Application of Computational Chemistry Methods to the Prediction of Electronic Structure in Nickel Dithiolene Complexes

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1. INTRODUCTION

Advances in the science of computational chemistry over the past 20 years, the widespread availability and increasing ease of use of computational chemistry software, and an exponential reduction in the cost and size of extremely powerful computer hardware now make some degree of computational predictive capability for physical properties (e.g. solubility, electronic and vibrational spectra, reactivity, molecular configuration, and chirality) within the reach of nearly every laboratory that is involved in new materials research and development. Previously, researchers out of necessity would have to follow an empirical approach of synthesizing, isolating, characterizing, and purifying hundreds of different compounds in order to establish structure-property relationships that could be used to further direct the design and development effort toward the desired goal. Of these hundreds of compounds synthesized, only a handful would have the necessary combination of physical characteristics to be deemed worthy of further study and development. As can be imagined, this process is extremely time consuming, labor intensive (weeks to months to completely synthesize and characterize each compound), costly, and sometimes highly frustrating for organic chemists engaged in the synthesis of new materials—especially for those with limited resources. Modern hardware and user-friendly software now make it possible to model new compounds and their physical properties with remarkable accuracy within a few hours or days. Only a few years ago it would have taken from weeks to months of work to achieve the same results.

Nowhere has there been more evidence of the predictive capability of computational chemistry than in the pharmaceutical industry, where computational molecular design techniques have been used to great advantage for a number of years in the rapid development of new drugs with enhanced biological activity and specificity at lower cost. More recently, computational chemical methods have been applied to the molecular engineering and design of liquid crystal materials for use in the multibillion-dollar information display industry and the optoelectronic, photonics, military, scientific, and life sciences sectors. In all of these examples, the vast majority of the target materials systems consist of organic molecules containing combinations of carbon, hydrogen, nitrogen, sulfur, fluorine, and phosphorous, for which the computational algorithms and procedures have been well defined in a large body of existing literature. Modeling of compounds containing other elements (in particular, transition metal organometallics) represents a substantial challenge for several reasons: (1) the scarcity of previous literature references on the subject, (2) the lack of parameter files (basis sets) that can adequately account for the unique nature of the coordinate-covalent bonds that are formed in these materials, (3) the intensive computational resources required to accomplish the calculations, and (4) the scarcity of software capable of modeling organometallics.

In the research described in this paper, a computational modeling methodology employing both molecular mechanics and *ab initio* computational methods was developed and used to calculate the expected electronic absorbance spectra in the near-IR region for both existing and novel zerovalent transition metal dithiolene near-IR dye complexes containing nickel as the central metal atom. This is believed to be the first time that calculations of this nature have been attempted in nickel dithiolene systems, or in any other transition metal organometallic complex. This new computational capability now makes it possible to determine, before synthesis, the effect of structural changes in either the dithiolene core, the ligands (or both) on the physical and optical properties of the complexes and accelerate their development for applications in optical devices.

2. NICKEL DITHIOLENE COMPLEXES

Transition metal dithiolenes are composed of a central metal atom (in this case, nickel) bonded to four sulfur atoms, which in turn are bonded to four carbon atoms to form a square planar geometry (Figure 1) composed of two five-member planar rings (the *dithiolene* core).

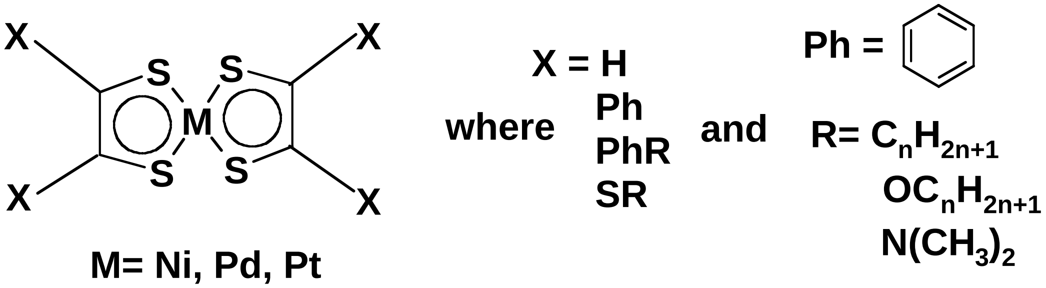


Figure 1. The base structure of the nickel dithiolene system

The metal atom is zerovalent, due to overlap of d-orbitals on the metal with the extended π-electron system of the dithiolene core. As a result, the bonding in the complex is coordinate covalent and possesses very little (if any) ionic character. The high degree of electron delocalization results in a very intense electronic absorbance transition in the near-IR region (600-1600 nm, depending on structure). The zerovalent nature of the complexes makes them highly soluble in nonpolar organic solvents such as benzene, toluene, and hexane, which makes them unique among both metal complexes and other near-IR dyes. The terminal R groups can be selected from a large number of substituents (alkyl, alkoxy, aryl, thioether), and these terminal groups can have a large effect on the physical properties of the complexes.

Nickel dithiolenes are both thermally and photochemically stable, and thus have been of interest for a number of years as passive absorbers in xerography, as Q-switching absorbers for lasers, and for optical power limiting and all-optical switching. Most recently, they are of special interest as dye dopants for liquid crystal near-IR devices for optical modulation, switching and night vision/avionics imaging. Their high solubility in nonpolar organic solvents also renders them highly soluble in liquid crystals, which is a distinct advantage over other near-IR dyes that are primarily ionic in nature and thus have poor solubility in organic host media. They can also possess liquid crystal phases in their own right, depending on the structure of the complex and the number and position of the functional groups attached. This property is a distinct advantage for use in liquid crystal systems, as it allows them to be used at much higher concentrations in the host material without adversely affecting the unique physical and optical properties of the liquid crystal host. The recent increased technological importance of these materials in near-IR optical modulation devices based on liquid crystals, along with the challenging nature of the modeling task, makes these interesting materials an ideal subject for study.

3. COMPUTATIONAL MODELING TECHNIQUES

Modeling of electronic transition states in organometallic systems represents a significant technical and computational challenge. There is a scarcity of both previous literature references on the subject and, even more significantly, a very limited number of basis sets that adequately account for the unusual coordinate-covalent bonding in these materials. Because of the complexity of the calculations, substantial computational resources are also required.

In general, the process of modeling the electronic absorbance spectra is composed of three key steps:

- Minimization of the free energy of the molecular structure using molecular mechanics methods.
- Determination of the electronic distribution in the molecule and calculation of the available electronic energy levels and excited states.

- Calculation of the allowable ground-state to excited-state transitions that are responsible for the electronic absorbance spectrum.

Molecular mechanics calculations use Newtonian mechanics and empirical force fields to model the potential energy of an atom in its molecular structure. This process examines the chemical bonds of a molecular structure to generate a particular molecular conformation that represents an energy-minimized state with respect to bond angles, electrostatic repulsions, and steric factors. This energy-minimized structure represents an approximate equilibrium conformation that must be further refined using quantum mechanical methods.

The electronic distribution within the molecule and its effect on the energy-minimized equilibrium molecular conformation can be determined by using either semi-empirical or *ab initio* quantum mechanical computation methods. Semi-empirical methods use some approximations in order to achieve reduced computation times. They are used primarily in situations when a certain degree of computational accuracy can be sacrificed in exchange for reduced computational resources and run time. *Ab initio* methods provide a much more detailed and accurate description of the quantum mechanical aspects of a molecular structure, but do so at a cost of increased computational resource requirements and time. The substantially better accuracy of a*b initio* calculations make them the preferred method for modeling the exceedingly complex electronic distribution and excited state transitions found in organometallic compounds.

Ab initio calculations are based on a detailed description of the quantum mechanical aspects of a molecular structure using the Schrödinger equation, defined as

$$H_{op}\Psi = E\Psi$$

where H_{op} is defined as the Hamiltonian operator, Ψ as the wavefunction of the system, and E as the energy of the system. The Hamiltonian of the system represents its kinetic and potential energy. In a three-dimensional system, the Hamiltonian operator is defined as

$$H_{op}\Psi = \frac{-h^2}{8\pi^2 m}\left[\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right] + U\Psi$$

where h is Planck's constant and m is the mass of an electron. The terms x, y, and z are the Cartesian coordinates of an electron with respect to the nucleus, while U refers to the potential energy of the system.[1]

A wavefunction is a mathematical expression that describes the wave nature of an electron after certain restrictions are placed upon it by basis sets, which give specific information on the electronic structure and orbitals of the atoms as well as describing the path and behavior of electrons. The wavefunction expression is a group of Gaussian Type Orbital (GTO) equations for which the generic equation is

$$\Psi = Nx^l y^m z^n e^{-\alpha r^2}$$

Again, the x, y, and z are the Cartesian coordinates. The variables l, m, and n are positive integer values that describe the angular momentum of the orbital, while r is the distance to the center of the atom. The variable N is the normalization constant, and the variable α represents the orbital exponent of the Gaussian function. All of these variables change as different methods are used and different molecules are examined.

While it is impossible to solve the Schrödinger equation for a many-electron system, various methods can be used to approximate certain values in the equation to make it solvable. The Hartree-Fock method is based on the use of three approximations to estimate the many-electron wavefunction: (1) The Born-Oppenheimer approximation, which assumes that all nuclei are motionless with respect to the electron; (2) The Linear Combination of Atomic Orbitals (LCAO) approximation, which assumes that electron orbitals may be expressed as one-electron basis functions centered on each atom, and (3) the Hartree-Fock approximation, which assumes that the sum of all single-electron calculations of a molecule is the same as the multi-electron calculation of the molecule. Because of errors associated with the Hartree-Fock approximation, the entire Hartree-Fock computational method becomes less accurate with increasing molecular size.[2]

Density Function Theory (DFT) makes use of a different approach. Unlike the Hartree-Fock method, where the calculations start with an exact Hamiltonian and have approximate wavefunctions written in terms of a product of one-electron functions, the DFT method replaces the many-electron wavefunction with electronic density as the basic quantity.[3] Although not as well established and time-tested as the Hartree-Fock method, the DFT method is widely employed in the field of computational chemistry and is considered to be a good method to use with transition metal complexes.

The expected excited-state electronic transitions are determined by including the configuration interaction (CI) model in the *ab initio* quantum mechanical calculations. The CI model is derived from Hartree-Fock calculations that are expanded to incorporate electron promotion and changing shell levels.

4. MODELING IN NICKEL DITHIOLENE SYSTEMS

Following the general approach outlined in the previous section, a modeling methodology was developed to determine the electronic spectrum of nickel dithiolene complexes in the near-IR region. A series of nickel dithiolene systems that had previously been prepared and reported in the literature by Mueller-Westerhoff[4] was modeled and the calculated wavelengths were compared to the experimental literature data to test the accuracy of the modeling method. Because there is no single software package that can accomplish all of the steps required to calculate the electronic spectrum for the nickel dithiolene complexes, it became necessary to use several different software packages on two different computing platforms and develop methods to allow interchange of data and parameters between the various software packages. Table 1 gives an overview of the computational tasks that summarizes the details of the hardware and software used to perform the computations.

Computational task	**Software**	**Hardware**
Molecular mechanics optimization	Spartan 4.0[5]	2 GHz dual-processor Intel XEON server
Output-input file conversion	OpenBabel[6]	
Ab initio calculations	General Atomic and Molecular Electronic Structure System (GAMESS) [7]	SGI Altix Server (16-2.5 GHz Itanium 2 processors)
Electronic spectra generation	WebMO[8]	

Table 1: A summary of the computational tasks and resources utilized for the calculation of near-IR spectral transitions in nickel dithiolenes

Spartan was used to actually build the molecule and to run molecular mechanics optimization. The output file of optimized atom coordinates was then transferred to GAMESS using OpenBabel. Specifying the appropriate conditions under which to conduct the *ab initio* calculations using GAMESS proved to be extremely challenging for a number of reasons. Parameter options and appropriate basis sets for the calculations must both be selected and specified properly in order to achieve accurate and useful results. This process is non-trivial under the best of circumstances, because there are a large number of calculation options and not all of these options are universally applicable to all calculation types or molecular systems. For relatively small organic molecules there is existing literature to guide in the selection of appropriate options and parameter sets, but in the case of nickel dithiolenes there is no pre-existing body of literature from which to draw guidance. Therefore, it became necessary to determine the proper calculation conditions based on: (1) extensive study of the general literature on *ab initio* molecular modeling theory, (2) review of the handful of existing references on *ab initio* modeling in unrelated transition metals and their complexes, and (3) testing of the selected modeling parameters and conditions by means of an iterative trial and error process.

The calculation options for GAMESS that were critical in obtaining an accurate model of the electronic distribution in the nickel dithiolene complexes are described below:

- *SCFTYP (self-consistent field wavefunction)*- specifies the basic calculation type that is used. For our work, the Restricted Hartree-Fock[9] (RHF) and Density Functional Theory[10] (DFT) options were used. The RHF method was ultimately chosen for the final calculations because (1) it was found to be more accurate than the DFT method in initial test trials, and (2) because the CI calculations that are required to calculate the absorbance spectra are based on the RHF calculations, they cannot be run concurrently with the DFT option.

- *GBASIS-* specifies the type of basis set used for the calculation and what type of basis set function to choose. The minimal basis sets (GBASIS=STO) and split-valence basis sets (GBASIS=N31) were chosen initially because they were two of the few basis sets that supported both nickel and the other atoms commonly contained in organic compounds (and consequently were the only ones capable of producing accurate calculations for the electronic structure of nickel dithiolenes). The minimal basis set used was STO-3G.[11-12] The 3G indicates the use of three Gaussian functions. Split-valence basis sets used were 6-31G with six Gaussian functions (indicated by the 6), and 6-31G(d),[13] which includes both six Gaussian functions and functions that incorporate *d*-orbital calculations. The split-valence basis sets proved to be more accurate because they correctly predicted that valence electrons do most of the bonding. The inclusion of *d*-orbitals increases the accuracy of the calculations.
- *SCF and DIRSCF*- specify whether the self-consistent field wavefunction will be calculated directly or indirectly.[14] Hartree-Fock calculations make use of a large number of two-electron repulsion integrals that are stored and retrieved from hard disk storage. The direct SCF calculation reevaluates the integrals directly without storing to disk during each Hartree-Fock iteration, which dramatically speeds up processing time.
- *CITYP* (Configuration Interaction Model Type) – includes and specifies CI models in the *ab initio* calculations for electronic spectra calculations. The CI method used for determining the electronic structure of a compound was configuration interaction single-promotion (CIS) because it gave accurate results within a reasonable time.[15]
- *NSTATE*- specifies how many different peaks in the electronic spectrum should be solved for during the calculations. The optimal value for NSTATE was found to be 10

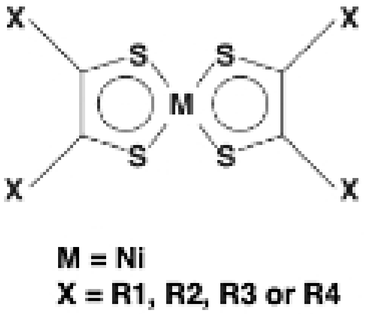
because lower values generated inaccurate results while higher values significantly increased calculation times without any significant gain in accuracy.

- *DAMP* - aids in allowing the system to converge to an energy minimum state during SCF calculations[16-17]. *Ab initio* calculations were found to fail consistently in nickel dithiolene systems unless this crucial option is added.

The computational conditions listed above were used to verify the accuracy of the computational method and test its ability to predict near-IR electronic absorbance bands in novel, yet-to-be synthesized nickel dithiolene complexes.

5. COMPUTATIONAL RESULTS

Figure 2 below shows the calculated wavelength of near-IR absorbance bands using the new computational method together with the experimental wavelength reported in the literature by Mueller-Westerhoff[18] for a number of different solvents.

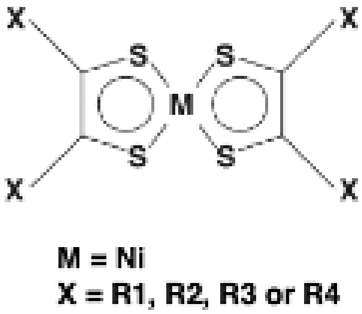


Terminal Group	Experimental Solvent	Experimental Wavelength (nm)	Calculated Wavelength (nm)
R=H	Hexane	720	720.91
R=CH_3	$CHCl_3$	774	843.08
R=CF_3	Pentane	715	775.05
R=S-C_4H_9	$CHCl_3$	1104	1012.31
R=C_6H_5	$CHCl_3$	866	845.19
R=2-Napthyl	$CHCl_3$	905	993.08
R_1,R_4=H; R_2,R_3=C_6H_5	CH_2Cl_2	805	857.78

Figure 2. The near-IR absorbance wavelengths for several nickel dithiolene compounds previously prepared and reported in the literature. The experimental wavelength is the actual wavelength of the near-IR absorbance band in the experimental solvent. The calculated wavelength represents the prediction of the new computational method.

The experimental wavelengths were measured using certain solvents. This may offset the calculated wavelengths. However, a Pearson correlation of the calculated near-IR absorbance data to the corresponding experimental near-IR data was determined for the compounds in Figure 2. The Pearson correlation *r* is a measure of the fit of a least-squares linear regression through the data set. Likewise, the correlation coefficient R^2 describes the proportion of the points that can be accounted for by the linear regression. Calculation of a correlation coefficient R^2 between the experimental and calculated near-IR wavelength data yields a value of 0.91, which represents an excellent correlation between calculated and experimental results for a majority of the compounds modeled. The computational model currently assumes that the compound is in a vacuum. The excellent correlation is strong evidence of the predictive capability of the computational method developed in this work and validates its use in predicting electronic transition states in yet-to-be-explored nickel dithiolene systems. The following section describes the first steps in this direction.

The new computational method described in the previous sections was applied to a series of nickel dithiolene systems with ligands of varying structure in order to establish structure-property relationships that could be used in the design of new materials with an advantageous combination of physical and optical properties (high host solubility, large absorbance oscillator strength, and control of the peak absorbance maximum through ligand selection). The goal of this initial effort was to determine what structural features would allow the main near-IR absorbance band to be shifted to longer wavelengths without negatively impacting the solubility in a liquid crystal host material. Figure 3 below shows the predicted near-IR wavelength maxima for several nickel dithiolene compounds with varying terminal groups. The figure also includes for reference one nickel dithiolene complex with C_6 alkyl terminal groups that has been previously synthesized.



Terminal Groups	Experimental Wavelength (nm)	Predicted Wavelength (nm)
R=C_6H_5	866	845.19
R = S-H	?	1053
R = S-Ph	?	972
R_1, R_4 = S-H ; R_2, R_3 = S-Ph	?	1004
R_1, R_4 = H ; R_2, R_3 = S-Ph	?	1038
R_1, R_4 = H ; R_2, R_3 = S-H	?	1055

Figure 3: Predicted electronic spectral maxima for a series of candidate nickel dithiolene compounds that have yet to be synthesized. The first entry in the table is a compound that has been synthesized and included for reference.

One significant trend that can be observed on examination of the table is that the near-IR peak wavelength is red-shifted when sulfur-containing groups are bonded directly to the dithiolene core, whereas the near-IR maximum is blue-shifted in the case where phenyl groups are bonded directly to the dithiolene core. This observed trend is somewhat counter-intuitive, as it is normally accepted that the addition of aromatic groups in conjugation with another aromatic structure generally shifts the absorbance maximum of the molecule to *longer* wavelengths because of resonance stabilization (the energy gap between electron levels is reduced, thus allowing electronic state transitions to occur at lower energy and longer wavelengths). Clearly the *d*-orbitals on the sulfur-containing terminal groups are providing a greater degree of resonance stabilization than the phenyl groups. The nature of this stabilization is not yet understood, and will be investigated in the future.

One serious problem that was encountered with the model was the inability of GAMESS to produce accurate electronic spectral data for compounds containing nitrogen atoms. Failures in computation were routinely encountered in every attempt to model nitrogen-containing nickel dithiolene structures. In an attempt to determine the source of the problem, we modeled some very simple, classical nitrogen-containing organic compounds using the method and came up with similar results. The source of the problem at this point is still unresolved, but it appears to be a basic functional issue with GAMESS itself and not with our specific computational methodology or parameter files. An investigation into this issue is ongoing.

5. CONCLUSION

A computational method has been developed that can accurately predict the electronic spectra of nickel dithiolenes. It now becomes possible to model new nickel dithiolenes prior to synthesis so that synthesis efforts can be concentrated only on those compounds that by theoretical predictions have the best chance of showing the desired physical and optical properties for device applications. A large number of trials can be run to see how different terminal groups will affect the electronic spectrum. One limitation of the current method is that the accuracy of the Hartree-Fock calculations is substantially reduced as the size of the molecule increases. DFT calculations may provide a workaround to this problem and should be investigated as an alternative. A more serious limitation is the current inability of GAMESS to accurately calculate electronic spectra when nitrogen atoms are included in the terminal groups. Future investigations will concentrate on improving the model to overcome these two limitations as well as further applying its predictive capability to new nickel dithiolene compounds in the low-to-medium molecular weight range.

ACKNOWLEDGEMENTS

1. Laboratory for Laser Energetics for providing the tools and facilities for research
2. Mr. Kenneth Marshall – Advisor
3. Dr. R. Stephen Craxton – Program Director
4. Mr. Anthony G. Noto – Mentor

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