f1min=-15.0;
    f1max=15.0;
    f2min=0.0;
   f2max=15.0;
8
    frinc=f1(2)-f1(1);
8
    xmin=floor((flmin-f1(1))/frinc)+1;
```

```
xmax=floor((flmax-fl(1))/frinc)+1;
    ymin=floor((f2min-f2(1))/frinc)+1;
    ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax), f2(ymin:ymax), ZR(ymin:ymax, xmin:xmax), 10, 'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
%LDM1152 [13C2]PSQ HYSCORE Simulation Dimer & Ion Pair
%_____
clear;
Sys0.S = 1/2;
Sys0.g = 2.00575;
Sys0.Nucs = '13C, 13C, 13C, 13C';
Sys0.A = [2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0;2.1713 2.7757 0];
Sys1.S = 1/2;
Sys1.q = 2.00575;
Sys1.Nucs = '13C, 13C';
Sys1.A = [-1.5741 13.5674 0.44;-1.5741 13.5674 0.44];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1, x2, y1, p1] = saffron(Sys0, Exp, Opt);
[x1, x2, y2, p2] = saffron(Sys1, Exp, Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd)) + (real(p2.fd));
ZR = zeros(512, 512);
% Set threshhold for contour at 10% max amplitude
    Zthresh = 0.02*max(max(Z));
   for iy=1:512,
       for ix = 1:512,
           if Z(ix, iy) < Zthresh,
              ZR(ix, iy) = Zthresh;
           else
              ZR(ix, iy) = Z(ix, iy);
```

```
end
       end;
   end;
   f1min=-15.0;
   f1max=15.0;
   f2min=0.0;
   f2max=15.0;
   frinc=f1(2)-f1(1);
   xmin=floor((flmin-fl(1))/frinc)+1;
   xmax=floor((flmax-fl(1))/frinc)+1;
   ymin=floor((f2min-f2(1))/frinc)+1;
   ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax),f2(ymin:ymax),ZR(ymin:ymax,xmin:xmax),20,'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
return;
% LDM2134 [13C2](3,6-(OMe)2-PSQ) HYSCORE Tris Complex
clear;
Sys0.S = 1/2;
Sys0.g = 2.0057;
Sys0.Nucs = '13C, 13C, 13C, 13C, 13C, 13C';
Sys0.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1,x2,y1,p1] = saffron(Sys0,Exp,Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd));
% set threshhold for contour at 10% max amplitude
```

```
Zthresh = 0.01*max(max(Z));
   for iy=1:512,
       for ix = 1:512,
           if Z(ix,iy) < Zthresh,</pre>
              ZR(ix, iy) = Zthresh;
           else
              ZR(ix, iy) = Z(ix, iy);
           end
       end;
   end;
00
   f1min=-7.0;
   f1max=7.0;
   f2min=0.0;
   f2max=7.0;
8
   frinc=f1(2)-f1(1);
8
   xmin=floor((flmin-fl(1))/frinc)+1;
   xmax=floor((flmax-fl(1))/frinc)+1;
    ymin=floor((f2min-f2(1))/frinc)+1;
   ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax),f2(ymin:ymax),ZR(ymin:ymax,xmin:xmax),10,'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
% LDM2134 [13C2](3,6-(OMe)2-PSQ) HYSCORE Dimer Simulation
clear;
Sys0.S = 1/2;
Sys0.q = 2.0057;
Sys0.Nucs = '13C, 13C, 13C, 13C';
Sys0.A = [0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
```

```
[x1, x2, y1, p1] = saffron(Sys0, Exp, Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd));
% set threshhold for contour at 10% max amplitude
   Zthresh = 0.05*max(max(Z));
   for iy=1:512,
       for ix = 1:512,
           if Z(ix,iy) < Zthresh,</pre>
              ZR(ix,iy) = Zthresh;
           else
              ZR(ix, iy) = Z(ix, iy);
           end
       end;
   end;
00
   f1min=-15.0;
   f1max=15.0;
   f2min=0.0;
   f2max=15.0;
8
   frinc=f1(2)-f1(1);
8
   xmin=floor((flmin-fl(1))/frinc)+1;
   xmax=floor((flmax-fl(1))/frinc)+1;
   ymin=floor((f2min-f2(1))/frinc)+1;
    ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax),f2(ymin:ymax),ZR(ymin:ymax,xmin:xmax),10,'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
%LDM2134 [13C2](3,6-(OMe)2-PSQ) HYSCORE Simulation Molecule
<u><u><u></u></u></u>
clear;
```

```
Sys0.S = 1/2;
Sys0.g = 2.00575;
Sys0.Nucs = '13C,13C';
Sys0.A_ = [-0.4155 16.1325 0.63;-0.4155 16.1325 0.63];
```

```
\% Load the experimental Parameters
```

```
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1,x2,y1,p1] = saffron(Sys0,Exp,Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd));
% set threshhold for contour at 10% max amplitude
    Zthresh = 0.05*max(max(Z));
    for iy=1:512,
        for ix = 1:512,
            if Z(ix,iy) < Zthresh,</pre>
               ZR(ix,iy) = Zthresh;
            else
               ZR(ix, iy) = Z(ix, iy);
            end
        end;
    end;
00
    f1min=-25.0;
    f1max=25.0;
    f2min=0.0;
    f2max=25.0;
00
    frinc=f1(2)-f1(1);
00
    xmin=floor((flmin-f1(1))/frinc)+1;
    xmax=floor((flmax-fl(1))/frinc)+1;
    ymin=floor((f2min-f2(1))/frinc)+1;
    ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax),f2(ymin:ymax),ZR(ymin:ymax,xmin:xmax),10,'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
```
```
%LDM2134 [13C2](3,6-(OMe)2-PSQ) HYSCORE Simulation All Components
$_____
clear;
% Species 1
Sys1.S = 1/2;
Sysl.g = 2.0057;
Sys1.Nucs = '13C,13C,13C,13C,13C,13C'; % Treating the nuclei seperately
Sys1.A = [0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064 0;0.9758 1.3064
0;0.9758 1.3064 0;0.9758 1.3064 0];
% Species 2
Sys2.S = 1/2;
Sys2.g = 2.0057;
Sys2.Nucs = '13C,13C';
Sys2.A = [-0.4155 16.1325 0.63;-0.4155 16.1325 0.63];
% Species 3
Sys3.S = 1/2;
Sys3.q = 2.0057;
Sys3.Nucs = '13C, 13C, 13C, 13C';
Sys3.A = [0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0;0.3849 7.9653 0];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1, x2, y1, p1] = saffron(Sys1, Exp, Opt);
[x1, x2, y2, p2] = saffron(Sys2, Exp, Opt);
[x1, x2, y3, p3] = saffron(Sys3, Exp, Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd)) + (real(p2.fd)) + (real(p3.fd));
% set threshhold for contour at 10% max amplitude
   Zthresh = 0.01*max(max(Z));
   for iy=1:512,
        for ix = 1:512,
           if Z(ix,iy) < Zthresh,</pre>
              ZR(ix, iy) = Zthresh;
           else
```

```
ZR(ix, iy) = Z(ix, iy);
            end
        end;
    end;
8
    f1min=-25.0;
    f1max=0.0;
    f2min=0.0;
    f2max=25.0;
00
    frinc=f1(2)-f1(1);
9
    xmin=floor((flmin-f1(1))/frinc)+1;
    xmax=floor((flmax-fl(1))/frinc)+1;
    ymin=floor((f2min-f2(1))/frinc)+1;
    ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax),f2(ymin:ymax),ZR(ymin:ymax,xmin:xmax),15,'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
```

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Chapter 3. The Influence of Lewis Acidity on Spin Density Delocalization

3.1 Introduction

In the previous chapter, it was shown that the wave function of the unpaired spin density can be, and is, influenced by a variety of factors. DFT results predicted an overall decrease in average carbonyl carbon unpaired spin density when examining a family of 3,6-R₂-PSQ molecules moving from electron-donating groups to electron-withdrawing groups. This showed a spin polarization effect based on substituent choice. When examining NaPSQ, Na-[¹³C₂]PSQ, Na(3,6-(OMe)₂-PSQ) and Na([¹³C₂]3,6-(OMe)₂-PSQ) by EPR and ESEEM, however, the trend predicted by DFT was also true for unpaired spin density at the nucleus (isotropic coupling), but not unpaired spin density in p-orbitals (dipolar coupling). ¹H- a_{iso} values were smaller for 3,6-(OMe)₂-PSQ than PSQ, as well as ¹³C- a_{iso} values. ESEEM results contrasted with these as dipolar values were found with the opposite trend. For both dimer and ion-pair molecules, [¹³C₂]3,6-(OMe)₂-PSQ was found to have larger *T* values than [¹³C₂]PSQ. In this chapter Na⁺ is replaced with a Zn(tren)²⁺ unit and examined is the effect(s) Lewis acidity has on unpaired spin density distribution.

The purpose of this chapter is to explore spin density delocalization in phenanthrenesemiquinone when covalently bound to a d^{10} metal, specifically Zn^{II} . Zn^{II} was chosen to mimic the ionic radius of Ni^{II}, due to the interest in Ni-SQ complexes. Ni^{II} has an ionic radius of 83 pm (octahedral, high spin,) and Zn^{II} has an ionic radius of 88 pm¹, making zinc an appropriate d^{10} model for Ni^{II} complexes. The importance of having a d^{10} model is to study what effect an M^{II} ion has on spin density in a bound, organic radical ligand, in the absence of exchange coupling. Since our ultimate goal is to understand the effects of exchange coupling on

spin density delocalization/polarization, we wish to first know what would happen when the semiquinone is bound to a non-paramagnetic metal, in a similar chemical environment to [Ni(tren)(PSQ)](BPh₄). In addition, the hyperfine coupling constants of NaPSQ will be compared to those of Zn-PSQ, to assess the effect of an M^{II} ion on spin density delocalization.

The system of study is seen below in Figure 1 and is molecularly analogous to the aforementioned Ni^{II} complex. The system contains tris(2-aminoethyl)amine (tren), an ancillary ligand used to occupy coordination sites on zinc, and a single PSQ moiety. This system has been previously studied², albeit with a tetraazzmacrocyle in the place of tren, but only as a spectroscopic baseline for its Ni^{II} analogue. Steady-state electronic absorption features were compared and assigned based on the Zn^{II} compound and its absence of any d-d transitions in the visible region of the spectrum. No synthetic or physical characterization was provided by the study. Other studies that targeted Zn^{II}-SQ species concentrated on bis-semiquinone systems that exhibited triplet ground states^{3–5}. These studies were focused on super exchange interactions between the ligands as well as interligand electron transfer and valence tautomerism.



Figure 3-1. Molecular structure of [Zn(tren)(3,6-R₂-PSQ)]⁺.

Additionally, Ga^{III} was chosen to assess spin density at the metal center. Zn has an I = 0 nucleus and thus no hyperfine would be seen from EPR experiments, whereas Ga has two I = 3/2

nuclei, ⁶⁹Ga and ⁷¹Ga, and therefore the hyperfine coupling can be measured. These compounds will be essential to the analysis of spin density delocalization as it provides hyperfine information at the metal center, and hyperfine information at the carbonyl carbons for a M^{III} ion. Although there is no hyperfine coupling available for M^{II} ions in this study, it will still be advantageous to compare M^I (Na) and M^{III} ions hyperfine interactions, both at the metal and the carbonyl carbons. This will give a much fuller picture of the interplay between ligand and metal, when an unpaired electron is involved.

Of course this is not the first study to employ Ga^{III} as a diamagnetic stand-in for a paramagnetic metal. Fehir⁶ has studied $[Ga(tren)(3,6-NO_2-PSQ)]^{2+}$ as well as $[Ga(tren)(2,7-NO_2-PSQ)]^{2+}$ complexes. This study was conducted to uncover spin density delocalization as a mechanism of substituent placement. It was found that the 2,7 isomer shifted the spin density onto the N atoms of the NO₂ groups to a greater extent than in the 3,6 isomer. There is, however, a slight possibility that some of the ¹⁴N hyperfine interaction could be a result of N ligating atoms from the tren capping ligand. Hyperfine coupling at the Gallium nucleus was said to be consistent with a Ga^{III}_2 iminosemiquinone complex synthesized and studied by Wieghardt and coworkers.⁷

McCusker and coworkers have studied $[Ga_2(tren)_2(CA)]^{3+}$ complexes in which two $Ga(tren)^{3+}$ units are binding to a tetraoxolene (CA) ligand where one side possesses semiquinone character, and the other side, catecholate, giving an S = $\frac{1}{2}$ system. This study found the two gallium nuclei had comparable hyperfine parameters and yet smaller than the hyperfine coupling constants of the carbonyl carbons of the free CA ligand. This system also served as a template for studying analogous Cr^{III} complexes⁸. DFT and CW-EPR have been carried out on a [Ga(tren)(PSQ)](BPh_4) complex and its' isotopologue, [Ga(tren)([9,10-1^3C_2]PSQ)](BPh_4), in an

attempt to measure spin density at the gallium nucleus; the ability to explore hyperfine interactions at the ligating metal are made possible by the I = 3/2 gallium nucleus. Attempts were made to isolate and study a Cd^{II}-PSQ complex to elucidate hyperfine coupling at a M^{II} center, and compare to Zn^{II} and Ni^{II}; however, the complex was unable to be isolated. In lieu of obtaining said Cd^{II} complex, the information obtained from the Ga^{III} complex aided in drawing conclusions regarding spin density delocalization across the semiquinone ligand to the metal center.

A density functional theory (DFT) has been conducted in addition to the EPR study to examine the possibilities of a substituent effect. Zn^{II} - and Ga^{III} -3,6-R₂-PSQ complexes were examined, and only in the case of Ga^{III} complexes was a trend found comparing average oxygen spin density and average carbon spin density. In both cases, however, the magnitude of spin density on carbonyl carbon atoms was greater than on oxygen atoms.

Continuous Wave EPR (cw-EPR) experiments of $[Zn(tren)(PSQ)](BPh_4)$ and its ¹³C isotopologue as well as $[Ga(tren)(PSQ)](BPh_4)_2$ and its ¹³C isotopologue were conducted. For $[Zn(tren)(PSQ)](BPh_4)$ and $[Zn(tren)(^{13}C_2PSQ)](BPh_4)$ the treatment was similar to that of the free ligands; room temperature CW spectra were taken at varying field modulation values to uncover proton a_{iso} values, ESEEM experiments to uncover axial (anisotropic) and rhombic contributions to the hyperfine interaction. Results of HYSCORE experiments are also presented to aid in the interpretation of the ESEEM data.

3.2 Experimental

General Methods. Reagents were purchased from commercially available sources and used without further purification unless otherwise stated. Stabilizer-free tetrahydrofuran was purchased from Fisher Scientific and either distilled over sodium metal and benzophenone and freeze, pump, thawed to remove O₂, or taken from a dry still with a solvent bomb. Elemental analyses and electro-spray ionization ESI mass spectra were obtained through the analytical facilities at Michigan State University. GC mass spectra were obtained on a Hewlett Packard G1800D GCD system equipped with an electron ionization detector. NMR spectra were collected on Agilent DDR2 500 MHz Spectrometers equipped with 7600A autosamplers at the Max T. Rogers NMR Facility at Michigan State University.

Synthesis. [Zn(tren)(OH₂)₂](ClO₄)₂ (1). The synthesis of this compound is based on an unpublished procedure. 2.55 g (6.8 mmol) Zn(ClO₄)₂·6H₂O was added to a stirring ethanolic solution of 1 g (6.8 mmol) of tren and immediately a colorless precipitate crashed out of solution. The reaction was stirred for an additional hour to ensure complete complexation. The colorless solid was then filtered, washed with EtOH and dried on an aspirator. Yield: (>100%). MS [GC m/z (rel. int.)]: C₆H₂₁N₄O₂Zn⁺ 245.07 (100%), ClO₄⁻ 98.95 (100%).

[Zn(tren)(PSQ)](BPh4) (2). The synthesis of this compound is based on an unpublished procedure. In a dry box, a THF solution of 297 mg (1.41 mmol) 9,10-phenanthrenequinone was made and an excess of sodium metal (5x5x5 mm³ chunks) were added and the reaction was stirred overnight. The clear/deep red catecholate solution was filtered to remove the unreacted sodium. In a separate flask, 564 mg (1.26 mmol) [Zn(tren)(OH₂)](ClO₄)₂ was suspended in MeOH and the catecholate solution was added to this, drop-wise. As the catecholate solution was added, the reaction mixture changed from colorless/cloudy to yellow/clear. This was stirred overnight and the following day 483 mg (1.41 mmol) [Fc](PF₆) in MeOH was added to produce a dark green reaction mixture. The mixture was then filtered to remove the ferrocene. A 20-fold excess of Na(BPh₄) (8.6 g, 25.2 mmol) was added to the filtrate and the reaction mixture was then transferred to a round bottom flask equipped with a gas flow adapter and pumped out of the dry box. The solution was then dried under a stream of N₂, and subsequently dried under vacuum. The resultant green powder was then taken up in dry, degassed CH₂Cl₂ (dried via dry still), by way of cannula transfer. In a secondary flask, hexanes was sparged with N₂ for 15-30 minutes and then cannula transferred to the CH₂Cl₂ flask to crash out a pale green solid. The solid was then filtered on a glass frit, washed with Et₂O and dried on an aspirator for a minimum amount of time and then pumped into a dry box. Yield: (18%). MS [ESI *m*/z (rel. int.)]: C₂₁H₃₁N₄O₃Zn⁺ (Complex · MeOH) 451.12 (10%). Analytical composition calculated for C₄₄H₄₆BN₄O₂Zn·0.5 CH₂Cl₂·0.05 CH₃OH: C, 68.33; H, 6.07; N, 7.15; Found: C, 68.52; H, 6.00; N, 6.94.

 $[Zn(tren)({}^{13}C_2-PSQ)](BPh_4)$ (3). This complex was synthesized analogously to complex 2. In a dry box, a THF solution of 56 mg (0.266 mmol) 9,10-phenanthrenequinone was made and an excess of sodium metal (5x5x5 mm³ chunks) were added and the reaction was stirred overnight. The clear/deep red catecholate solution was filtered to remove the unreacted sodium. In a separate flask, 106 mg (0.238 mmol) [Zn(tren)(OH₂)](ClO₄)₂ was suspended in MeOH and the catecholate solution was added to this, drop-wise. As the catecholate solution was added the reaction mixture changed from cloudy/colorless to yellow/clear. This was then stirred overnight and the following day 88 mg (0.266 mmol) [Fc](PF₆) in MeOH was added to produce a dark green reaction mixture. The mixture was then filtered to remove the ferrocene. A 20-fold excess of Na(BPh₄) (1.82 g, 5.32 mmol) was added to the filtrate and the reaction mixture was then transferred to a round bottom flask equipped with a gas flow adapter and pumped out of the dry box. The solution was then dried under a stream of N2, and subsequently dried under vacuum. The resultant green powder was then taken up in dry, degassed CH₂Cl₂ (dried via drystill), by way of cannula transfer. In a secondary flask, hexanes was sparged with N₂ for 15-30 minutes and then cannula transferred to the CH_2Cl_2 flask to crash out a pale green solid. The solid was then filtered on a glass frit, washed with Et₂O and dried in vacuo for a minimum amount of time and then pumped into a dry box. Yield: (47%). MS [ESI m/z (rel. int.)]: C₁₉¹³C₂H₃₁N₄O₃Zn⁺ (Complex MeOH) 453.18 (50%). Analytical composition calculated for ¹³C₂C₄₃H₄₆BN₄O₂Zn·H₂O·CH₃OH: C, 68.57; H, 6.63; N, 7.08; Found: C, 68.64; H, 6.43; N, 7.35.

[Fe(CsHs)2](BPh4) (4). The synthesis of this complex was based on methods developed in the literature⁹. A suspension was made of 1.0 g (5.4 mmol) of ferrocene in 40 mL of Acetone and 40 mL H₂O was made. This suspension was placed under N₂ and 1.22 g (7.6 mmol) anhydrous FeCl₃ was added and the orange suspension changed to deep blue. This was stirred for 20 minutes and 2.6 g (7.6 mmol) of Na(BPh4) was added, producing a dark blue precipitate. THF was added (ca. 200 mL) until all solids dissolved and this produced a light blue/milky white solution. The solution was filtered and the filtrate concentrated under a stream of N₂. A dark blue, fine crystalline powder resulted from concentrating the solvent. This solid was filtered, dried in vacuo and immediately stored in the glove box. The compound naturally decomposes (even under N₂) after several days. 1.2 grams of the dark blue, crystalline powder was recovered. Yield: (44%). MS [ESI (Hi-Res) m/z (rel. int.)]: C₁₀H₁₀Fe⁺ 186.0 (100%), C₂₄H₂₀B⁻ 319.2 (100%).

[Ga(tren)(PSO)](BPh4) (5). The synthesis of this compound is based on methods previously developed¹⁰. In a glove box, 99.9 mg (0.48 mmol) of PhenQ was taken up in THF, and 5x5x5 mm³ Na cubes were added to the stirring solution. After stirring overnight, a blood red solution persisted and was filtered. In a separate flask, 190 mg (0.43mmol) of GaI_3 was dissolved in 5 mL of MeOH and 0.06 mL (0.43 mmol) tren was added to the solution to produce a cloudy/yellow reaction mixture. The filtered PCat²⁻ solution was then added to the clear/colorless [Ga(tren)I₂]I solution to produce a yellow/clear reaction mixture and was stirred for 2 hours. The reaction mixture was then filtered and a concentrated MeOH solution of a 10fold excess of NaBPh₄ was added. The solvent volume was reduced by vacuum and the flask was covered and placed in the refrigerator (glove box). After several days a yellow crystalline precipitate had fallen out of solution to yield 200 mg (54 % yield) of Ga-PCat. The Ga-PCat complex was then dissolved in MeCN and 136 mg (0.269 mmol) of [Fc](BPh₄) was added to the stirring solution and immediately the color changed from bright yellow to brown-gold. This was stirred for 1 hour, after which the solution was filtered and an excess of NaBPh4 was added and the flask was swirled until all solids dissolved. 300 mL of degassed E_{t_2O} was added and the solution became cloudy. The flask was covered and placed in the fridge. A brown-gold crystalline solid had crashed out of solution after several days; this was filtered and washed with Et₂O. MS [ESI (Hi-Res) m/z (rel. int.)]: C₂₀H₂₆GaN₄O₂⁺ 423.13 (100%), C₂₄H₂₀B⁻ 319.2 (100%).

[Ga(tren)([9,10-¹³C₂]PSQ)](BPh4) (6). This compound was prepared in an analogous manner to 4. MS [ESI (Hi-Res) m/z (rel. int.)]: C₁₈¹³C₂H₂₆GaN₄O₂⁺ 425.13 (32%), C₂₄H₂₀B⁻ 319.2 (100%).

Physical Measurements. EPR Spectroscopy. All EPR data were collected on a Bruker Elexsys E-680X spectrometer, operating at X-band frequency (9.42-9.71 GHz). Low

temperature experiments were performed between 4-30 K using an Oxford Instruments liquid helium flow system equipped with a CF-935 cryostat and an ITC-503 temperature controller. Samples were prepared in a dry box in modified Wilmad Glass SQ-706 EPR tubes with 3.8 mm diameter. Prior to sample preparation, tubes were modified in the glass blowing lab at Michigan State University to contain a grated seal and vacuum adapter port. A vacuum was pulled on the sample tubes and then the vacuum ports were blown off at the grated seal, by hydrogen torch. Prior to collecting data, power-dependence experiments were conducted to ensure non-saturation of the detector. Continuous wave spectra were simulated using the garlic module of Easy Spin 4.5^{11,12,13}.

All pulsed experiments were conducted at X-band microwave frequency. ESEEM spectra were obtained using a three pulse sequence of 90°-τ-90°-T-90° with 90° pulse lengths of 16 ns. Tau values were chosen to suppress hyperfine contributions from weakly coupled protons. Echo amplitudes were integrated at FWHM and the T values were scanned from 40 ns to 6 µs with a 12 ns time increment. A four step phase-cycling procedure was used to eliminate unwanted 2-pulse echoes.¹⁴ Raw data were processed by phase shifting the spectra to remove the dispersion component from the time domain data. The in-phase portion of the data were normalized by dividing by a biexponential background decay function. These normalized data were then further processed by subtracting a second degree polynomial (DC-component of the signal), followed by application of a Hamming window. The data set was then zero-filled from 512 points to 1024 points and Fourier transformed. Frequency spectra are displayed as an absolute value of the transformed time domain data. ¹³C and ¹²C spectra are presented as one divided spectrum at each magnetic field value. After normalizing each time domain spectrum

individually, the ¹³C spectrum was divided by the ¹²C spectrum and the same work up procedure described above was applied¹⁵.

HYSCORE experiments were carried in a similar manner to the ESEEM experiments but with a four-pulse sequence of 90° - τ - 90° - t_1 - 180° - t_2 - 90° with a 180° pulse length of 16 ns. Echo amplitudes were measured at FWHM and τ values were chosen as stated above. T₁ and t₂ values were scanned from 40 ns to 2 µs with 16 ns time increments. Data sets were 128 points in both dimensions. A 4-step phase cycling program was used to filter out unwanted 2-pulse echoes.¹⁶ The real, or in-phase portion of the HYSCORE data were processed, in both dimensions, by first subtracting a 2° polynomial, then tapering the data with a Hamming window and zero-filling to 256 points. A two-dimensional fast Fourier transform was applied and absolute values taken. Data are presented as a two-dimensional contour plot. Each contour plot is presented at a threshold of 5-20% of the maximum peak amplitude (z-direction).

Spectra were fit using customized MATLAB scripts where EasySpin was used to perform spectral simulations and the fminsearch function in Matlab was used to optimize the calculation parameters. Fminsearch is a function that finds the minimum of an unconstrained multivariable function using a derivative-free method¹⁷. Residuals were calculated by squaring the difference of the experimental and simulated amplitudes. Goodness of fit for each spectral fit was assessed by calculating a χ^2 value with the following equation:

$$\chi_{n}^{2} = \frac{\Sigma_{i=1}^{N} \frac{\left(y_{i}^{exp} - y_{i}^{calc}\right)^{2}}{\sigma^{2}}}{N - L}$$
(3.1)

where the sum is taken over N points, y_i^{exp} and y_i^{calc} are the experimental and calculated y-axis values, σ is the standard deviation fixed at 2% of the maximum spectral amplitude and L is the number of adjustable variables.

Calculations. Calculations were performed with the Gaussian 03^{18} computational chemistry package on the supercomputing cluster HPCC (High Performance Computing Center) at Michigan State University. Structures were drawn in GaussView4 and were optimized on phenanthrenesemiquinones (S=1/2) using the unrestricted formalism with the B3LYP^{19–21} functional. Molecular geometries were optimized with the 6-31g(d,p)^{22–32} basis set and single point calculations were carried out with the 6-311g(d,p)^{33–36} basis set. Frequencies calculations were performed at the same level of theory as geometry optimizations. In addition the "pop=NPA" keyword command was used to calculate spin densities by natural population analyses (NPA)

3.3 Results and Discussion

Density Functional Theory. DFT analysis was carried out on the series of $[Zn(tren)(3,6-R_2-PSQ)]^+$ complexes, where $R = NH_2$, OMe, H, Br, CF₃, CN and NO₂. Initial structures were based on the crystal structure of $[Ni(tren)(PSQ)](BPh_4)$,¹⁰ as well as the $[Ni(tren)(3,6-R_2-PSQ)]^+$ complexes studied within Reference 10. The geometries were successfully optimized with the unrestricted form of the B3LYP functional and the 6-31g(d,p) basis set. Frequencies calculations were undertaken to ensure that a global minimum had been reached and no imaginary frequencies were found. Single point calculations and population analyses were then carried out with the same functional and the 6-311g(d,p) basis set. Spin density values were calculated by

subtracting the beta spin density from the alpha spin density for each atom and then averaging each value.

Examining unpaired spin density delocalization for complexes of this type is unprecedented in the literature. Most Zn-SQ complexes studied are bis-o-semiquinone complexes and are typically ground state triplets. Not unlike in this investigation, they are often studied to escape the complicated electronic structure issues present with paramagnetic metals; they provide a means to study the ligand in the same, if not very similar, geometric arrangement. Although many Zn-SQ complexes are biradicals, $[Zn(NH_3)_4(SQ)]^+$ has been studied by DFT, by Bencini and coworkers³⁷, and it does resemble the structure of the Zn-PSQ complex being studied in this chapter. The tetradentate ligand, tren, has been replaced with four ammonia ligands and the semiquinone ligand is o-benzosemiquinone. The ammonia ligands allow for a geometry closer to that of an octahedral complex, being free ligands and not connected to a central nitrogen atom connected by ethylene bridges, which can constrict the geometry from being completely octahedral. The other difference of this complex being benzosemiquinone, which does not have the same spin delocalization capabilities of phenanthrenesemiquinone. These differences are noted; however, they do not pose large differences with respect to the delocalization of the unpaired spin density. Bencini and coworkers found that less than 3% of the unpaired spin density resides on Zinc and the NH₃ ligands, while most of the unpaired spin is located on the SQ ligand. The Ni^{II} analogue was also studied and 49% of the unpaired spin is on Ni, 39% on the semiquinone ligand and 12% on the NH₃ ligands. These results are consistent with the findings of this study (as well as the following chapter); however, this comes with a caveat. The Natural Population Analysis did not calculate any unpaired spin density on zinc, but the Fermi analysis found an isotropic hyperfine coupling constant of -6.22 MHz, slightly greater than that of Na (-7.06 MHz). So it should be noted here that the NPA does not first calculate hyperfine coupling constants and then covert to spin density [in a similar routine that was carried out in Chapter 2 for the isotropic hyperfine coupling constants].

Figure 2 shows the graph of average carbonyl oxygen spin density versus average carbonyl carbon spin density. No linear correlation or functional dependence between the two quantities was found. It is noticeable that the average oxygen spin density has experienced a slight decrease and the carbonyl carbon spin density has increased by a factor of approximately two, relative to PSQ. However, the fact that the two quantities do not correlate indicate that the unpaired spin density found on each atom may be influenced more by its next nearest neighbors; i.e. unpaired spin density on oxygen may be more influenced by Zn and tren, and likewise, unpaired spin density on carbon may be more influenced by the phenanthrene ring system.

The average oxygen spin density does increase with increasing electronegativity. This is consistent with results from Fehir's calculations on $[Ni(tren)(3,6-R_2-PSQ)]^+$ complexes; indeed, even the ordering of increasing spin density on oxygen is consistent between the two studies. Compare this with the DFT results of Chapter 2 where there is no trend. The only derivative that attracts attentions is -NO₂, and it has the least amount of spin density at both the carbon and the oxygen, relative to the other derivatives.



Figure 3-2. Average Carbonyl carbon spin density versus average oxygen for $[Zn(tren)(3,6-R_2-PSQ)]^+$ Complexes.

Table 3-1. Average carbonyl carbon and oxygen spin density in Zn-PSQ and PSQ systems as calculated from NPA analysis.

Substituent	PSQ	Zn-PSQ	PSQ	Zn-PSQ
	Avg. $C(\rho)$	Avg. $C(\rho)$	Avg. $O(\rho)$	Avg. $O(\rho)$
Br	0.073	0.194	0.25	0.183
CF ₃	0.064	0.193	0.248	0.193
Н	0.082	0.2	0.254	0.185
NH_2	0.0877	0.192	0.247	0.152
NO ₂	0.042	0.185	0.205	0.196
OMe	0.081	0.199	0.249	0.163
CN	0.055	0.186	0.239	0.192

Relative to PSQ, for R = Br, CN and CF₃ oxygen spin density drops by ~20 %, while NO₂ remains essentially unaffected, and H, NH₂ and OMe drop by ~40 %. There does not seem to be

any correlation between change in oxygen spin density and ability to donate/accept π density or donate/accept σ density. There is a correlation, however, between electron withdrawing and electron donating groups. The electron donating substituents lost more oxygen spin density than their electron withdrawing counter parts.

Despite the drastic change in oxygen spin density, the carbonyl carbons experienced an even greater increase in spin density. A 50-60% increase was observed for each of the substituents upon complexation. The loss of the spin density at the oxygen does not equal the gain in spin density at the carbon, however; and in fact, the derivative that gained the greatest amount of unpaired spin density is $-NO_2$. Compared to all the other derivatives, $-NO_2$ barely lost any oxygen spin density. Although no correlation was observed between carbon and oxygen spin density, it was discovered that the carbonyl carbon spin density increases and the oxygen spin density decreases when bound to M^{II} ion with a full *d* shell. If the charge density at the metal was then increased to a M^{III} ion, what effect would that have on the spin density in the carbonyl groups?

To answer this inquiry, a similar set of calculations was undertaken for Ga^{III} complexes of the same type of molecular structure as the Zn^{II} complexes. Displayed below in Figure 3 is a plot of carbon versus oxygen spin density in $[Ga(tren)(3,6-R_2-PSQ)]^{2+}$ complexes where $R = NH_2$, OMe, H, Br, CF₃, CN and NO₂. This is the first instance where a somewhat modest correlation coefficient has been achieved. The magnitude of unpaired spin density at the oxygen atoms has decreased dramatically while carbon unpaired spin density has remained in approximately the same range, with respect to the Zn-PSQ PSQ systems. Table 2 compares the carbonyl spin density between the free radical, Zn-PSQ and Ga-PSQ compounds. These results illustrate that

Lewis acidity and/or metal complexation potentially has an effect on spin density delocalization in PSQ type systems.

It is observed that in moving from the free radical to the Zn^{II} complex, the spin density at the oxygen decreases by approximately 20-40%, then another 40-56% decrease in the Ga^{III} complexes. It has been seen in [Ni(tren)(3,6-R₂-PSQ)]⁺ and [Cr(tren)(3,6-R₂-PSQ)]²⁺ complexes that a drastic decrease in average oxygen spin density occurs when comparing average oxygen spin density.

At the carbonyl carbons, however, the effect is not as straight forward. It was previously discussed that the Zn^{II} polarizes more spin density onto the carbons, but only for R = H and electron withdrawing derivatives does the carbon spin density decrease in moving from M^{II} to M^{III} . On the other hand, for electron donating substituents, the carbonyl spin density decreases.



Figure 3-3. Average Carbonyl carbon spin density versus average oxygen for $[Ga(tren)(3,6-R_2-PSQ)]^{2+}$ Complexes.

Table 3-2. Carbon and Oxygen spin density in $3,6-R_2$ -PSQ radical anions, $[Zn(tren)(PSQ)]^+$ and $[Ga(tren)(PSQ)]^{2+}$ complexes.

Substituent	PSQ C (ρ)	Zn-PSQ C (ρ)	Ga-PSQ C (ρ)	PSQ Ο (ρ)	Zn-PSQ Ο (ρ)	Ga-PSQ Ο (ρ)
Br	0.073	0.194	0.197	0.25	0.183	0.102
CF3	0.064	0.193	0.216	0.248	0.193	0.125
Н	0.082	0.2	0.214	0.254	0.185	0.111
NH2	0.0877	0.192	0.161	0.247	0.152	0.066
NO2	0.042	0.185	0.213	0.205	0.196	0.127
OMe	0.081	0.199	0.18	0.249	0.163	0.08
CN	0.055	0.186	0.203	0.239	0.192	0.115

It is quite apparent from the above results that Lewis acidity perturbs the spin density in the carbonyl groups. It is not apparent, however, as to why the oxygen spin density decreases by

such a magnitude, or why the carbon spin density increases to such a magnitude, in moving from free radical to M^{II}, to M^{III}. Following the synthesis section, the carbonyl carbon and proton spin density values will be assessed by EPR.

Synthesis. The d¹⁰-semiquinone complexes were synthesized based on procedures previously published. Figure 4 shows the several oxidations states of phenanthrenequinone (or any



Figure 3-4. Oxidation states of phenanthrenequinone.

quinone). Typically, quinones and semiquinones are not sought after as nucleophiles. Although transition metal-quinone complexes have been prepared^{38,39}, quinones have very low binding affinities, most likely due to the low nucleophilicity of the carbonyl oxygen atoms; their one electron reduced forms, semiquinones, also suffer from low binding affinities. The low charge density at the oxygen atoms (one negative charge delocalized across several atoms) is responsible for the low binding affinity. Additionally, the radical character of the ligand can lend itself to side reactions and formation of oligomers. The two-electron reduced form, catecholates, have high negative charge density on the oxygen atoms and are strong nucleophiles. Therefore, by exploiting the redox nature of the quinone, one can easily use the nucleophilicity of the catecholate to bind to a metal and subsequently use chemical oxidants to produce metal-semiquinone species. The major stipulation in these reactions is that the

semiquinone and catecholate forms are, generally, extremely air and moisture sensitive, especially in solution. Therefore, these reactions are carried out in dry boxes and on Schlenk lines.

For both Zn^{II} and Ga^{III} products, phenanthrenequinone was first taken up in dry THF and reduced with an excess of sodium metal. The filtered catecholate solution was then added to stirring solutions of metal-tren precursor complexes, either in THF or MeOH and produced yellow-amber/clear reaction mixtures. Zn-PCat complexes were made with Zn(tren)(ClO₄)₂, which was prepared by adding Zn(ClO₄)₂·6 H₂O to a stirring, EtOH solution of tren. After which a colorless precipitate crashes out of solution. Ga-PCat complexes, however, were synthesized by adding tren to a solution of GaI₃, producing [Ga(tren)I₂]I in solution.

Following complexation of PCat²⁻ to Zn^{II}, the solution was oxidized with a ferrocenium salt to produce a dark, forest green-colored solution, reminiscent of the NaPSQ ion pair. This was filtered (to remove any ferrocene that had precipitated out of solution) and the complex was metathesized with an excess of Na(BPh₄) to produce the BPh₄ salt. The identity of the complex was confirmed by ESI mass spectrometry results, as well as elemental analysis. Both the ¹²C and ¹³C complexes were found with a methanol molecule attached to the complex.

The Ga-PCat complexes were also oxidized by a ferrocenium salt, although the resultant semiquinone was a brown-gold-colored solution. This complex was also metathesized with Na(BPh₄) and finally recrystallized in a solution of MeCN, by adding Et₂O and letting it set over several days. The identity of the ¹²C and ¹³C complexes were confirmed by Hi-Res Mass Spec results.

CW-EPR.

In the previous chapter, CW-EPR was found to be a powerful technique; multiple ¹³C- a_{iso} values were found for both NaPSQ and Na(3,6-(OMe)₂-PSQ) compounds. It was shown that NaPSQ had larger a_{iso} values, in both the ion-pair and dimer compounds; however, when comparing dipolar values, the situation was reversed. Also, it was observed that the substituent has an influence on the paired ion. For NaPSQ, ²³Na- $a_{iso} = 1.32$ MHz while for Na(3,6-(OMe)₂-PSQ) ²³Na- $a_{iso} = 1.17$ MHz. It should also be noted that the Fermi contact integrals for NaPSQ and Na(3,6-(OMe)₂-PSQ) were 7.06 MHz and 6.98 MHz, respectively. Although there is a large difference in magnitude, both the observed and calculated a_{iso} values conformed to the trend that NaPSQ had a larger value.

Moving forward, those experimental results and calculations from Chapter 2 will be compared to Zn^{II}- and Ga^{III}-tren type complexes. Although Zn^{II} has an ionic radius that is similar to Ni^{II}, utilizing zinc does pose a discontinuity to the study, though. Unlike Na and Ga, the hyperfine coupling at Zn cannot be measured using a standard Zn source. ⁶⁴Zn makes of 48% of the natural abundance of all Zn isotopes and has no nuclear spin. The only Zn isotope with nuclear spin is ⁶⁷Zn with I = 5/2 and its natural abundance is 4.1%, making it difficult to measure contributions to the hyperfine coupling at X-band microwave frequencies. There was an attempt to synthesize a Cd^{II} analogue which has two isotopes with nuclear spin, ¹¹¹Cd and ¹¹³Cd, each with $I = \frac{1}{2}$; however, the identity of this complex could not be confirmed. So, although there are computational results from DFT calculations, there will be no hyperfine data for this complex.

A second caveat to this study deals with the Ga-PSQ complex. In addition to CW data, ESEEM and HYSCORE analyses of the anisotropic contribution to the hyperfine coupling would round out the study of delocalization of unpaired spin density; however, the physical observable

for these experiments is the formation of a spin echo. The ability to produce an echo lies with the molecule in question, and in the case of this study, no echo was observed for either **5** or **6**. Efforts were made to find an echo by increasing the concentration of the samples and even increasing the microwave power to the point of saturating the detector, but all of these efforts were to no avail. It is also possible that this molecule has a spin lattice relaxation time, T_2 , which is fast compared to the detector. If this is the case, then it would be possible to observe an echo at higher operating frequencies. Pulsed Studies of Ga-SQ complexes at W-band, for example, are known⁸.

Despite the inability to observe a spin echo, the CW spectra were obtained and hyperfine coupling for both 69,71 Ga and 13 C were detected. The CW spectrum (black) and simulation (red) of [Ga(tren)(PSQ)](BPh₄)₂ are shown below in Figure 5. Unlike the PSQ ion-pair compounds, only hyperfine coupling to gallium is observed. The coupling is large enough that no coupling from ring protons could be detected. Gallium has two isotopes with nuclear spin, 69 Ga and 71 Ga, each with I = 3/2. EasySpin computes a single value that is a weighted average of the two isotopes, based on the formula:

$$\bar{A} = A(^{69}Ga)w(^{69}Ga) + A(^{71}Ga)w(^{71}Ga)$$
(3.2)

Only the weighted average will be presented from here on.

The spectrum was fit with $a_{iso} = 19.73$ MHz. This value is consistent with other Ga-SQ complexes. For complexes of the form $[Ga_2(tren)(SQ)]^{3+}$, McCusker and coworkers have found ${}^{69,71}Ga-a_{iso} = 10.03$ MHz and 10.36 MHz, and this is for the case where a single electron is delocalized across a six-membered ring onto two Ga^{III} ions.⁸ A pentacoordinated Ga complex of the formula [Ga(3,5-di-tert-butyl-*o*-iminosemiquinone)(3,5-di-tert-butyl-*o*-iminocatecholate)(pyridyl)] exhibited ${}^{69,71}Ga-a_{iso} = 40.71$ MHz.⁴⁰ This hyperfine coupling is

roughly twice the simulated value of **5**, however the iminosemiquinone has a six-membered-ring and thus less atoms to delocalize the unpaired spin density, relative to PSQ. Lastly, Fehir has found 69,71 Ga- $a_{iso} = 17.37$ MHz for [Ga(tren)(3,6-(NO₂)₂-PSQ)](BF₄)₂.⁴¹ This compound being the closest, structurally, to the Ga-PSQ complex studied in this chapter. Although more compounds are not involved, it may be pertinent to note that Ga^{III} has a smaller isotropic hyperfine coupling in this compound, relative to **5**, leading one to the conclusion that perhaps the -NO₂ groups are polarizing the unpaired spin density away from gallium.

To contrast the experimental observations with theoretical results, there are two points to consider. The first deals with comparing the observed 69,71 Ga- $a_{iso} = 19.73$ MHz hyperfine coupling constant with the calculated value of 20.79 MHz. For a direct comparison, the observed constant gives the calculation validation and it seems rather accurate. If the observed 69,71 Ga- $a_{iso} = 17.37$ MHz hyperfine coupling constant for [Ga(tren)(3,6-(NO₂)₂-PSQ)](BF₄)₂ were compared with the calculated value of 22.25 MHz, then, if only the DFT results were considered, one could draw the opposite conclusion to the one above. Here it seems that the -NO₂ groups would be polarizing unpaired spin density toward gallium, but this only takes into account DFT results and the experimental results do not have enough merit to propose a trend from one derivative to another. If there were more experimental results to consider from varying derivatives, then one could propose such a trend.

Secondly, the theoretical results are a contradiction. The fermi contact integral is 20.79 MHz; however, the calculated spin density at gallium is zero. It should be considered here that in the above DFT section, the results displayed are from that of the natural population analysis, and in this section only the Fermi contact integrals are being considered. It was stated previously that these two entities are calculated both separately, and with differing methods. The Fermi method

does predict a hyperfine coupling constant at the gallium nucleus and this agrees with the observed results, as well as predicting unpaired spin density at gallium. One last caveat to the Fermi contact integrals: only ⁶⁹Ga- a_{iso} values are calculated, ⁷¹Ga is not considered. Due to this, the calculated Fermi contact integrals are inherently lower than the weighted average or ⁷¹Ga. The magnetic moment of ⁷¹Ga is larger than the magnetic moment of ⁶⁹Ga, 2.56 versus 2.02, respectively (where the magnetic moment is a ratio of μ/μ_N).



Figure 3-5. 10 K CW spectrum (black) and simulation (red) of **5**, $[Ga(tren)(PSQ)](BPh_4)_2$. Simulation parameters: g = 2.00535, lwpp = 0.71 mT, 0.28 mT, a_{iso} values: ^{69,71}Ga = 19.73 MHz. Experimental parameters: 9.72 GHz μ W frequency, 0.63 mW power, 3460 G center field, 200 G sweep width, 1 G modulation amplitude, 512 points. $\chi^2 = 0.23$.



Figure 3-6. 10 K CW spectrum (black) and simulation (red) of **6**, $[Ga(tren)([^{13}C_2]PSQ)](BPh_4)_2$. Simulation parameters: g = 2.00532, lwpp = 1.09 mT Lorentzian + 0.57 mT Gaussian, a_{iso} values: $^{69,71}Ga = 19.73$ MHz, ^{13}C - a_{iso} values: 27.77 MHz, 32.10 MHz. Experimental parameters: 9.72 GHz μ W frequency, 0.016 mW power, 3460 G center field, 200 G sweep width, 1 G modulation amplitude, 512 points. $\chi^2 = 0.22$.

Moving on from hyperfine at the metal, hyperfine coupling at the carbonyl carbon atoms are considered. Pictured above in Figure 6 is the room temperature spectrum CW spectrum of **6**, $[Ga(tren)([^{13}C_2]PSQ)](BPh_4)_2$ (black) and its simulation (red). The immediate observation from the simulation of **6**, is that the ^{13}C - a_{iso} is large relative to any other compound in this study, including the Zn-PSQ complex below. DFT predicts Fermi contact integrals of 7.29 MHz and 7.20 MHz for the two carbonyl carbons, which is high compared to what has been observed thus far, but 27.77 MHz and 32.10 MHz seems excessive. Unfortunately, these results cannot be directly compared to any other study in the literature, but for such strong hyperfine coupling at the carbonyl carbon atoms, they can be compared to the trianion of chloranilic acid. Broze and

Luz⁴² report a ¹³C- $a_{iso} = 22.9$ MHz for the carbonyl carbon atoms. This tetraoxolene ligand consists of four carbonyl groups total (two *o*-quinone groups on one six-membered ring), and so for a coupling this large to be measured on a free ligand, one might expect the coupling decrease upon complexation. This is yet to be measured, but, ¹³C- a_{iso} does increase for PSQ when bonded to Ga; this was both observed experimentally and predicted by DFT.



Figure 3-7. Room temperature CW spectrum (black) and simulation (red) of **2**, [Zn(tren)(PSQ)](BPh₄) at 20 mG modulation amplitude. Simulation parameters: g = 2.0071; a_{iso} values: $H_{3,6} = 5.90$, $H_{1,8} = 4.01$, $H_{2,7} = 1.96$, $H_{4,5} = 1.01$; Peak to peak line width: 0.0136 mT Gaussian 0.0107 mT Lorentzian broadening. Experimental parameters: 9.42 GHz microwave frequency, 0.80 μ W microwave power, 3353 G centerfield, 50 G sweep width, 20 mG modulation amplitude, 1024 points. $\chi^2 = 0.45$.

The experimental spectrum and simulation of **2**, [Zn(tren)(PSQ)](BPh4), can be seen in Figure 7. The spectrum was fit with four nonequivalent sets of two protons each, line broadening parameters with Gaussian and Lorentzian (Gaussian plus Lorentzian, or, Voigtian) components, and an isotropic *g* value. A total of 81 lines is expected from four nonequivalent groups with 2 protons each; however, only a total of 31 lines were observed in the 20 mG spectrum. Phenanthrenequinone has been previously studied as a free ion, reduced by zinc metal in alkaline media. The hyperfine information provided by the analyses from that study merely provided two hyperfine couplings, produced from two groups of four protons each.⁴³ This arrangement is not the case as there are four groups of chemically equivalent protons. Table 3 compares ¹H-*a*_{iso} values obtained from the simulations and those predicted by the Fermi analysis in DFT. The obtained values from the simulations prove to be in fine agreement with calculated Fermi contact integrals. DFT values calculated have asymmetry in their values, but these were taken to be equivalent in order to simplify the simulation.

Table 3-3. Calculated Fermi contact integrals and ${}^{1}\text{H}-a_{iso}$ values of **2** obtained from simulations of CW spectra, in MHz.

	H _{3,6}	H _{1,8}	H _{2,7}	H _{4,5}
aiso/MHz	5.90	4.01	1.96	1.01
Fermi Contact/MHz	-5.57,-5.29-	5.61,-5.4	1.82,1.67	1.43,1.22

The ¹H- a_{iso} values are comparable to those of NaPSQ, albeit with slightly higher hyperfine coupling constants, therefore no strong conclusions can be drawn from these results alone relating to the influence of Lewis acidity on unpaired spin density distribution. Though, the line shape alone of this radical is drastically different than that of NaPSQ, and due to the metal. In Kazuhiro's study of ion-pairs of PSQ, one can see the effect of the metal just by line shape alone.

So not only has it been seen that substituents have an effect on line shape and coupling, but also the ion has a profound effect as well. This stems from various physical properties of the nuclei involved, as well as the local magnetic environment of the molecule. Though, the protons involved due not experience the greatest effect of the zinc ion, the carbonyl carbons change in hyperfine is discussed below.



Figure 3-8. Room temperature CW spectrum (black) and simulation (red) of **3**, [Zn(tren)([¹³C₂]PSQ)](BPh₄) at 20 mG modulation amplitude. Simulation parameters: g = 2.007107; ¹³C- a_{iso} values: 1.08 MHz and 2.78 MHz; Peak to peak line width: 0.0246 mT Gaussian plus 0.0247 mT Lorentzian broadening. Experimental parameters: 9.39 GHz microwave frequency, 0.80 mW microwave power, 3320 G centerfield, 50 G sweep width, 20 mG modulation amplitude, 1024 points. $\chi^2 = 0.93$.

Displayed in Figure 8 is the CW spectrum and simulation of **3**, $[Zn(tren)([^{13}C_2]PSQ)](BPh_4)$. The spectrum resembles that of Na[¹³C₂]PSQ quite well, indicating initially that ¹³C hyperfine coupling had a similar effect on the spectrum. The coupling was within the same range as well; ¹³C- $a_{iso} = 1.08$ MHz and 2.78 MHz for **3**, where ¹³C- $a_{iso} = 1.57$ MHz for Na[¹³C₂]PSQ ion pair. This may indicate that an M^{II} ion does not necessarily have an effect on the hyperfine coupling, per se. However, the effect of the Zn(tren)²⁺ fragment does have an effect on the hyperfine coupling and that is manifested as asymmetry in the isotropic coupling of the carbonyl carbon atoms. The ¹H hyperfine couplings were not found to be asymmetrical, however. It is possible that the perturbations (from Zn^{II}) on the ¹H hyperfine couplings of "proton pairs" are small and therefore do not constitute distinguishing differences between the pairs of protons.

DFT calculations predicted dissimilar spin density values for the carbonyl carbon atoms (0.20 versus 0.19) however, the disparity in the Fermi contact coupling is more telling. DFT predicted ${}^{13}\text{C}-a_{iso} = 0.71$ MHz and 2.17 MHz for the carbonyl carbon atoms; this is some validation for DFT and the Fermi analysis correctly calculating spin properties for the types of molecules in this study. Although the exact magnitudes of the isotropic hyperfine couplings were not predicted, the disparity of the "delocalization" of the hyperfine coupling was correctly predicted.

	H3,6	H1,8	H2,7	H4,5	Сс=0
$ ho(\mathrm{N})_{\mathrm{obs}}$	0.0013	0.0009	0.00043	0.00022	0.0024,
					0.0009
$ ho(\mathrm{N})_{\mathrm{calc}}$	0.00125,	0.00125,	0.0004,	0.00032,	0.00193,
	0.0012	0.0012	0.00037	0.00027	0.00063

Table 3-4. Calculated spin density values at ¹H and ¹³C nuclei for **2** and **3**.

Table 4 compares the calculated isotropic spin densities with the spin density values obtained from the fits. As with the hyperfine coupling constants, the calculated values do agree with the values obtained from fitting the spectra. Additionally, these values are comparable to spin density values for NaPSQ and Na(3,6-(OMe)₂-PSQ).

To summarize the results of the CW experiments, the isotropic hyperfine coupling constants found for Zn-PSQ are comparable to those found for the ion-pairs of Chapter 2. And unfortunately, there does not seem to be a great effect of Lewis acidity on unpaired spin delocalization. This is unfortunate because as the study moves towards unraveling the intricacies of the Ni-PSQ system, it would have been advantageous to learn something about the spin properties of this system in the absence of the paramagnetic Ni^{II} ion. The greatest outlier of this section are the results of fitting the Ga-PSQ spectra. The ^{69,71}Ga- a_{iso} and ¹³C- a_{iso} hyperfine coupling constants are much larger than the hyperfine coupling constants of any of the other semiquinones examined within this study; however, the hyperfine coupling at gallium is in agreement with other gallium complexes where a paramagnetic ligand is bonded to gallium. So perhaps Lewis acidity does have an effect on unpaired spin density local, but it is not manifested in M^I or M^{II} type ions but M^{III} and ions of higher charge.

It must be added, though, that a calculation was performed in which the Ga^{III} ion was replaced with Ge^{IV}, and the flowing Fermi contact integrals were obtained: 73 Ge = 1.99 MHz, $^{13}C_{C=O}$ = 6.17 MHz and 5.46 MHz. So while the carbonyl carbon Fermi contact integrals are high, they are not of the magnitude of the carbonyl carbon atoms of the Ga-PSQ complex, and are of the same magnitude of the Zn-PSQ complex, as well as the ion-pairs of Chapter 2. It could be that the hyperfine interactions of Ga-PSQ are truly an anomaly and inherent to Ga-SQ complexes in general. Additionally, due to complications from ESEEM experiments, a spin echo could not be
found originating from Ga-PSQ, therefore the hyperfine coupling within these complexes could not be further explored.

ESEEM. In Chapter 2 it was shown that the dipolar contribution to the hyperfine coupling dominated the coupling in NaPSQ and Na(3,6-(OMe)₂-PSQ). This was evident for the ion-pair, dimer and tris complex (Na(3,6-(OMe)₂-PSQ) only). For the Zn-PSQ complex studied in this chapter, however, there is a single species being analyzed. Tris(2-aminoethyl)amine provides for only a single semiquinone moiety to bond to the metal, so in the future it may be pertinent to use such a concept for complexes of the type $[M^{I}(tren)(SQ)]$. It was also concluded from the previous section that the Lewis acidity provided by Zn^{II} did not have an effect on the isotropic hyperfine coupling, either for protons or carbonyl carbons.

The frequency domain spectrum and simulation are displayed below in Figure 9, below. The spin Hamiltonian used to model the Zn-PSQ system has the form:

$$\widehat{H} = g_e \beta_e B \widehat{S}_Z + A_{ZZ} \widehat{S}_Z \widehat{I}_Z + A_{XZ} \widehat{S}_Z \widehat{I}_X - g_N \beta_N B \widehat{I}_Z$$
(3.3)

where the first and last terms are the electronic and nuclear Zeeman interactions, respectively, and the middle terms are the electron-nuclear hyperfine coupling terms. The hyperfine parameters were as follows: C_1 , $a_{iso} = 1.08$ MHz, T = 2.84 MHz; C_2 , $a_{iso} = 2.78$ MHz, T = 2.46MHz. These hyperfine coupling parameters were arrived upon by holding the isotropic values constant and varying the dipolar values until a reasonable fit was reached.

The simulation accounts for three out of the four resonances from 0 - 6 MHz. The frequency domain spectra show peaks at 0.7, 2.17, 3.06, 4.36 MHz and a large hump centered at ~11.8 MHz. None of these resonances correspond to the ¹³C Larmor frequency of 3.70 MHz at 345.5 mT magnetic field. The large hump at 11.54 MHz is most likely a result of proton anisotropy

from **2**. This can be seen in the comparison spectrum in Figure 11. These features were suppressed by using the division technique; however, the origin of this resonance is **2**, Zn-PSQ.



Figure 3-9. ${}^{13}C/{}^{12}C$ Zn-PSQ ESEEM frequency domain spectrum and fit. Simulation parameters: C₁: $a_{iso} = 1.08$ MHz, T = 2.84 MHz $\rho = 0$; C₂: $a_{iso} = 2.78$, T = 2.46, $\rho = 0$. Experimental parameters: Field = 345.5 mT, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns τ and 40 ns starting time value.

Although DFT calculations proved useful when comparing results to theory in the CW section, the predicted anisotropic couplings do not contrast well with the simulated values. DFT calculated the following values: C_1 , $a_{iso} = 0.71$ MHz, T = 17.97 MHz; C_2 , $a_{iso} = 2.17$ MHz, T = 19.14 MHz. These dipolar values are more comparable with dipolar couplings of the NaPSQ ion pair ($a_{iso} = 1.5741$ MHz, T = 13.5674 MHz). Isotropic ¹³C coupling constants of **3** showed to be comparable to NaPSQ and Na(3,6-(OMe)₂-PSQ), which leads to the conclusion that the Zn^{II} ion has no effect on the hyperfine coupling, but when considering the dipolar coupling, this conclusion becomes invalid. It is now evident then, that Zn^{II} may not have an influence on the isotropic coupling, which is a result of unpaired spin density in σ -type orbitals, but rather it has an effect on the dipolar coupling, which is a result of the unpaired spin density in π -type orbitals. The case may be that the main effect on the isotropic coupling, simply arises due to the asymmetry introduced by the [Zn(tren)]²⁺ unit. This notion remains to be untested, however. The reduction in dipolar coupling is likely due to the Lewis acidity of the Zn^{II}, but it is unclear, in a mechanistic sense, how this is occurring. It would be pertinent to the future of this study to study changes in hyperfine coupling at the metal center.



Figure 3-10. ¹³C/¹²C Zn-PSQ ESEEM time domain spectrum and fit. Simulation parameters: C₁: $a_{iso} = 1.08$ MHz, T = 2.84 MHz $\rho = 0$; C₂: $a_{iso} = 2.78$, T = 2.46, $\rho = 0$. Experimental parameters: Field = 345.5 mT, 3 pulse ESEEM sequence, 12 ns time increment, 136 ns τ and 40 ns starting time value.



Figure 3-11. Comparison of 2 (blue) and 3 (red) ESEEM spectra. Fourier transforms were normalized to compare features from each spectrum.

HYSCORE. Consistent with ESEEM of Zn-SQ type species, there have not been explorations into the anisotropic hyperfine couplings of such complexes, and therefore HYSCORE spectra are virtually unknown from this field as well. There have been instances of exchanging Fe^{II} with Zn^{II} in Q_A and Q_B sites of bacterial reaction centers that contain ubisemiquinone; however, these zinc ions do not seem to interact with the oxygen atoms of ubisemiquinone, rather they are part of the biochemical system at large.⁴⁴

Figure 12 shows the first and second quadrants of the HYSCORE spectrum of **3** at 345.5 mT. As a reminder from Chapter 2, cross peaks that occur in the first quadrant signify weak couplings, i.e. couplings where $A < 2v_{Larmor}$, and cross peaks that occur in the second quadrant are indicative of strong coupling, i.e., couplings where $A > 2v_{Larmor}$. On-diagonal peaks are a consequence of the two-dimensional technique, where resonances from ESEEM are projected onto each other. Off-diagonal peaks arise due to cross-coupling of ω_{α} and ω_{β} frequencies originating from the same hyperfine coupling.



Figure 3-12. HYSCORE spectrum of **3**, Zn-¹³C₂PSQ. Experimental conditions: 345.5 mT magnetic field, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 time values.

The most intense off-diagonal peaks observed for this spectrum are at (2.9,4.5) and (4.5,2.9) centered about the ${}^{13}C_{\nu}$ frequency (3.69 MHz at 345.5 mT). These off-diagonal peaks are weak, relative to all of the diagonal peaks except (4.15,4.15), but they are present and it justifies the use of ${}^{13}C$ -labeling. These cross-peaks are not present in the HYSCORE spectrum of **2** (spectrum in Chapter 3 Appendix). It would have been ideal to detect off diagonal peaks corresponding to

 ${}^{13}C_{\nu}$ frequencies, or even observe resonances in quadrant two, where strong couplings occur. A second spectra of **3** can be seen in Figure 13 where the threshold in the *z*-direction is much lower, so as to see weak cross coupling in the second quadrant.



Figure 3-13. HYSCORE spectrum of **3**, $Zn^{-13}C_2PSQ$. Experimental conditions: 345.5 mT magnetic field, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 time values. A lower *z*-threshold was used to accentuate weak cross-couplings in quadrant two.

These less prominent, off-diagonal peaks were not expected, as the dipolar hyperfine coupling constants were small and within the same range as the isotropic hyperfine coupling constants. However, the simulation of quadrants one and two (Figures 14 and 15), based on the ESEEM simulation parameters, clearly shows off-diagonal resonances in the second quadrant and in the same vicinity of the observed off-diagonal resonances.



Figure 3-14. HYSCORE simulation (red) and spectrum (black) of **3**, Zn-¹³C₂PSQ. Experimental conditions: 345.5 mT magnetic field, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 time values. Simulation parameters: g = 2.0033; ¹³C₁, $a_{iso} = 1.08$ MHz, T = 2.84 MHz; ¹³C₂, $a_{iso} = 2.78$ MHz, T = 2.46 MHz; HYSCORE pulse sequence.



Figure 3-15. HYSCORE simulation (red) and spectrum (black) of **3**, Zn-[¹³C₂]PSQ in quadrant one. Experimental conditions: 345.5 mT magnetic field, 16 ns time increment, 136 ns tau, 36 ns starting t_1 and t_2 time values. Simulation parameters: g = 2.0033; ¹³C₁, $a_{iso} = 1.08$ MHz, T = 2.84 MHz; ¹³C₂, $a_{iso} = 2.78$ MHz, T = 2.46 MHz; HYSCORE pulse sequence.

Similarly, the knowledge gained from the HYSCORE spectrum of **3** is likely less important than comparison to NaPSQ ion pair and dimer, and Ni-PSQ. The HSYCORE spectrum of **3** is more comparable to that of the NaPSQ dimer, than the ion-pair, in that both spectra show the effect of delocalization of a single radical across a binding metal (Na and Zn) to an ancillary ligand (PhenQ and tren). The dimer was simulated to show equal delocalization across the four carbonyl carbon atoms, which agrees with the spectra, both HYSCORE and ESEEM. **3** was simulated to have asymmetrical distribution of hyperfine between two carbonyl carbons; it remains to be observed what is causing this but it could be hypothesized that it is dependent on the [Zn(tren)] unit. Exploring this possibility may require isotopic labelling of tren nitrogen

atoms with ¹⁵N atoms. This addition would be done in the absence of ¹³C nuclei, so as to accentuate ¹⁵N hyperfine coupling. Alternatively, tren protons could be replaced with ²H atoms (I = 1), which would allow faster relaxation of the ¹⁴N nuclei (I = 1) and pronounce the ¹³C effect.

3.4 Conclusions and Future Work

At the outset of this project it was desired to know the effect of Lewis Acidity on spin density distribution, and to further understand spin density distribution in M^{n+} -SQ complexes. It was found for Zn^{II}-PSQ, that upon complexation the dipolar portion collapsed to be within range of the isotropic coupling. This stands to be the main effect for bonding with a M^{II} ion with an ancillary ligand. Recall from Chapter 2 that for both ion-pair and dimer molecules, the lowest dipolar coupling was 2.77 MHz for NaPSQ, but was 7.96 MHz for Na(3,6-(OMe)₂-PSQ). Although, to conclude that carbonyl carbon dipolar hyperfine coupling decreases drastically as a result of complexation of a semiquinone to a metal would be short-sided. Attempts were made to study the ESEEM spectra of Ga-PSQ and Ga-¹³C₂PSQ, but no spin echo was located and therefore no ESEEM spectra were taken; therefore, there is no information on carbonyl carbon dipolar coupling for M^{III} -PSQ complexes.

As for the isotropic values of Ga-PSQ and Ga-¹³C₂PSQ, the magnitude increased by more than a factor of two (relative to all other compounds studied in this chapter and Chapter 2) in the case of both carbonyl carbon atoms and gallium. It can be hypothesized that this is most likely a consequence resulting from the bonding of the oxygen atoms to the Ga^{III} ion. The ^{69,71}Ga- a_{iso} values were in agreement with similar complexes from literature. It would be advantageous to further this study using Cd^{II} in place of Zn^{II} to gain hyperfine information at the metal center for M^{II} -SQ type complexes. This could then be compared to the hyperfine interactions at gallium and sodium, and possibly a trend, or more concrete theory could be had.

An interesting observation from the DFT portion of this chapter was the magnitude that the spin density shifts as it binds to Zn^{II} and Ga^{III}. These findings suggest that the metal causes spin density to polarize more towards the carbonyl carbon atoms. The carbonyl carbon hyperfine coupling constants did decrease relative to the free ligands in Chapter 2. It would be helpful for this study to expand by increasing the number of molecules studied. This would solidify the findings in this chapter.

In addition to having a Ga-SQ complex that exhibits a spin echo, it would be advantageous to study the substituent effects predicted by DFT. As was seen by the CW spectrum of **5**, the ¹³C nuclei have such a line broadening effect that it completely masks all other hyperfine coupling. Field modulation studies would be useful for molecules of this type once a suitable system is found. And if a suitable system is found then it may be prudent to pursue ¹⁷O labeling in order to determine if the predicted loss in oxygen spin density is a real trend. A combination of ¹³C and ¹⁷O labeling (in separate molecules) could prove and or disprove this prediction.

Now that it has been assessed what happens to hyperfine interactions at the carbonyl carbon in free radicals and radicals bound by M^{II} and M^{III} type ions, the next chapter will focus on the effect of adding an exchange interaction with unpaired spins on the M^{II} ion.

APPENDIX

APPENDIX

CW-EPR

```
function res = LDM2120cw1 fit(hpar)
% LDM2120 Ga-PSQ 20K 1 G Mod. Amp. Simulation & Fit
%------
% Load the experimental spectrum
[B, spc, params] = eprload('LDM2120cw10.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = spc/(max(spc)-min(spc)); % Normalizes the data
lmin = 112; % min point to start w/in the data set
lmax = 412; % max point to stop w/in data set
% Simulation Parameters to give the least-squares fitting program a place
% to start.
Sys0.S = 1/2;
Sys0.q = 2.00535;
Sys0.lwpp = [0.710 0.2815]; % mT
Sys0.Nucs = 'Ga';
Sys0.n = 1;
Sys0.A = 19.7295; % MHz
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000, params.A1SW*1000];
Exp.ModAmp = 0.1; % mT
Exp.nPoints = params.XPTS;
Exp.Temperature = 20;
% Call the simulation program
[B,sim] = pepper(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
offset = Edata(lmin); % corrects for baseline offset
Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end;
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
return;
```

```
function res = LDM2120 13C fit(hpar)
% LDM2120 13C Ga-[13C2]PSQ Room Temp. 1 G Mod. Amp. Simulation & Fit
%_____
% Load the experimental spectrum
[B, spc, params] = eprload('ldm2120 13cwA.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = spc/(max(spc)-min(spc)); % Normalizes the data
lmin = 51; % min point to start w/in the data set (depends on # of points in
data set, 512)
lmax = 472; % max point to stop w/in data set
% Simulation Parameters to give the least-squares fitting program a place
% to start.
Sys0.S = 1/2;
Sys0.g = 2.00532;
Sys0.lwpp = [1.0939 0.5693]; % mT
Sys0.Nucs = 'Ga, 13C, 13C'; %
Sys0.n = [1 1 1]; %
Sys0.A = [19.7295 27.7707 32.1071]; % MHz
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000,params.A1SW*1000];
Exp.ModAmp = 0.1; % mT
Exp.nPoints = params.XPTS;
Exp.Temperature = 20;
% Call the simulation program
[B,sim] = pepper(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
offset = Edata(lmin); % corrects for baseline offset
Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end;
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
return;
```

```
function res = LDM2163 RT 20mG fit(hpar)
% LDM2163 Zn-PSQ Room Temp. 20 mG Mod. Amp. Simulation & Fit
%_____
% Load the experimental spectrum
[B,spc,params] = eprload('LDM2163cw 0.02G RT.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = spc/(max(spc)-min(spc)); % Normalizes the data
lmin = 370; % min point to start w/in the data set
lmax = 638; % max point to stop w/in data set
% Simulation Parameters to give the least-squares fitting program a place
% to start.
Sys0.S = 1/2;
Sys0.g = 2.0071;
Sys0.lwpp = [0.0136 0.0107]; % mT
Sys0.Nucs = '1H,1H,1H,1H'; % Treating the nuclei seperately
Sys0.n = [2 2 2 2]; % 4 classes of 1H nuclei
Sys0.A = [1.0135 1.957 4.0089 5.904]; % MHz
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000,params.A1SW*1000];
Exp.ModAmp = 0.002; % mT
Exp.nPoints = params.XPTS;
% Call the simulation program
[B,sim] = garlic(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
offset = Edata(lmin); % corrects for baseline offset
Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end:
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
return;
```

```
function res = LDM2189_RT 20mG fit(hpar)
% LDM2189 Zn-[13C2]PSQ Room Temp. 20 mG Mod. Amp. Simulation & Fit
%_____
% Load the experimental spectrum
[B,spc,params] = eprload('LDM2189cw 0.02G RT.DTA'); %Loads the spectrum
B=B/10; %Gauss to mT
Edata = spc/(max(spc)-min(spc)); % Normalizes the data
lmin = 340; % min point to start w/in the data set
lmax = 680; % max point to stop w/in data set
% Simulation Parameters to give the least-squares fitting program a place
% to start.
Sys0.S = 1/2;
Sys0.g = 2.007107;
Sys0.lwpp = [0.0246 0.0247]; % mT
Sys0.Nucs = '1H,1H,1H,1H,13C,13C'; % Treating the nuclei seperately
Sys0.n = [2 2 2 2 1 1]; % 4 1H & 2 13C
Sys0.A = [1.0135 1.957 4.0089 5.904 1.0871 2.7845]; % MHz
% Load the experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.CenterSweep = [params.A1CT*1000,params.A1SW*1000];
Exp.ModAmp = 0.002; % mT
Exp.nPoints = params.XPTS;
% Call the simulation program
[B,sim] = garlic(Sys0,Exp);
Cdata = sim/(max(sim)-min(sim)); % Normalizes the simulation
offset = Edata(lmin); % corrects for baseline offset
Cdata = Cdata + offset; % Corrected baseline
% Calculation of residual
res = 0.0;
for ipt = lmin:lmax,
   res = res + (Cdata(ipt) - Edata(ipt))^2;
end:
plot(B(lmin:lmax),Cdata(lmin:lmax),' r',B(lmin:lmax),Edata(lmin:lmax),' k');
return;
```

```
function res = LDM2189ESEEMtime fit(hpar)
% LDM2189 Time Domain Sim/Fit Using 2189 time domain divided by 2163
% (Zn-[13C2]PSQ) / (Zn-PSQ)
8-----
% Load the experimental spectrum
[time,amp] = eprload('LDM2189 3p3455G136ERat.DTA');
Amp = real(amp)/(max(real(amp))); % Normalizes the data
time = (time/1000);
lmin = 1;
lmax = 512;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.0033;
Sys0.Nucs = '13C,13C'; % Treating the nuclei differently
Sys0.n = [1 1]; % 2 classes of 13C nuclei
Sys0.A = [1.0871 2.8425 0; 2.7845 2.4614 0]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012;
Exp.tau = 0.136;
Exp.T = 0.04;
Opt.nKnots = 91;
[x,y] = saffron(Sys0,Exp,Opt);
Y = real(y)/max(real(y)); % Normalizes the simulation
res = 0;
for ipt = lmin:lmax,
   res = res + (Y(ipt) - Amp(ipt))^2;
end;
plot(x(lmin:lmax),Y(lmin:lmax), ' r',time(lmin:lmax),Amp(lmin:lmax),' k');
return;
```

```
function res = LDM2189ESEEMfit(hpar)
% LDM2189div2136 Frequency Domain Sim/Fit
% (Zn-[13C2]PSQ) / (Zn-PSQ)
$-----
% Load the experimental spectrum
[larmor, intens] = eprload('LDM2189 3p3455G136spN.DTA');
larmor = larmor*1000; %GHz -> MHz
lmin = 1;
lmax = 186;
% Simulation Parameters
Sys0.S = 1/2;
Sys0.g = 2.0033;
Sys0.Nucs = '13C,13C'; % Treating the nuclei seperately
Sys0.n = [1 1]; % 2 classes of 13C nuclei
Sys0.A = [1.0871 2.8425 0; 2.7845 2.4614 0]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012;
Exp.tau = 0.136;
Exp.T = 0.04;
Opt.nKnots = 91;
[x,y] = saffron(Sys0,Exp,Opt);
ESnormDAL; % Normalizes the simulation
res = 0;
for ipt = (lmin):lmax,
   res = res + (spec(ipt) - intens(ipt))^2;
end;
plot(larmor(lmin:lmax), intens(lmin:lmax), ' k', f(lmin:lmax), spec(lmin:lmax), '
r');
return;
```

```
% LDM2189 HYSCORE Spectrum Zn-[13C2]PSQ
% Load the experimental spectrum
[x,Z,params]=eprload('LDM2189 hysc3455G136sp.DTA');
f1=x\{1,1\}*1000.;
f2=x\{1,2\}*1000.;
% Plot the spectrum
contour(f1, f2, Z);
% Edit the plot?
ans=input('Edit Contour plot (y/n)? ','s');
 if(ans=='y'),
    hyscedit;
 end
return;
% LDM2189 HYSCORE Molecule Simulation Zn-[13C2]PSQ
%_____
clear;
Sys0.S = 1/2;
Sys0.g = 2.0033;
Sys0.Nucs = '13C, 13C';
Sys0.A_ = [1.0871 2.8425 0; 2.7845 2.4614 0];
% Load the experimental Parameters
Exp.Field = 345.5;
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016;
Exp.tau = 0.136;
Exp.t1 = 0.036;
Exp.t2 = 0.036;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1,x2,y1,p1] = saffron(Sys0,Exp,Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = (real(p1.fd));
% set threshhold for contour at 10% max amplitude
   Zthresh = 0.05*max(max(Z));
   for iy=1:512,
       for ix = 1:512,
```

```
if Z(ix,iy) < Zthresh,</pre>
               ZR(ix,iy) = Zthresh;
            else
               ZR(ix, iy) = Z(ix, iy);
            end
        end;
    end;
8
    f1min=-9.0;
    f1max=9.0;
    f2min=0.0;
    f2max=9.0;
00
    frinc=f1(2)-f1(1);
8
    xmin=floor((flmin-f1(1))/frinc)+1;
    xmax=floor((flmax-f1(1))/frinc)+1;
    ymin=floor((f2min-f2(1))/frinc)+1;
    ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax),f2(ymin:ymax),ZR(ymin:ymax,xmin:xmax),10,'r');
xlabel('f1 (MHz)');
ylabel('f2 (MHz)');
grid;
```

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Chapter 4. Measuring Spin Density Delocalization in Ni^{II}-Phenanthrenesemiquinone Complexes

4.1 Introduction

This chapter aims to monitor spin density in the presence of an exchange interaction and assess if the method of using 13 C as a spin label correlates with theoretical results. Recall from Chapter 1 that a DFT study was carried out to study the average oxygen spin density as a function of calculated exchange coupling constant, *J*, as seen in Figure 1.



Figure 4-1. Average oxygen spin density versus *J*, reproduced from Reference 1.



Figure 4-2. Molecular structure of $[Ni(tren)(3,6-R_2-PSQ)]^+$ (where tren = tris(2-amineoethyl)amine and 3,6-R₂-PSQ = 3,6-R₂-Phenanthrenesemiquinone) complexes.

The structure of the complexes studied can be seen below in Figure 2. These calculations were explained in Chapter 1, however, to restate, the importance of these calculations in this body of work is as a backdrop for why the choice has been made to further study these molecules. It is our desire to understand these compounds with respect to their spin properties, in light of the fact that the magnitude of *J* has not be measured except when $R = NH_2^{-1}$. The purpose of these calculations was to uncover any theoretical trend between substituent (derivative of [Ni(tren)(3,6-R₂-PSQ)]⁺, and the magnitude of exchange coupling, *J*. A linear trend was found, correlating *J* with the average oxygen atom spin density of certain substituents; specifically, electron donating groups were found to have lower *J* values and lower average oxygen spin density values. The spin density values were obtained by mathematical manipulation of spin density values that were calculated by DFT with Natural Population Analysis (NPA) from the Natural Bond Order (NBO) package within Gaussian03²⁻⁴.

What is being correlated here are two values that cannot be measured directly, by conventional methods. Exchange coupling constants can be extrapolated from variable temperature magnetic susceptibility measurements, or directly by inelastic neutron scattering, while spin populations can be obtained from neutron diffraction experiments. All three techniques require a solid, crystalline sample. Regardless of the more unconventional means that require synchrotron light sources, spin density populations can be calculated from hyperfine coupling constants⁵, as it has been accomplished in this work in the preceding chapters; this formula that has been used only takes into account the isotropic hyperfine coupling. This coupling is a result of the resident electron density at the nucleus (*s*-orbital). Therefore, building on what has been accomplished from DFT calculations, the hyperfine parameters that have been simulated will be compared to the hyperfine parameters calculated. When referred to in this chapter, the term spin density will be directly relating to the aforementioned calculations.

It has also been previously stated why we chose to use ¹³C-spin labeling instead of ¹⁷O; however, as a reminder, there is no correlation between carbonyl carbon spin density and *J* with respect to these compounds as seen in Figure 3. These are theoretical results and thus are not necessarily a perfect reflection of what the experimental results will be. Therefore, by using ¹³C as an isotopic label at the carbonyl carbon atoms, it is an experiment in and of itself as to whether or not ¹³C labeling of molecules of the type $[TM(tren)([^{13}C_2]PSQ)]^{n+}$ (where TM = transition metal and n = 0, 1, 2, 3...n) is a sound method for tracking changes in spin density from one complex to the next within a series of molecules.



Figure 4-3. Average carbonyl carbon spin density versus J.

It has been seen in Chapter 2 that the isotropic hyperfine coupling constants obtained from the CW experiments create a map of the spin density at each nucleus. Between the two compounds studied it was suggested that a substituent effect was operative, decreasing the isotropic spin density at the carbonyl carbons in 3,6-(OMe)₂-PSQ relative to PSQ. It was also apparent in the overall line shape of the CW spectra that installment of methoxy groups to the phenanthrenequinone backbone created a perturbation in the spin density distribution. However, when studying the low temperature ESEEM time domain and Fourier transform spectra, it was observed that the dipolar hyperfine coupling constants (electron density in π – type orbitals), were larger in Na[¹³C₂]3,6-(OMe)₂-PSQ when compared to Na[¹³C₂]PSQ. The isotropic coupling constants were smaller for $[^{13}C_2]3,6-(OMe)_2$ -PSQ type radicals, compared to Na $[^{13}C_2]$ PSQ type radicals, as well.

Although ESEEM and HYSCORE have been used for decades to study transition metal complexes⁶, there have not been many reports concerning synthetic, non-biologically related, paramagnetic transition metal complexes bound to organic radical ligands. Indeed, most of the literature focuses on biological molecules, where it can be difficult to determine structures that are operative in biological processes. A combination of EPR techniques are often used to help determine structural parameters from EPR data. Here, however, our intention is to gain carbonyl carbon hyperfine coupling constants to ascertain as to what, if any effect is to be had on the coupling from electron exchange.

4.2 Experimental

General Methods. Reagents were purchased from commercially available sources and used without further purification unless otherwise stated. Stabilizer-free tetrahydrofuran was purchased from Fisher Scientific and either distilled over sodium metal and benzophenone and freeze, pump, thawed to remove O_2 , or taken from a dry still with a solvent bomb. Elemental analyses and electro-spray ionization ESI mass spectra were obtained through the analytical facilities at Michigan State University.

Synthesis. Ni(tren)Cl₂ (1). The procedure for the preparation of this compound has been previously reported.¹ To a stirring solution of 2.38 g (10.0 mmol) NiCl₂·6H₂0 in absolute ethanol 1.5 mL (10.0 mmol) of tren was added. The solution is stirred for one hour during which a light purple precipitate forms. The reaction mixture is filtered using a medium frit. The precipitate is then washed with distilled ethanol, recrystallized from hot ethanol to produce a light blue microcrystalline product. The light blue microcrystalline product can be filtered with a fine frit into the same filtrate from the first filtration. This was left out overnight to produce dark blue crystals. The product should be stored in a desiccator or dry box because it is highly hygroscopic. Recrystallized yield: 37.15%. Anal. calcd. for $C_6H_{18}Cl_2N_4Ni \cdot H_2O$: C, 24.52; H, 6.86; N, 19.07; Found: C, 24.50; H, 6.74; N, 19.01.

[Ni(tren)(PSQ)](BPh₄) (2). The procedure for the preparation of this compound has been previously reported.¹ The entire reaction including recrystallizations were done in a dry box. 0.24 g (0.86 mmol) of Ni(tren)Cl₂ was dissolved in 20 mL methanol. This solution was added to a 20 mL methanol solution of 0.20 g (0.96 mmol) 9,10-phenanthrenecatechol and 0.076 g (1.9 mmol) NaOH powder. The gold colored reaction mixture was stirred for 30 minutes and then oxidized with 0.32 g (0.96 mmol) of [FeCp₂](PF₆), and the color changed to dark brown. The solution was then stirred for another 15 minutes and filtered using a medium frit. A concentrated methanol solution of 3.3 g (9.6 mmol) NaBPh₄ was added drop wise to the filtered reaction mixture and it was left out to crystallize. A dark brown microcrystalline product was recovered. The crystals were washed with methanol (10 mL x 3) and ether (10 mL x 3) and dried in vacuo. The product can be recrystallized by adding 200 mL of ether to a concentrated acetonitrile solution of the complex. The dark brown crystals were then filtered off with a fine frit. The product should be stored under N₂. Recrystallized yield: 54.7%. Anal. Calcd. From C₄₄H₄7BN₄NiO₂: C, 72.06; H, 6.46; N, 7.64; found: C, 72.02; H, 6.57; N, 8.00.

[Ni(tren)([9,10-¹³C₂]PSQ)](BPh₄) (3). This compound was prepared analogously to compound 2. Recrystallized yield: 20%. MS [ESI (Hi-Res) m/z (rel. int.)]: C₁₈¹³C₂H₂₆N₄NiO₂⁺⁻ 414.1478 (100%), C₂₄H₂₀B⁻ 319.1663 (100%).

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Physical Measurements. EPR Spectroscopy. All EPR data were collected on a Bruker Elexsys E-680X spectrometer, operating at X-band frequency (9.42-9.71 GHz). Low temperature experiments were performed between 4-30 K using an Oxford Instruments liquid helium flow system equipped with a CF-935 cryostat and an ITC-503 temperature controller. Samples were prepared in a dry box in modified Wilmad Glass SQ-706 EPR tubes with 3.8 mm diameter. Prior to sample preparation, tubes were modified in the glass blowing lab at Michigan State University to contain a grated seal and vacuum adapter port. A vacuum was pulled on the sample tubes and then the vacuum ports were blown off at the grated seal, by hydrogen torch. Prior to collecting data, power-dependence experiments were conducted to ensure non-saturation of the detector. Continuous wave spectra were simulated using the garlic module of Easy Spin 4.5^{7,8,9}.

All pulsed experiments were conducted at X-band microwave frequency. ESEEM spectra were obtained using a three pulse sequence of 90° - τ - 90° -T- 90° with 90° pulse lengths of 16 ns. Tau values were chosen to suppress hyperfine contributions from weakly coupled protons. Echo amplitudes were integrated at FWHM and the T values were scanned from 40 ns to 6 µs with a 12 ns time increment. A four step phase-cycling procedure was used to eliminate unwanted 2-pulse echoes.¹⁰ Raw data were processed by phase shifting the spectra to remove the dispersion component from the time domain data. The in-phase portion of the data were normalized by dividing by a biexponential background decay function. These normalized data were then further processed by subtracting a second degree polynomial (DC-component of the signal), followed by application of a Hamming window. The data set was then zero-filled from 512 points to 1024 points and Fourier transformed. Frequency spectra are displayed as an absolute value of the transformed time domain data. ¹³C and ¹²C spectra are presented as one divided

spectrum at each magnetic field value. After normalizing each time domain spectrum individually, the ¹³C spectrum was divided by the ¹²C spectrum and the same work up procedure described above was applied¹¹.

HYSCORE experiments were carried in a similar manner to the ESEEM experiments but with a four-pulse sequence of 90°- τ -90°- t_1 -180°- t_2 -90° with a 180° pulse length of 16 ns. Echo amplitudes were measured at FWHM and τ values were chosen as stated above. T₁ and t₂ values were scanned from 40 ns to 2 µs with 16 ns time increments. Data sets were 128 points in both dimensions. A 4-step phase cycling program was used to filter out unwanted 2-pulse echoes.¹² The real, or in-phase portion of the HYSCORE data were processed, in both dimensions, by first subtracting a 2° polynomial, then tapering the data with a Hamming window and zero-filling to 256 points. A two-dimensional fast Fourier transform was applied and absolute values taken. Data are presented as a two-dimensional contour plot. Each contour plot is presented at a threshold of 5-20% of the maximum peak amplitude (z-direction).

Spectra were fit using customized MATLAB scripts where EasySpin was used to perform spectral simulations and the fminsearch function in Matlab was used to optimize the calculation parameters. Fminsearch is a function that finds the minimum of an unconstrained multivariable function using a derivative-free method¹³. Residuals were calculated by squaring the difference of the experimental and simulated amplitudes. Goodness of fit for each spectral fit was assessed by calculating a χ^2 value with the following equation:

$$\chi_n^2 = \frac{\sum_{i=1}^N \frac{(y_i^{exp} - y_i^{calc})^2}{\sigma^2}}{N - L}$$
(4.1)

where the sum is taken over *N* points, y_i^{exp} and y_i^{calc} are the experimental and calculated y-axis values, σ is the standard deviation fixed at 2% of the maximum spectral amplitude and *L* is the number of adjustable variables. The χ^2 values in this chapter are not good signs of merit for the spectra in this chapter, due to the difficult nature of modeling exchange-coupled molecules properly.

4.3 Results and Discussion.

Synthesis. Complexes of this type are typically prepared from a metal precursor complex that contains an ancillary ligand and good leaving groups. The ancillary ligand ultimately serves the purpose of occupying coordination sites while simultaneously discouraging any spin polarization. A catecholate is then added to the metal precursor complex and subsequently oxidized. A general scheme for the synthesis of the compounds studied can be seen in Figure 4 (both ¹²C, **2**, and ¹³C, **3**, were prepared analogously).





The complex precursor, Ni(tren)Cl₂ (1), was prepared by adding tren to the NiCl₂·6 H₂O salt. The salt is neon green and upon addition of tren, the H₂O molecules are displaced, and the neon green changes to bright royal blue, as a result of strong absorption in the red¹⁴. After stirring for several minutes, a light blue crystalline powder crashes out of solution. This precipitate is then filtered and washed with cold ethanol. The complex is then recrystallized from hot ethanol, filtered and stored in a desiccator. Hydrolyzed versions of this complex are light purple.

Complex 2 was made by first placing 9,10-phenanthrenecatechol (PCatH₂) (synthesized by a previous lab mate) in MeOH with 2 equivalents of NaOH. By adding NaOH, this creates an acid-base reaction, producing H₂O as the side product. Following this step, Ni(tren)Cl₂ is added to this stirring PCat²⁻ reaction mixture, producing a gold-brown colored solution. The remaining steps for synthesizing this compound are outlined below.

The above steps were altered to increase the yield of the ¹³C-labeled complex. PCatH₂ is synthesized from phenanthrenequinone (PhenQ), and this is one more step than what is necessary for synthesizing **3**. As performed in Chapters 2 and 3 of this dissertation, PhenQ can be reduced chemically be excess sodium metal. By reducing the number of compounds to be made, this creates a likelihood for increasing the yield of the final complex. PCatH₂ is highly hygroscopic and must be immediately stored away from sources of hydration. In addition to this, earlier attempts were made to incorporate ¹⁷O atoms into the quinone ligand, so as to measure ¹⁷O hyperfine coupling constants and gain spin density information at the center of the exchange interaction. By having ¹⁷O atoms on the quinone, it would be desirable to have a route in which ¹⁶O sources would not interact with these isotopes. It would be possible that, during the acid-base reaction, the oxygen atoms from HO- would exchange with the ¹⁷O nuclei on the resulting catecholate. It is noted that this would be a slim chance, but ¹⁷O-labeling may be in the future of this project.

Complexes 2 and 3 were prepared by first performing a two electron reduction with excess sodium metal. The sodium metal was cut in light mineral oil into 5x5x5 mm3 cubes and

prior to pumping into the glove box the oil was removed as much as possible. Before adding the sodium metal to the THF solution of phenanthrenequinone, the sodium chunks were washed with dry THF and then added to the reaction flask. Upon addition the solution changes to dark green, corresponding to the semiquinone oxidation state. After stirring overnight, a blood red solution persisted for Na₂PCat. The catecholate complex was then filtered to remove all unreacted sodium metal.

After filtration, the catecholate compound were added to Ni(tren)Cl₂ and produced dark brown-gold reflecting complexation of PCat²⁻ to Ni(tren)²⁺ and formation of NaCl. This compound was then stirred overnight, to ensure complexation of the catecholate to Ni^{II}. The catecholate complexes were then oxidized by one electron with a methanolic solution of [Fc](PF₆) and produced a dark brown solution. After oxidation, the compound was filtered to remove any ferrocene produced by the reaction. In order to encourage crystal formation, a 20fold excess of NaBPH₄ was added, in MeOH solution, to the filtrates of the two complexes.

In the case of complexes 2 and 3, after sitting overnight small brown-black platelets had crashed out of solution. These were filtered and washed with MeOH and Et₂O. The platelettes were then dissolved in a minimum amount of MeCN and then 500 mL of degassed Et₂O was added to crash out the product. 495 mG (54.7%) and 150 mg (20%) of 2 and 3 were collected as dark brown crystals and microcrystals, respectively. Percent yields were not reported for similar complexes prepared by Gatteschi¹⁵ or Bencini and Dei¹⁶

CW-EPR. The Ni-PSQ systems are considered to be in the limit of strong exchange, in which the exchange coupling parameter is much greater than any of the other spin parameters. This comes about due to the fact that exchange coupling constants have been unable to be

measured by typical means, i.e. variable temperature magnetic susceptibility^{1,15,16}, which means that the energy of the interaction is greater than magnetometers have been able to detect. In addition, large *J* values predicted by DFT¹. Typically, molecules with a ground state that does not support the symmetry of the system must be described in such a manner to include effects that arise from this mismatch. In particular, the ground state configuration of the Ni-SQ systems, which have an S = 1 spin center interacting with an $S = \frac{1}{2}$ spin center are described with zero-field splitting effects. Because the ground state is a quartet (variable temperature magnetic susceptibility¹), and the symmetry of the system must be lifted, in which Kramer's doublets are produced (Figure 5).



Figure 4-5. Zero field splitting diagram for a quartet ground state.
As stated these are zero field effects and arise in the absence of magnetic field. However, when placed in a magnetic field, the degeneracy of the Kramer's doublets are lifted and transitions between the $m_s = \pm 1/2$ and $m_s = \pm 3/2$ can occur. Figure 7 shows the CW spectra of **2** and **3**. The physical origins of this line shape have been described previsously¹. The large absorptive feature near *g*-4 has been assigned to transitions within the $m_s = \pm 3/2$ manifold, which have been allowed by the breaking of the degeneracy of the Kramer's doublets. The feature near *g*-2 comes from transition in the $m_s = \pm 1/2$ manifold.



Figure 4-6. 7 K CW spectrum and simulation of **2**, [Ni(tren)(PSQ)](BPh₄). Simulation parameters: S = [1,1/2], $g_{xx} = g_{yy} = 2.08$, $g_{zz} = 2.44$, D = 49,000 MHz (1.63 cm⁻¹), E = 6200 MHz (0.21 cm⁻¹), electron exchange = -6.1 cm⁻¹ (-182,647.9 MHz), HStrain = (2200,1100,90) MHz, DStrain = 38,000 MHz, 2,900 MHz. Experimental conditions: 4 K, 9.41 GHz microwave operating frequency, 0.8 mT modulation amplitude, 4000 G sweep, 260 mT center field and 2048 points.

This line shape has been observed in other Ni^{II}-radical complexes^{15–18}; however, for some of these citations, simulation parameters have been listed but the line shape has not been produced (explicitly, no simulated spectrum was shown in the text), most likely due to the level of difficult of reproducing the spectrum or there was not even an attempt to simulate the experimental spectrum. A Ni-Phenoxyl system studied by Wieghardt and coworkers, contained a feature similar to the one produced by the simulation above¹⁸; however the line shape was not able to be reproduced. Attempts to reproduce the line shape in this study were focused on the ¹²C isotopologue, seeing as the majority of the line shape between the two spectra are the same.



Figure 4-7. 7 K CW spectra of 2 (black), $[Ni(tren)(PSQ)](BPh_4)$, and 3 (blue), $[Ni(tren)([^{13}C_2]PSQ)](BPh_4)$.

The Hamiltonian used to model these complexes is displayed below:

$$\widehat{H} = g_e \beta_e B \widehat{S} + \widehat{S} \cdot D \cdot \widehat{S} + J \cdot \widehat{S}_1 \cdot \widehat{S}_2$$
(4.2)

The first term is the electronic Zeeman where g_e gyromagnetic ratio for an electron, which is 2.0023. The second term is the zero field splitting term and describes the energy of the splitting of the Kramer's doublets. D is a diagonal tensor and can be explained mathematically, in terms of its eigenframe:

$$\boldsymbol{D} = \begin{pmatrix} D_x & 0 & 0\\ 0 & D_y & 0\\ 0 & 0 & D_z \end{pmatrix} = \begin{pmatrix} -\frac{1}{3}D + E & 0 & 0\\ 0 & -\frac{1}{3}D - E & 0\\ 0 & 0 & \frac{2}{3}D \end{pmatrix}$$
(4.3)

where $D = (3/2)D_z$ and $E = (D_x - D_y)/2$, and D is the axial parameter and E is the rhombicity parameter. It is tradition to represent the D and E parameters in terms of an E/D ratio; however, in this work, in an effort to maintain clarity between the simulation parameters and the discussion of the data, D and E will be discussed individually. The last term is the exchange coupling term where J is exchange coupling constant, typically quantified in cm⁻¹, and S_1 and S_2 are the individual spin centers. Again, to be transparent between the simulations and the discussion J will be reported in both cm⁻¹ and MHz.

The simulation presented above in Figure 6 was accomplished with several parameters. First, a spin system must be defined, and in this situation there is a ferromagnetically coupled system where the spin centers are S = 1 (octahedral Ni^{II}) and S = 1/2 (PSQ), and in EasySpin this must be defined explicitly as [1,1/2] for syntax purposes. In each of the subsequent parameters, values must be defined for both spin centers for values that arise due to S > 1. Next, the g values are considered; for this system, an isotropic g can be considered, however this is an axial system and the g-values are $g_{zz} = 2.44$, $g_{xx} = g_{yy} = 2.08$ for S = 1 and an isotropic g = 2.00 for S = 1/2. The zero-field splitting parameters are D = 49,000 MHz (1.63 cm⁻¹) and E = 6,200 MHz (0.21 cm⁻¹) for S =1 and there are none for S = $\frac{1}{2}$. The electron exchange (represented as "ee" in EasySpin) is next considered, and it should be noted that this is isotropic exchange, and can also be represented as J with other parameters. For this simulation ee = -218,846 MHz (-7.3 cm⁻¹), this diverges from experimental measurements and will discussed below. Lastly the line broadening parameters are considered. The first considered is DStrain, which EasySpin defines as "Widths (FWHM) in MHz of the Gaussian distributions of the scalar parameters D and E that specify the D matrix of the zero-field interaction. If FWHM_E is omitted, it defaults to zero"⁷. For this complex, the *DStrain* and *EStrain* values are 38,000 MHz and 2,900 MHz, respectively for S = 1 and 0 for S = 1/2. And finally, HStrain, this line-broadening parameter accounts for unresolved hyperfine couplings. These values are expressed in terms of their contributions along the x, y and z axes, and EasySpin defines as "Residual line width (full width at half height, FWHM), in MHz, describing broadening due to unresolved hyperfine couplings. The three components are the Gaussian line widths in the x, y and z direction of the molecular frame"⁷. The values are $HStrain_x = 2,200$ MHz, $HStrain_y = 1,100$ MHz and $HStrain_z = 90$ MHz.

These simulation parameters do not come without critique, and although the major portions and features of the line shape of 2 have been reproduced, it has not been fit. The major contributor to this is the exchange coupling parameter *ee*, or electron exchange. As stated above this is the isotropic exchange coupling describing the energy of the coupling between the two spin centers. There was a major effort to use any/all of the EasySpin tools to correctly describing the exchange interaction of this molecule, but none quite worked properly. The electronic structure of the interaction is described in the simulation as a combination of zero-field splitting and isotropic exchange coupling; however, another way to describe this interaction would be to instead use isotropic and anisotropic exchange. This would be a valid interpretation of the coupling indeed, due to the fact that the organic radical resides largely in a π -type orbital. EasySpin does accommodate for systems with anisotropic, or dipolar, exchange with the *eeD* parameter, but there was simply no effect to the line shape of the simulation when using this parameter as outlined in the EasySpin documentation.

Even more obviously, the magnitude of the electron exchange here is -7.3 cm⁻¹ and this is not consistent with variable temperature magnetic susceptibility measurements that the author of this work and others have measured for this compound^{17,16} and similar Ni-SQ complexes¹⁵. By these measurements, temperature dependence was only observed for [Ni(tren)(3,6-(NH₂)₂-PSQ](BPh₄) by Fehir, and a coupling constant of -109 cm⁻¹ was found. At the very least, an idea of what the exchange coupling could be is several times larger than what is predicted by the simulation. Additionally, Gatteschi and coworkers estimated that for $[Ni(CTH)DTBSQ]PF_6$ (where CTH = dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetrade and is similar in function to tren, and DTBSQ = 3,5-di-tert-butylsemiquinone) a lower limit on the energy separation between the quartet ground state and doublet excited state could be 400 cm⁻¹. It is acknowledged that the electron exchange is most likely stronger in this complex when compared to [Ni(tren)(PSQ)](BPh4) due to the DTBSQ ligand having less of an ability to delocalize the electron density of the radical; however to calculate this lower limit, the data of the two complexes is similar enough to use this number as a benchmark. To conclude with this line of critique, the electron exchange parameter of the simulation in Figure 6 is off by at two orders of magnitude.

The sharp, downward facing feature in the g-2 region could be a qualitative marker for the magnitude of the exchange coupling. Fehir¹ recorded the EPR spectra of [Ni(tren)(3,6-R₂-

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PSQ)](BPh₄) complexes (where $R = NH_2$, H and NO₂), and these are featured in the figure below. As it can be seen from the spectra and the aforementioned exchange coupling constant, the -NH₂ derivative exhibits the lowest magnitude of coupling and has a derivative like feature in contrast to the features of the -H and -NO₂ derivatives. It is possible that this is a physical observable for the magnitude of the exchange coupling. As the exchange coupling becomes smaller in magnitude, then the shape of the *g*-2 feature become more derivative in nature. A simple study with Easy Spin shows that this can be the case.



Figure 4-8. EPR spectra of $[Ni(tren)(3,6-R_2-PSQ)](BPh_4)$ complexes where R = H (red, bottom), NH₂ (blue, middle) and NO₂ (green, top). Spectra taken from Reference 1.

By taking the same script to simulate complex 2 and modifying the electron exchange parameter (exchange coupling), the simulation reproduces the same observation that was seen in Figure 8. When the exchange coupling is sufficiently small, the feature at g-2 becomes derivative in nature, and as the exchange coupling is increased, this feature decreases in intensity and moves away from the derivative shape. Although the values being used are inconsistent with what has been observed experimentally, the simulation shows similar line shapes to those being produced by actual compounds. If this parameter is improved upon, then exchange coupling constants could be reliably predicted by simulation software for hybrid metal-organic radical type exchange coupled molecules. Additionally, this would replace the need for isotopic labeling and would demonstrate the effect a specific substituent has on spin polarization. That being said, isotopic labeling has been quite instrumental in this studying for tracking changes in molecular structure, based on the common them of phenanthrenesemiquinone.



Figure 4-9. Comparison of various electron exchange (exchange coupling) values for Ni-PSQ based on simulation parameters for Ni-PSQ.

More could be detailed about the inaccuracies of this simulation but the real hurdle that should be cleared is development of a sound theoretical approach to simulate molecules of this type. Much has been accomplished in the field of exchange-coupled transition metal-organic radical systems, there is however, still room for a more precise understanding of the quantum mechanical underpinnings of these systems that accommodate exchangeable electrons and their energetics.

ESEEM. In an effort to fully characterize the hyperfine coupling as a function of magnetic field value, ESEEM spectra were taken at various field points along the CW spectrum. It is practice in the area of ESEEM where $S > \frac{1}{2}$ to study the hyperfine interaction at not just g-2 but at several points in the spectrum. ESEEM spectra were taken at 334, 260 and 180 mT for both **2** and **3**. The presented spectra are divided spectra of the ¹³C and ¹²C spectra, utilizing the same Mims' division technique of Chapters 2 and 3. Time domain spectra were normalized with a biexponential prior to division, and then worked up with the usual procedure as outlined in the experimental section of this chapter.

In Figure 8 is displayed the ESEEM Fourier transform of Ni-[$^{13}C_2$]PSQ/NiPSQ taken at 334 mT with $\tau = 140$ ns and its simulation. The corresponding divided time domain spectrum and simulation are displayed in Figure 9. It is immediately apparent that there exists some disagreement in the time domain simulation with the Fourier transform simulation. At this point it is imperative to explain the approach used to model these complexes.

The EasySpin program used to simulate ESEEM spectra is Saffron and Saffron only supports systems with one spin center; seeing as there are two spin centers in the complexes being studied, this is the first fork in the road to be overcome. The most obvious way to continue forward would be to simply model the system as a quartet, S = 3/2, and move on. This was the first approach to fitting these spectra. The model spin system would include the same parameters as the CW model, excluding electron exchange and replacing the spin-coupled system with a single spin center of S = 3/2. This approach was attempted several times over but a good agreement amongst the hyperfine parameters could not be accounted for. Resonances could be

produced, but the peak placement was askew and this was not the case when $S = \frac{1}{2}$. Thus, it was decided to move forward using a spin system consisting of a $S = \frac{1}{2}$ spin center, with the axial *g* values and HStrain line broadening parameters of the CW simulation. As it will be seen, the majority of the discussion on hyperfine parameters stems from analysis of the ESEEM collected at 334 mT, which is located in the g-2 area of spectrum, where organic radicals are observed. Since it is the prerogative of this work to study the hyperfine interaction at the carbonyl carbon nuclei on the organic radical portion of the complex, it was decided that there is validity to using this approach.

Another layer of complexity was owed from the fact that no hyperfine coupling parameters were afforded from the CW simulations. In Chapters 2 and 3 the approach for simulating ESEEM spectra was eased by knowing ${}^{13}C$ - a_{iso} constants from the CW simulations. This provided a template of only four unknowns, the two dipolar constants and two rhombicity constants. The rhombicity values were held at zero until acceptable dipolar values were reached, and lastly the rhombicity values were varied between 0 - 1 until a good fit had been achieved. With the ESEEM simulations of this chapter, however, the entirety of the hyperfine parameters was unknown, making this task of simulating the spectra much more arduous than in previous chapters. The hyperfine parameters were unable to be determined from the CW spectra due to the exchange coupling and zero field splitting; these values were much greater then menial hyperfine coupling constants and thus washed out any fine structure that would have been otherwise observed. It would be possible to study the CW spectra at higher microwave frequencies, such as W-band (~94 GHz), which would provide for higher resolution and the possibility of observing hyperfine coupling. There was also an effort to uncover the isotropic

coupling constants using Davies' ENDOR experiments, but the results of **2** matched those of **3**; the spectra were nearly identical.



Figure 4-10. ¹³C/¹²C NiPSQ ESEEM Fourier transform (black) and fit (red). Simulation parameters: S = ¹/₂, $g_{xx} = g_{yy} = 2.08$, $g_{zz} = 2.44$, HStrain = (2200,1100,90) MHz, C₁: $a_{iso} = -2.11$ MHz, T = 3.29 MHz $\rho = 0.433$ MHz; C₂: $a_{iso} = 1.58$ MHz, T = 6.32 MHz, $\rho = 0.03$ MHz. Experimental conditions: 334 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 3 pulse ESEEM sequence, 140 ns τ , 40 ns acquisition trigger and 12 ns increments.

In continuing with the idea of discrepancy between time and frequency domain spectra, it was acknowledged early on in the simulation process that this disparity would ultimately exist in one form or another. And although the time domain data are the raw data and the frequency domain spectra are but the result of mathematical treatment of the time domain data followed by Fourier transformation, in collaboration with simulating the HYSCORE spectra, it was decided to use hyperfine values that were more consistent with the Fourier transformations of the time domain data. Simulations that favor the time domain spectra will also be presented, but only in brief.



Figure 4-11. ¹³C/¹²C NiPSQ ESEEM Fourier transform (black) and fit (red). Simulation parameters: S = ¹/₂, $g_{xx} = g_{yy} = 2.08$, $g_{zz} = 2.44$, HStrain = (2200,1100,90) MHz, C₁: $a_{iso} = -2.11$ MHz, T = 3.29 MHz $\rho = 0.433$ MHz; C₂: $a_{iso} = 1.58$ MHz, T = 6.32 MHz, $\rho = 0.03$ MHz. Experimental conditions: 334 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 3 pulse ESEEM sequence, 140 ns τ , 40 ns acquisition trigger and 12 ns increments.

The spectrum was simulated by treating the carbonyl carbon nuclei in an asymmetric manner. Prior to this treatment, the nuclei were treated equivalently, as if the unpaired electron density were delocalized evenly between the two. As it was stated above, the spectra were also simulated with the same *g* and *HStrain* values as the CW spectrum. The final hyperfine values

were achieved by varying the isotropic and dipolar values in both the time and frequency domain spectra until all the major features were represented. This process was cumbersome and time consuming. The Matlab function fminsearch was then used to find global minima for these values. Once the isotropic and dipolar constants were settled, the rhombicity values were varied to achieve the lowest residual value possible.

The values achieved from the simulations are as follows: $C1-a_{iso} = -2.11$ MHz, C1-T = 3.29MHz, $C1-\rho = 0.433$ MHz; $C2-a_{iso} = 1.58$ MHz, C2-T = 6.32 MHz, $C2-\rho = 0.03$ MHz. Near g-2, the simulated spectrum shows a sharp feature at 6.07, followed by small humps at 11.93 and 17.7 MHz, none of which directly correspond to nuclear Larmor frequencies. At 334 mT. $^{13}\mathrm{C}_{\upsilon}$ = 3.57 MHz, however owing to the fact that this is a divided spectrum, this large feature is most likely due to a large dipolar coupling. Table 3 (see below) shows the hyperfine parameters for this spectrum. These hyperfine parameters show that upon complexation to a paramagnetic metal, the spin density does shift. Recall from Chapter 2 that for the ion-pair, the carbonyl carbon nuclei had hyperfine values of $a_{iso} = -1.57$ MHz and T = 13.57 MHz. Comparing these two sets of results shows that there is little change in isotropic coupling constant, but a large change in dipolar coupling. Including the results of Chapter 3 where the isotropic and dipolar hyperfine coupling constants of $[Zn(tren)([^{13}C_2]PSQ)](BPh_4)$ were in the range of 1 - 3 MHz. Perhaps it is the situation that the isotropic coupling is rather unperturbed by complexation, and the dipolar coupling is more delocalized across the carbonyl bond, certainly this is within the realm of possibilities. It would be beneficial to study more carbon positions within the phenanthrene ring system as well as the oxygen nuclei, across the series of compounds studied in this dissertation. Indeed, by theory the majority of the radical spin density resides on the oxygen nuclei.

With regards to the theoretical interpretation of the electronic structure, DFT predicts the following hyperfine parameters: $C1-a_{iso} = 1.147$ MHz, C1-T = 19.31 MHz, $C1-\rho = 0.08$ MHz; $C2-a_{iso} = -1.634$ MHz, C2-T = 13.96 MHz, $C2-\rho = 0.12$ MHz. These values relate well with the hyperfine parameters of the ion-pairs of Chapter 2, but do not predict well the results of the simulations in this chapter. It is worth noting that the predicted signs of the hyperfine coupling are in agreement with simulated values. The computational program ORCA (developed by Frank Neese) was also consulted to attempt to study the spin properties however the results were similar to those produced by Gaussian03 and Gaussian09.

Table 4-1. Hyperfine coupling parameters obtained from Ni-[¹³C₂]PSQ/NiPSQ ESEEM.

	aiso/MHz	<i>T</i> /MHz	$ ho/\mathrm{MHz}$
Carbon 1	-2.11	3.29	0.433
Carbon 2	1.58	6.32	0.03

It was mentioned at the beginning of this section that a secondary set of hyperfine parameters were found and would be briefly covered. Below, Figures 12 and 13 show the parameter set for values optimized for the time domain data. At first inspection, these coupling constants describe the time data more accurately than the values above; however, after scrutinizing the Fourier transform spectrum, it is noticed that only the resonance at 6.07 MHz is well represented. Again, after comparing the two parameter sets with both ESEEM and HYSCORE experimental spectra, it was determined that the first set was a better representation of the spectra than the second set.



Figure 4-12. ¹³C/¹²C NiPSQ ESEEM Fourier transform (black) and fit (red). Simulation parameters: $S = \frac{1}{2}$, $g_{xx} = g_{yy} = 2.08$, $g_{zz} = 2.44$, HStrain = (2200,1100,90) MHz, C_1 : $a_{iso} = -4.09$ MHz, T = 1.535 MHz $\rho = 0.0$ MHz; C_2 : $a_{iso} = 1.07$ MHz, T = 6.36 MHz, $\rho = 0.19$ MHz. Experimental conditions: 334 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 3 pulse ESEEM sequence, 140 ns τ , 40 ns acquisition trigger and 12 ns increments.



Figure 4-13. ¹³C/¹²C NiPSQ ESEEM Fourier transform (black) and fit (red). Simulation parameters: $S = \frac{1}{2}$, $g_{xx} = g_{yy} = 2.08$, $g_{zz} = 2.44$, HStrain = (2200,1100,90) MHz, C_1 : $a_{iso} = -4.09$ MHz, T = 1.535 MHz $\rho = 0.0$ MHz; C_2 : $a_{iso} = 1.07$ MHz, T = 6.36 MHz, $\rho = 0.19$ MHz. Experimental conditions: 334 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 3 pulse ESEEM sequence, 140 ns τ , 40 ns acquisition trigger and 12 ns increments.

Stacked ESEEM spectra of the ¹³C/¹²C NiPSQ spectra are seen in Figure 14. It is utterly apparent from this figure that the bulk effect of the carbonyl carbon nuclei occurs at 334 mT, near g-2 for these molecules. The g-2 region is where organic radicals typically experience resonance with the scanning magnetic field in a bath of microwave energy. So the fact that the ¹³C effect is highest at g-2 is not a surprise, for the portion of the radical wavefunction giving rise to this resonance is associated, solely, with the semiquinone ligand.

It is noted here that these data are atypical of hyperfine effects when examining the hyperfine parameters across the spectrum of system with S > 1. It is typical for the hyperfine coupling

constants to increase in intensity moving from high magnetic field values to lower magnetic field values. The opposite trend is observed in the stacked spectrum; EasySpin predicts an increase in the echo amplitude as well. This can be seen in Figure 13, which is a Fourier transform spectrum of the data collected at 260 mT.



Figure 4-14. Overlaid ESEEM spectra of ${}^{13}C/{}^{12}C$ Ni-PSQ: 334 mT (black), 260 mT (red) and 180 mT (blue).



Figure 4-15. ¹³C/¹²C NiPSQ ESEEM Fourier transform (black) and fit (red). Simulation parameters: $S = \frac{1}{2}$, $g_{xx} = g_{yy} = 2.08$, $g_{zz} = 2.44$, HStrain = (2200,1100,90) MHz, C₁: $a_{iso} = -2.11$ MHz, T = 3.29 MHz $\rho = 0.433$ MHz; C₂: $a_{iso} = 1.58$ MHz, T = 6.32 MHz, $\rho = 0.03$ MHz. Experimental conditions: 260 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 3 pulse ESEEM sequence, 92 ns τ , 40 ns acquisition trigger and 12 ns increments.

Before moving on to the HYSCORE section, it is worth mentioning that this type of study in nearly unprecedented. Hybrid metal-organic radical complexes are not well studied within the areas of ESEEM and HYSCORE, especially of the type the transition metal-semiquinone type, undergoing exchange coupling. Additionally, synthetic transition metal complexes are not well studied either, the ESEEM and HYSCORE techniques have been traditionally been used to aid in the structural characterization of biological molecules, as well as biological reactions.

HYSCORE. HYSCORE data were collected at 4 K and are presented respective to their compounds, and not as divided spectra. Spectra presented are from data collected at 334 mT (140 ns τ) and 260 mT (92 ns τ) for **2** and **3**. Two quadrants in each spectra are shown; quadrant 1 (Q1) on the right and quadrant 2 (Q2) on the left. The other two quadrants (not displayed) are reflections of quadrants 1 and 2 and are a consequence of the two dimensional Fourier transformation (2D-FT). The z-scale is presented colorimetrically, with yellow being the most intense and dark blue being the least intense. The spectra were simulated with the same spin system and hyperfine parameters as the ESEEM spectra above.

The purpose of this study is twofold. Primarily, it would be advantageous to know what other components of the spin system are operative in the presence and absence of ¹³C-labelling. the identity of the peak at 6 MHz in each system would be desirable to know, since it does not directly correspond to any of the Larmor frequencies available in the molecule. Secondly,

Figures 16 and 17 correspond to **3** and **2** HYSCORE spectra at 334 mT, respectively. The ¹³C spectrum will be assessed first, followed by the ¹²C spectra. The large feature at 6.1 MHz that lies on the diagonal in Q1 is due to the ridges at (1.6,3.1) and (6.1,1.6), centered about the on diagonal peak 3.7 MHz, which corresponds to the ¹³C_v at 334 mT (3.69 MHz). Also contributing to the peak at 6.1 MHz would be the smaller peaks in the same ridge at (2.8,3.1) as well as (5.6,2.0). The side ridges centered about the ¹H_v at 14.2 MHz are most likely from tren protons and arise as a consequence of spin polarization through the sigma bonding system of the Ni(tren) fragment. In addition to this, these side ridges centered about ¹H_v are present in both spectra.



Figure 4-16. HYSCORE 2D-FT spectrum of **3** acquired at 4 K. Experimental conditions: 334 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 4 pulse HYSCORE sequence, 140 ns τ , 40 ns acquisition trigger (both dimensions) 16 ns increments and 256 x 256 points.



Figure 4-17. HYSCORE 2D-FT spectrum of **2** acquired at 4 K. Experimental conditions: 334 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 4 pulse HYSCORE sequence, 140 ns τ , 40 ns acquisition trigger (both dimensions) 16 ns increments and 256 x 256 points.

If hyperfine coupling from spin polarization to protons is observed, then it is not a stretch for ¹⁴N hyperfine interactions to be present as well. Indeed, in Q2 ridges centered about the third harmonic of the ¹⁴N_v frequency (1.02 MHz) at -3.2 MHz could be due to ¹⁴N hyperfine, but in order to test this ¹⁵N-labelling could be employed. By installing I = $\frac{1}{2}$ nuclei for I = 1 nuclei, this could cause the proton and nitrogen atoms to relax faster by coupling and a decrease in signal might be observed. It would also be advantageous to create a per-methylated tren analogue of these compounds to witness a loss in signal from proton couplings (centered about 14 MHz).

Within the ¹²C spectrum, the features responsible from tren are observed in Q1 around 14.1 MHz. The on-diagonal peak at 3.67 MHz arises from small resonances in the ESEEM 1D spectrum, most likely from natural abundance of ¹³C in the molecule. The main purpose of this spectrum, however, is to serve as a comparison to the ¹³C spectrum, and it easily seen that the effects induced by the ¹³C spin label are not present and other contributors from both spectra are present and some even more intense than in the ¹³C spectrum. This illustrates the strength of using ¹³C as an isotopic label for tracking changes in hyperfine coupling in these molecules.



Figure 4-18. HYSCORE 2D-FT simulation (red) and spectrum of **3** acquired at 4 K. Simulation parameters: $S = \frac{1}{2}$, $g_{xx} = g_{yy} = 2.08$, $g_{zz} = 2.44$, HStrain = (2200,1100,90) MHz, C₁: $a_{iso} = -2.11$ MHz, T = 3.29 MHz $\rho = 0.433$ MHz; C₂: $a_{iso} = 1.58$ MHz, T = 6.32 MHz, $\rho = 0.03$ MHz. Experimental conditions: 334 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 4 pulse HYSCORE sequence, 140 ns τ , 40 ns acquisition trigger (both dimensions) 16 ns increments and 256 x 256 points.

In the above figure, the simulation for the spectrum taken 334 mT is shown in red, plotted over the experimental 2D-FT. The simulation does quite well in representing most of the features stemming from the carbon-13 hyperfine, especially in Q1. The major feature in Q1 untouched by the simulation is the on-diagonal peak at 11.47 MHz, which is not even a harmonic of ¹³C_v. In the strong coupling regime, in Q2, the simulation covers the ridges centered about the peak at (-5.61,5.61). These ridges are a bit atypical in their form in that strong coupling in Q2 usually yields peaks (or ridges) that are parallel to the diagonal line. The Q1 ridges are more reminiscent of typical HYSCORE spectra where the ridges/resonances are perpendicular to the diagonal¹⁹. The other off-diagonal resonances in Q2 at (-9.52, 5.86) and (-5.86,9.52) are also present in the NiPSQ 2D-FT spectrum.

Below are the HYSCORE 260 mT spectra, for complexes **3** and **2**, respectively. Effects in Q1, relative to the 334 mT spectrum, that are present, are the tren features, along with baseline effects likely from the ¹³C label. The effects from ¹³C are minimalized, or much less intense, at this magnetic field value, as was seen in the ESEEM spectrum at the same magnetic field value. The decrease in echo amplitude (intensity) could be due to the occurrence that the magnetic field axis is no longer parallel to the magnetic axis of the ¹³C coupling at g 2, and therefore can no longer detect a response from being off resonance with the ligand-centralized radical.

The most prominent new feature in this spectrum, relative to the 334 mT spectrum, are the more intense features in Q2, centered about -5.2 MHz. Due to the absence of these features from the ¹²C spectrum at 260 mT, it is assumed that this is an effect of the ¹³C hyperfine coupling. Also, in Q1, not only has the intensity (*z*-axis) dwindled in the 0 - 7 MHz range, but also it appears that the proton HYSCORE has expanded. As for spectra collected at magnetic field values lower than 260 mT, the HYSCORE effect becomes dominated by ¹H hyperfine, while ¹³C

HYSCORE has completely vanished. It is fair to conclude that the ¹³C HYSCORE is most prominent at g-2 due to the nature of the delocalized electron density on the carbonyl carbon nuclei.



Figure 4-19. HYSCORE 2D-FT spectrum of **3** acquired at 4 K. Experimental conditions: 260 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 4 pulse HYSCORE sequence, 92 ns τ , 40 ns acquisition trigger (both dimensions) 16 ns increments and 256 x 256 points.



Figure 4-20. HYSCORE 2D-FT spectrum of **2** acquired at 4 K. Experimental conditions: 260 mT magnetic field, 9.71 GHz microwave frequency, 4 K, 4 pulse HYSCORE sequence, 92 ns τ , 40 ns acquisition trigger (both dimensions) 16 ns increments and 256 x 256 points.

The HYSCORE experiments found that the ¹³C hyperfine coupling was vast and rich in both the weak coupling (Q1) and strong coupling (Q2) regimes. This notion is also supported by the ESEEM results; however, due to the second dimension, the HYSCORE spectra not only bring more information to the table regarding hyperfine sublevel structure, but they also bring an aesthetic quality that draws attention to these more subversive details. These spectra are invaluable in showing the great disparity between **2** and **3** as far as ¹³C hyperfine is concerned and also in displaying the common hyperfine elements active in both complexes.

4.4 Conclusions and Future Work

The results and observations produced in this Chapter have possibly raised more questions than answers with regards to tracking hyperfine coupling in transition metal-organic radical complexes that experience an electron exchange interaction. The original idea behind this research was to use an isotopic label to observe changed in hyperfine coupling between various derivatives of the type [Ni(tren)(3,6-R₂-PSQ)]⁺. There have been other derivatives synthesized and characterized, and subjected to a treatment of cwEPR, ESEEM and HYSCORE measurements; however, the difficulty of modeling the spin system of these molecules has proved to be a task in and of itself. Efforts are ongoing to improve the accuracy of modeling these types of complexes in various forms.

The CW simulation of 2 does show both promise and concern. While unable to accurately represent the correct magnitude of exchange coupling, the line shape was able to be reproduced with decent accuracy. And, it was shown that the feature at g-2 is a possible marker for tracking the magnitude of exchange coupling. This will be promising to follow up on in future studies of molecules of this type, as well as tackle the theoretical efforts to accurately simulate the magnitude of the exchange coupling.

Interpretation of the ESEEM spectra showed that the data can actually be modeled well as a doublet system. The hyperfine coupling parameters discovered also showed that, like the $[Zn(tren)([^{13}C_2]PSQ)](BPh_4)$, the carbonyl carbon nuclei have a disproportionate amount of delocalized electron density. This is not surprising given that both complexes are within the C_s point group, and can even be approximated to be C_{2v}. It might be interesting to use a symmetric ancillary ligand or ligand system to occupy coordination sites and study the hyperfine coupling parameters to asses as to whether the delocalized electron density on the ligand can be controlled by the ligand, or it is merely a consequence of the bonding in a metal semiquinone complex. Examining the oxygen-metal bond lengths in such complexes is a means of characterizing the oxidation state of the semiquinone moiety. Catecholate ligands typically have symmetric bond lengths while semiquinones have slight discrepancies in the oxygen-metal bond lengths.²⁰

Finally, HYSCORE analysis of 2 and 3 yielded the potential for a great tool for characterizing differences in electronic structure of metal-radical complexes and their isotopologues. Also, HYSCORE could construed to be a more powerful technique for understanding hyperfine couplings that escape ESEEM analysis. The extra dimension is invaluable for studying the fine structure of open shell molecules. To state again, this research has been unique in that synthetic, exchange-coupled transition-metal complexes and their isotopologues are not usually studied with this level scrutiny. It is the hope of this author that HYSCORE and ESEEM analysis would be applied to more types of open-shell inorganic compounds in order for the field to grow. Currently, a majority of the research in the field resides in the biological realm, which does contain a good amount of inorganic chemistry, but it would be desirable for field and researchers if more studies would take advantage of these methods to further understand delocalization and its effects with regards to chemical reactivity and potential applications in technology.

APPENDIX

APPENDIX

CW-EPR

```
function res = LDM1056cw fit(hpar)
%LDM1056 Fit - McCracken & Stoll
% Load the Spectrum
[x,Edata,params]=eprload('LDM1052sh2CW.DTA');
Edata=Edata-Edata(1);
Edata = Edata/max(Edata);
Bdata=x/10.0;
lmin = 1;
lmax = 2048;
% Experimental Parameters
Exp.mwFreq = params.MWFQ/1.00e+09;
Exp.nPoints = params.XPTS;
Exp.CenterSweep=[params.A1CT*1000.,params.A1SW*1000.];
Exp.ModAmp = params.B0MA*1000.;
Exp.Temperature = 7.0;
Opt.nKnots = [91 4];
Opt.Output = 'summed';
% Simulation Parameters
Sys.S = [1.0 \ 0.5];
Sys.D = [49000 \ 6200; 0 \ 0];
Sys.ee = -6.1 \times 29979;
Sys.g = [2.44 2.08 2.08;2.00 2.00 2.00];
Sys.HStrain = [2200 1100 90];
Sys.DStrain = [38000 2900;0 0];
[B, spec, Trans] = pepper(Sys, Exp, Opt);
spec = spec/max(spec); % Normalize the simulation
res = 0.0;
for ipt = lmin:lmax,
    res = res + (spec(ipt) - Edata(ipt))^2;
end;
plot(B(lmin:lmax), spec(lmin:lmax), 'r', Bdata(lmin:lmax), Edata(lmin:lmax), 'k');
return;
```

ESEEM

```
function res = LDM1154 ESEEM 334mT 140tau Doublet Spec fit(hpar)
% LDM1154, Ni-[13C2]PSQ ESEEM FFT Sim/Fit
% Doublet - Saffron does NOT support systems w/ more than one spin
°
% Load the experimental spectrum
[freq,intens] = eprload('ldm1154div1052 334mT140sp.DTA');
freq = freq*1000;
lmin = 1;
lmax = 256;
% Simulation Parameters
Sys.S = 1/2; % Actually [1 1/2]
Sys.g = [2.44 \ 2.08 \ 2.08];
Sys.HStrain = [2200 1000 90];
Sys.Nucs = '13C, 13C';
Sys.n =[1 1];
Sys.A = [-2.11 3.288 0.433; 1.579 6.319 0.03]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 334; % Magnetic Field/millitesla
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.14; % Tau/microseconds
Exp.T = 0.04; % Starting T Value/microseconds
Opt.nKnots = 61;
[x,y] = saffron(Sys,Exp,Opt);
ESnormDAL; %Normalizes the simulation
res = 0;
for ipt = lmin:lmax,
   res = res + (spec(ipt) - intens(ipt))^2;
end;
plot(f(lmin:lmax), spec(lmin:lmax), ' r', freq(lmin:lmax), intens(lmin:lmax), '
k');
return;
```

```
function res = LDM1154_ESEEM 334mT 140tau Doublet Time fit(hpar)
% LDM1154, Ni-[13C2]PSQ ESEEM Time Sim/Fit
% Quartet - Saffron does NOT support systems w/ more than one spin
%-----
% Load the experimental spectrum
[time,amp] = eprload('ldm1154div1052 334mT140.DTA');
Amp = real(amp)/max(real(amp)); % Normalizes the data
time = (time/1000) + 0.14;
lmin = 1;
lmax = 256;
% Simulation Parameters
Sys.S = 1/2; % Actually [1 1/2]
Sys.g = [2.44 \ 2.08 \ 2.08];
Sys.HStrain = [2200 1000 90];
Sys.Nucs = '13C, 13C';
Sys.n =[1 1];
Sys.A = [-2.11 3.288 0.433; 1.579 6.319 0.03]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 334; % Magnetic Field/millitesla
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.14; % Tau/microseconds
Exp.T = 0.04; % Starting T Value/microseconds
[x,y] = saffron(Sys,Exp);
Y = real(y)/max(real(y)); % Normalizes the simulation
res = 0;
for ipt = lmin:lmax,
   res = res + (Y(ipt) - Amp(ipt))^2;
end;
plot(x(lmin:lmax),Y(lmin:lmax), ' r',time(lmin:lmax),Amp(lmin:lmax),' k');
return;
```

```
function res = LDM1154 ESEEM 260mT 92tau Doublet Spec fit(hpar)
% LDM1154, Ni-[13C2]PSQ ESEEM Time Sim/Fit 260 mT, 92 ns tau
% Doublet - Saffron does NOT support systems w/ more than one spin
%------
% Load the experimental spectrum
[freq,intens] = eprload('ldm1154div1052 260mT92sp.DTA');
freq = freq*1000;
lmin = 11;
lmax = 256;
% Simulation Parameters
Sys.S = 1/2; % Actually [1 1/2]
Sys.g = [2.44 \ 2.08 \ 2.08];
Sys.HStrain = [2200 1000 90];
Sys.Nucs = '13C, 13C';
Sys.n =[1 1];
Sys.A = [-2.11 3.288 0.433; 1.579 6.319 0.03]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 260; % Magnetic Field/millitesla
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.092; % Tau/microseconds
Exp.T = 0.04; % Starting T Value/microseconds
Opt.nKnots = 51;
[x,y] = saffron(Sys,Exp,Opt);
ESnormDAL; %Normalizes the simulation
res = 0;
for ipt = lmin:lmax,
   res = res + (spec(ipt) - intens(ipt))^2;
end;
plot(f(lmin:lmax), spec(lmin:lmax), ' r', freq(lmin:lmax), intens(lmin:lmax), '
k');
return;
```

```
function res = LDM1154 ESEEM 260mT 92tau Doublet Time fit(hpar)
% LDM1154, Ni-[13C2]PSQ ESEEM Time Sim/Fit 260 mT, 92 ns tau
% Doublet - Saffron does NOT support systems w/ more than one spin
8_____
% Load the experimental spectrum
[time,amp] = eprload('ldm1154div1052 260mT92.DTA');
Amp = real(amp)/max(real(amp)); % Normalizes the data
time = (time/1000) + 0.092;
lmin = 1;
lmax = 256;
% Simulation Parameters
Sys.S = 1/2; % Actually [1 1/2]
Sys.g = [2.44 \ 2.08 \ 2.08];
Sys.HStrain = [2200 1000 90];
Sys.Nucs = '13C, 13C';
Sys.n =[1 1];
Sys.A = [-2.11 3.288 0.433; 1.579 6.319 0.03]; % [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 260; % Magnetic Field/millitesla
Exp.Sequence = '3pESEEM';
Exp.dt = 0.012; % Time Increment/microseconds
Exp.tau = 0.092; % Tau/microseconds
Exp.T = 0.04; % Starting T Value/microseconds
Opt.nKnots = 51;
[x,y] = saffron(Sys,Exp,Opt);
Y = real(y)/max(real(y)); % Normalizes the simulation
res = 0;
for ipt = lmin:lmax,
   res = res + (Y(ipt) - Amp(ipt))^2;
end;
plot(x(lmin:lmax),Y(lmin:lmax), ' r',time(lmin:lmax),Amp(lmin:lmax),' k');
return;
```

HYSCORE

```
% LDM1154, Ni-[13C2]PSQ HYSCORE 2D-FT Simulation
% Quartet - Saffron does NOT support systems w/ more than one spin
%_____
clear;
Sys.S = 1/2; % Actually [1 1/2]
Sys.g = [2.44 \ 2.08 \ 2.08];
Sys.HStrain = [2200 1000 90];
Sys.Nucs = '13C, 13C';
Sys.n =[1 1];
Sys.A = [-2.11 3.288 0.433; 1.579 6.319 0.03];% [a-iso T rhombicity]
% Load the experimental Parameters
Exp.Field = 334; % Magnetic Field/millitesla
Exp.Sequence = 'HYSCORE';
Exp.dt = 0.016; % Time Increment/microseconds
Exp.tau = 0.14; % Tau/microseconds
Exp.t1 = 0.04; % Starting T Value/microseconds
Exp.t2 = 0.04;
Exp.nPoints = [256 256];
Opt.nKnots = 181;
[x1, x2, y, p1] = saffron(Sys, Exp, Opt);
% Plot the data
f1 = p1.f1;
f2 = p1.f2;
Z = real(p1.fd);
ZR = zeros(512, 512);
% Set threshhold for contour at 10% max amplitude
   Zthresh = 0.01*max(max(Z));
   for iy=1:512,
       for ix = 1:512,
           if Z(ix,iy) < Zthresh,</pre>
              ZR(ix, iy) = Zthresh;
           else
              ZR(ix, iy) = Z(ix, iy);
           end
       end;
   end;
   f1min=-15.0;
   f1max=15.0;
   f2min=0.0;
   f2max=15.0;
   frinc=f1(2)-f1(1);
```

```
xmin=floor((f1min-f1(1))/frinc)+1;
xmax=floor((f1max-f1(1))/frinc)+1;
ymin=floor((f2min-f2(1))/frinc)+1;
ymax=floor((f2max-f2(1))/frinc)+1;
contour(f1(xmin:xmax),f2(ymin:ymax),ZR(ymin:ymax,xmin:xmax),20,'r');
xlabel('f1 (MHz)');
ylabel('f1 (MHz)');
grid;
return;
```

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Chapter 5. Conclusions and Future Directions

5.1 Concluding Remarks

The goals of this research project entailed assessing whether or not a substituent effect was active in derivatives of 3,6-R₂-PSQs by investigating carbonyl carbon hyperfine interactions with CW and pulsed EPR techniques. In short, a substituent effect was observed, but only where R = H and OMe and only for organic radicals. The underpinnings of this research project necessitate for many derivatives to be synthesized, and not just organic radicals, but also for the Zn, Ga, and Ni complexes. Although this original goal was not achieved on a grand scale, what was achieved was an understanding of hyperfine fluctuations at the carbonyl carbon nuclei in PSQs when bound to Na⁺, Zn(tren)²⁺, Ga(tren)²⁺ and Ni(tren)²⁺. This does not qualify as a substituent effect, but what it does qualify as, is a study that shows the influence of Lewis acidity and exchange coupling on hyperfine coupling parameters.

Building on this notion, Table 1 shows the hyperfine parameters of all monosemiquinone complexes, excluding [Ga(tren)(PSQ)](BPh₄)₂ (no spin echo was observed). As an overarching theme, all isotropic coupling constants were on the scale of 0-3 MHz, regardless of sign. It is most likely the case that these constants are small because the radicals being studied are of aromatic nature and therefore the majority of the unpaired spin density is located in π – type orbitals. These findings are actually consistent with what has been found for the carbonyl carbons in ubisemiquinol oxidase. MacMillan and coworkers found carbonyl carbon *a* iso in the range of 0-1 MHz¹. These were organic radicals and the carbonyl oxygen nuclei were undergoing hydrogen bonding with nearby amino acid residues. For the metal complexes however, there aren't many examples of this kind of study in the literature and therefore real life comparisons are not easily found. Although, these results could be compared with theoretical results ad nauseam; however, this was not the point of this study.

Additionally, a comment is to be made for the low magnitude of these isotropic hyperfine interactions. It is thought that a majority of the spin density is contained within the carbonyl oxygen nuclei of semiquinones, and thus it is not a gross estimation that there could be a high concentration of spin density at the carbonyl carbon nuclei as well. This can be a decent estimation, but one should be careful in estimation; the isotropic values fond in this work were less than some ¹H- a_{iso} values. Again, due to the nature of these radicals, residing in π – type orbitals, a discrepancy should be noted that the isotropic and dipolar coupling constants do not necessarily track each other in magnitude. The results of the NaPSQ and Na(OMe)₂PSQ make this quite obvious.

 PSQ and N1-PSQ.

 NaPSQ
 Na(OMe)₂PSQ
 Zn-PSQ
 Ni-PSQ

 a_{iso}, T, ρ
 a_{iso}, T, ρ
 a_{iso}, T, ρ
 a_{iso}, T, ρ

 Carbon 1
 -1.57, 13.57, 0.44
 -0.41, 16.13, 0.63
 1.08, 2.84, 0
 -2.11, 3.29, 0.43

-0.41, 16.13, 0.63

2.78, 2.46, 0

1.58, 6.32, 0.03

-1.57, 13.57, 0.44

Carbon 2

Table 5-1. ¹³C Hyperfine parameters, in MHz, for NaPSQ Ion-Pair, Na(OMe)₂PSQ Ion-Pair Zn-PSQ and Ni-PSQ.

What is more interesting though, is the change in magnitude of the dipolar coupling across the series. The dipolar values are highest for the organic radicals, by an order of magnitude. The hyperfine interaction is quite contained within the semiquinone moiety, and has "nowhere to go" in comparison to the metal complexes. The dramatic decrease in magnitude of dipolar coupling from organic radical to metal complex could be explained by a spin delocalization mechanism, however these arguments would only be skeptical as there is no experimental data for the magnitude of hyperfine coupling that the metal/metal-tren system is experiencing. There is one exception of note, and that is the Ga-PSQ system, and that will be discussed below.

The study of organic radicals in Chapter 2 saw an interesting twist in that the simulations showed evidence of multiple species in solutions, rather than one ion pair; an ion-pair and dimer were found for NaPSQ and an ion-pair, dimer, and a "tris-like" complex for Na(OMe)₂PSQ. It is possible that in using sodium metal as a reductant, not only was the quinone reduced to a semiquinone but sodium also provided a surface for unwanted reactions. This situation made for a more serendipitous occasion than at first realization of the active multiple species.

The extra species in solution allowed for a more comprehensive study of radical delocalization. Although these complexes were not physically characterized, it was shown that it was not possible to properly simulate all features of the ESEEM spectrum without the additional species. For NaPSQ, the dimer showed that when an additional ligand is bound to an ion (or within close proximity), the unpaired spin density will be delocalized across the Na⁺ bridge, and onto the second ligand. This is a comparable effect to the delocalization in the Zn-PSQ system of Chapter 3; indeed, the isotropic and dipolar couplings are nearly identical. It would be interesting to synthesize each of these complexes (both isotopologues) and analyze their EPR, ESEEM and HYSCORE spectra and compare them to the spectra presented in this work. Lastly, if these individual complexes were realized, then to ultimately determine the validity of the analysis of Chapter 2, mixtures of the complexes could be made and then analyzed by CW and pulsed techniques.

Chapter 2 also afforded an interesting observation in that, in comparing the hyperfine parameters of NaPSQ and Na(OMe)₂PSQ, the isotropic couplings were larger from NaPSQ,

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while dipolar couplings were larger for Na(OMe)₂PSQ. This was true for both ion-pair and dimer compounds. The increase in dipolar coupling can be attributed to the methoxy groups; these are electron-donating groups and in this case the oxygen atoms donate into the π system of the phenanthrene ring.

Analysis of the d¹⁰-semiquinone complexes revealed some expected results and some unusual results. After analyzing the NaPSQ and Na(OMe)₂PSQ dimer systems, it was expected that the carbonyl carbon dipolar coupling may be on the order of 0 - 10 MHz for the Zn-PSQ and Ga-PSQ complexes. The hyperfine parameters for Zn-PSQ are listed in Table 1 and they are nearly identical to the parameters for the NaPSQ dimer ($a_{iso} = 2.17$ MHz, T = 2.77 MHz). It is possible that unpaired spin density of the radical has been delocalized across Zn and onto the amino groups. It would be interesting then to isotopically label the amino nitrogen nuclei with ¹⁵N; ¹⁴N ESEEM is a prominent field, but by using ¹⁵N the Mims' division technique could be used and only the tren nitrogen nuclei would be analyzed for their hyperfine parameters. Additionally, the amino protons could be labeled as ²H nuclei, this would give rise to ²H ESEEM and further analyze the delocalization as a function of ²H dipolar coupling.

Now, for the curious results of the Ga-PSQ complex. As a reminder, only isotropic coupling constants were found and the values are: 69,71 Ga- $a_{iso} = 19.73$ MHz, C1- $a_{iso} = 27.77$ MHz and C2- $a_{iso} = 32.10$ MHz. The isotropic hyperfine interaction at the gallium nucleus is consistent with other Ga-SQ complexes². The carbonyl carbon isotropic coupling constants were the real surprise, especially after analyzing all the complexes of this work; these values are much greater than any of the other isotropic coupling constants simulated. The objective of Chapter 3 was to determine if there was an effect of Lewis acidity on spin delocalization. It appeared that when comparing Zn-PSQ and [NaPSQ(PhenQ)], it was possible that the ancillary ligand had more of

an effect on spin delocalization than the ion itself. Including Ga-PSQ into that equation introduces yet another layer of complexity. The isotropic values are large enough to suggest that the dipolar values are minimal, but without ESEEM data, this is only a speculation. This gallium complex was to aid in answering the inquiry into spin delocalization, but is has created more questions than answers. A Cd^{II}-PSQ complex should be further pursued to examine hyperfine coupling at the metal center; ¹¹¹Cd and ¹¹³Cd have $I = \frac{1}{2}$ and their relative natural abundances are 12.8% and 12.22%, respectively. This would be an inexpensive means of studying spin delocalization in a d¹⁰, M^{II}-PSQ complex; this complex was pursued and even EPR, ESEEM and HYSCORE data were recorded, but the identity of the complex was unable to be determined by characterization techniques.

Finally, the Ni-PSQ study showed that there are still complications to be overcome in scrutinizing the spin delocalization mechanisms active in an exchange-coupled complex. Although the line shape of the Ni-PSQ complex was able to be recreated (to a certain degree), the model was inaccurate in its estimation of exchange coupling. The value in the model was much less than estimations for that specific complex and what has been found for similar complexes^{3,4}. Additionally, the simulated zero-field splitting parameters were also larger than what had been previously measured³. Although the magnitude was misrepresentative of the magnitude of the exchange coupling, varying this magnitude showed changes in the feature at g-2 and this may be indicative of a substituent effect. This should be pursued by examining the previously synthesized complexes, as well as by improving the simulation software to account for exchange coupling values that are more representative of the experimentally observed values.

The magnitude of the carbonyl carbon isotropic coupling constants fell within the range of what had been observed for the other compounds examined (excluding Ga-PSQ) and what had

been predicted by DFT. The dipolar coupling constants were of a similar magnitude to [NaPSQ(PhenQ)] dimer and Zn-PSQ, but were a mere fraction of what had been calculated by DFT. It was not surprising that dipolar coupling predictions were contrasting to the values measured; this was the case for Zn-PSQ as well, large dipolar values were calculated and values simulated were vastly lower in magnitude.

Despite these short-comings, the HYSCORE spectra and analysis afforded a decent understanding of the hyperfine interaction at the carbonyl carbon nuclei. The variance between Ni-PSQ and Ni-[$^{13}C_2$]PSQ was stark in that the hyperfine coupling was obvious and had rich fine structure that could not be observed from ESEEM and especially the CW spectrum, where any hyperfine coupling was completely unresolved and swamped out by the large exchange interaction. The ESEEM simulations and spin system proved to be a good match for simulating the HYSCORE spectra as well. Recall that the ESEEM and HYSCORE spectra were modeled as a doublet, instead of a quartet. The simulation achieved accurate simulation of both strong and weak hyperfine couplings.

What remains to be accomplished by these simulations was an accurate portrayal of the echo amplitude (or intensity) of the resonances in both ESEEM and HYSCORE simulations. Specifically, the height of the peaks typically increases when investigating lower magnetic field values compared to higher magnetic field values. This effect was unable to be reproduced by either a double or quartet system; the doublet systems were pursued due to accuracy of peak position prediction. Again, this could be due to the origin of the radical being housed in orbitals on the PSQ moiety.

5.2 Future Directions

The goal of this project was to measure hyperfine interactions and the heart of a direct exchange interaction despite not having a measure J. It would be advantageous to devise a system where J values are easily measured by variable temperature magnetic susceptibility and spin density information could be obtained by means of EPR. Such a system would therefore need a nucleus at which spin density could be measured. This would be the most advantageous situation to learn about the abilities of substituents and metal centers to polarize/delocalize spin density.

In the course of looking for a system in which this could be done, two systems have been examined that follow the same structural motif as the metal complexes studied within this work, phenazinesemiquinone (PazSQ) and anthracenesemiquinone (ASQ). Both of which can be seen below, in Figure 1.



Figure 5-1. Molecular structures of [Ni(tren)(ASQ)]⁺ (top) and [Ni(tren)(PazSQ)]⁺ (bottom).

A DFT evaluation was undertaken to examine the ability of these systems to polarize spin density with various substituents and determine their corresponding exchange coupling constants. The initial geometries were created in GaussView4⁵ from the [Ni(tren)(PSQ)]⁺ structure. Calculations were performed in Guassian03⁶ for [Ni(tren)(4,5-R₂-PazSQ)]⁺ and in Gaussian09⁶ for [Ni(tren)(4,5-R₂-ASQ)]. Calculations were performed with the unrestricted formalism and the B3LYP^{7–9} functional (UB3LYP is the appropriate syntax for input files). Geometries were optimized with the 6-31G(d,p)^{10–20} basis set and single point calculations were carried out with the 6-311g(d,p)^{21–24} basis set. Frequencies were checked so as to ensure that no imaginary frequencies existed in the course of optimizing the geometry.

The broken symmetry approach was used to model these compounds. The Hamiltonian used to describe these molecules is of the form $\hat{H} = J\hat{S_1} \cdot \hat{S_2}$, where S_1 and S_2 are the spin operators for the individual spin centers and *J* is the exchange coupling constant. Complexes were optimized as quartet states and single point calculations were done for the quartet and doublet states with the quartet optimized geometry. *J* values were obtained by the following equation developed by Yamaguchi and coworkers²⁵:

$$J = 2 \frac{E_{HS} - E_{BS}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}}$$
(1)

Where E_{HS} is the energy of the high spin state (quartet) and E_{BS} (doublet) is the energy of the broken symmetry state, and $\langle S^2 \rangle_{HS}$ and $\langle S^2 \rangle_{BS}$ are the spin expectation values for the high spin and broken symmetry states, respectively. Spin density values were calculated as stated in previous chapters: beta spin densities were subtracted from alpha spin densities for individual atoms and then the values were averaged over either the two oxygen atoms, or nitrogen atoms.

Displayed below in Figure 2 are the results for Ni-ASQ, where the substituents are in the 4,5 positions, on the back of the anthracene ring.



[Ni(tren)(4,5-R₂-AnthraSQ)]⁺ J vs. Avg. Oxygen Spin Density

Figure 5-2. Average oxygen spin density versus *J* for $[Ni(tren)(4,5-R_2-ASQ)]^+$ complexes. A linear trend between the average oxygen spin density and *J* is observed, just as in the case of the 3,6-R₂-PSQ series. The main difference here is that the trend is not necessarily associated with electron withdrawing/donating groups. The two major observations from the Ni-PSQ series was a linear relationship, as well as electron donating groups were associated with lower *J* values and electron withdrawing groups were associated with larger *J* values. This of course makes it all the more interesting to study both series of compounds experimentally. Although the advantage with the ASQ series is that the *J* values are approximately half of the calculated values

compare to the NiPSQ series. *J* was able to be experimentally determined for [Ni(tren)(3,6-NH₂-PSQ)](BPh₄) and it was found to -119 cm⁻¹, while the calculated value was -209 cm⁻¹. If this overestimation of the *J* value is true for the Ni-ASQ complexes then these would be prime targets to be pursued for experimental studies.

Displayed below is J versus oxygen spin density for $[Ni(tren)(4,5-R_2-PazSQ)]^+$ complexes.



Figure 5-3. Average oxygen spin density versus *J* for $[Ni(tren)(4,5-R_2-PazSQ)]^+$ complexes.

A linear trend is also observed but here the J values are much greater than the values calculated for the Ni-PSQ series, which nearly solidifies the inevitability that J values for these compounds will not be able to be determined experimentally; however, these compounds have a N atom in between the exchange center and the substituents, making it convenient to study hyperfine coupling parameters by ¹⁴N-ESEEM and HYSCORE.

These are two possible avenues to pursue when considering future directions for projects in the same vein of this work. Additional studies were undertaken to calculate J for α -diimine complexes; these are ligands where the carbonyl oxygen nuclei have been replaced with nitrogen nuclei. The idea here is that ¹⁴N is the most abundant form of nitrogen and it has I = 1, which means that the hyperfine coupling could be measured by ESEEM. These calculations are not presented here, but in each complex that was examined, the calculated J values were greater than those of Ni-PSQ, thus it would be unlikely that J values could be experimentally determined. One last consideration for future studies would be to add a bridge between the metal and SQ so as to have a super-exchanged complex. The exchange coupling may then be a more suitable magnitude to be measured by variable temperature magnetic susceptibility.

5.3 Final Remarks

EPR is a powerful tool for investigating the hyperfine structure of various types of systems. CW-EPR measurements will often provide isotropic couplings, ESEEM measurements measure dipolar couplings and HYSCORE spectra show the landscape of the hyperfine coupling throughout the molecule. It has been established in this work and elsewhere^{26,27} that this can be a strong method for investigating the spin properties of exchange-coupled inorganic complexes as well as organic radicals and organic-based radical-metal complexes.

¹³C-labelling of the quinone moiety has shown to be an interesting means of studying the hyperfine coupling in the compounds studied here. While not providing for a clear correlation of

hyperfine coupling and delocalization between PSQs, Zn-PSQ and Ni-PSQ, it was shown that the isotropic coupling is rather consistent among all these types of compounds, and the main entity to examine is the dipolar coupling. The dipolar coupling showed obvious changes depending on the type of molecule being examined. This study will provide a backdrop for a more extensive study including multiple derivatives, as well as lay the foundation for more ESEEM and HYSCORE studies of synthesized inorganic complexes experiencing some form of exchange coupling. REFERENCES

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