

**Computational Modeling of Spectral Properties of Azobenzene Derivatives**

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## Abstract

Azobenzenes have been noted for their ability to undergo isomerization between the straight *trans* isomer and the bent *cis* isomer with visible light and UV irradiation, respectively. Their photochemically induced isomerization make them highly useful in optical switching devices. Time-dependent density functional theory (TDDFT) can model highly complex molecules like azobenzenes accurately, efficiently, and cost-effectively. In this study, TDDFT was used for the first time to model the absorption spectra of several azobenzene derivatives. The results show a reasonably good association between the theoretical and experimental values for the absorbance spectra of the azobenzenes. The ultimate goal is to use azobenzenes as terminal functional groups attached to nickel dithiolene metal complexes (which are well known to have an intense near IR absorbance band) to create photoswitchable absorbers with high sensitivity in the near IR region. Such systems are of special interest for liquid crystal device applications for near IR optical switching, modulation, and sensor protection applications.

## 1. Introduction

Azobenzenes are noted for the ease in which they undergo reversible photochemically induced isomerization. When the more thermodynamically stable, rod-like *trans* state is exposed to UV irradiation, it transforms into the bent *cis* state (Fig 1). Upon exposure to either visible light irradiation or elevated temperature, the less stable *cis* state is converted back into the *trans* state. This rapid and reversible isomerization makes azobenzenes useful as dopants for liquid crystal systems because of their ability to change the optical properties, such as birefringence and selective reflection, of the liquid crystal host[1].

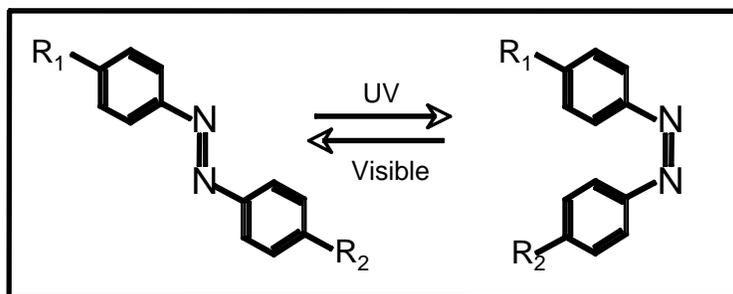


Fig. 1: Photochemically induced isomerization of azobenzenes. The terminal groups  $R_1$  and  $R_2$  can be any aliphatic, aromatic, or halogen substituent.

Nickel dithiolenes (Fig 2) are noted for properties that make them useful as liquid crystal dyes. They have intense long-wavelength absorption (600 nm to 1600 nm), a zerovalent core structure, high solubility in nonpolar solvents, and high thermal and optical stability. These properties make nickel dithiolenes good photodetectors. They are also capable of absorbing IR laser radiation and releasing short pulses upon saturation. Lastly, they are useful in IR sensor protection, tunable to absorb wavelengths from 600 nm to 1600 nm. There are several applications in photonics, telecommunications, military sensor protection, and laser systems [5].

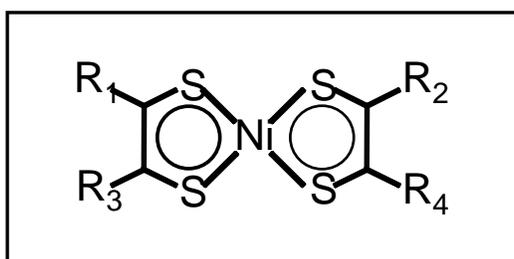


Fig. 2: Structure of nickel dithiolenes dye molecules. Different dyes are formed by substitutions of the R groups. The R groups are typically hydrogens, alkyl or alkoxy substituted phenyl groups, or alkylthio ether groups.

Nickel dithiolenes with azobenzene terminal groups, or azobenzene substituted nickel dithiolenes, have the potential to be rapid and reversible photoswitchable absorbers with high absorption in the near IR region. The nickel dithiolene core would be attached to the terminal azobenzene groups with linkage groups that promoted the extensive electron delocalization of the entire molecule. However, nickel dithiolenes are synthesized through a costly and time consuming, multi-step synthesis process. Conventional trial-and-error synthesis would be extremely inefficient considering that synthesis of azobenzene substituted nickel dithiolenes would require even greater resources and effort. Furthermore, large quantities would need to be synthesized in order to establish physical properties. Using computational chemistry, physical properties of only the most promising complexes would be predicted prior to synthesis. Rather than wasting resources through trial-and-error synthesis, computers can calculate complex structures and properties such as the absorbance spectra of molecules in hours or days.

In this study, a new computational method, time-dependent density functional theory (TDDFT) was applied to several azobenzene derivatives to successfully predict their spectral properties. Then TDDFT was applied to nickel dithiolene dyes substituted with the above-mentioned azobenzene derivatives. However, free energy convergence problems impeded with the modeling of the complex. Improper basis function selections caused the free energy to cycle in loops. The computers had trouble mapping the electron sharing between the nickel dithiolene cores and azobenzene terminal groups. Since larger molecules have diminished success and accuracy in convergence, and take a substantially longer time to compute, the azobenzene substituted nickel dithiolene dyes could not be modeled.

## 2. Previous Research

Previous attempts at modeling nickel dithiolenes have employed different computational methods for excited state calculations. Semiempirical methods use existing experimental data with approximations to fit the calculations according to known parameters. These semiempirical methods provide rapid computational time, but with reduced accuracy[2]. The Hartree-Fock method uses approximations of the electron wave function derived directly from theoretical principles. This method has better accuracy, but a longer computational time and is generally only successful in smaller molecules to which the theoretical principles better apply[3]. Lastly, the density functional theory (DFT) method bases calculations on a 3-D electron density function rather than numerous electron wave functions[4]. Though it does hold the advantage of being able to model highly complex molecules accurately, the computational time increases rapidly with structural complexity.

Time-dependent density functional theory (TDDFT) computations follow the evolution of electron density in a perturbed system as a function of time[1]. An impulse potential containing all frequencies is applied to “disturb” the molecular system while in the ground state. Frequency-dependent time evolution of the electron density is used to calculate the electronic absorbance spectra. This method provides both high computational accuracy and reduced computational times.

TDDFT has previously been employed in the modeling of the absorbance spectra of an extensive set of nickel dithiolenes for the first time by Marshall *et al* [5]. In this work, the density function was evaluated using Gaussian 03, an electronic structure program that predicts the energies, molecular structures, and vibrational frequencies of molecular systems,

along with numerous molecular properties derived from these basic computation types [6]. The theoretical values were in excellent agreement with the experimental results with a mean absolute error of only 0.034 eV, when a mean absolute error of less than 0.2 eV is considered accurate [5]. This study builds upon the modeling of nickel dithiolene dyes with TDDFT. Once the absorbance spectra of azobenzenes were modeled, TDDFT could be applied to azobenzene substituted nickel dithiolene dyes.

### 3. Methodology

The methodology of this study is shown in Fig 3. The first step involved the use of Spartan (Wavefunction Inc.), a computational chemistry software package used for generation of the molecular structure of the candidate molecules [7].

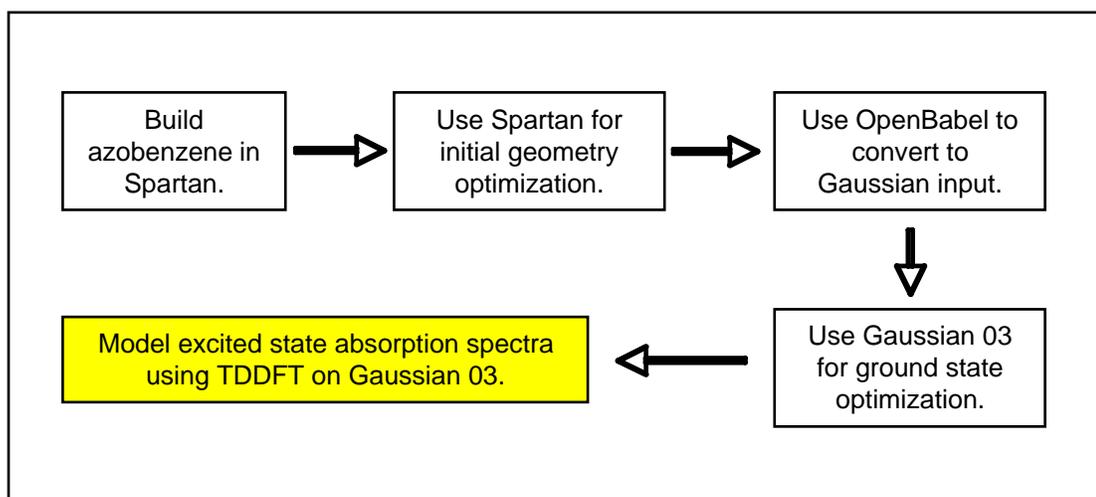


Fig. 3: Overview of the computational methodology used for the TDDFT calculations.

Spartan was also used for the initial geometry optimization, which is an important step for mapping the general structure. Spartan provides Cartesian coordinates for the approximate structures based on the bond lengths and angles of existing molecules. OpenBabel, a

chemical language translator, converted the Cartesian coordinates generated by Spartan into a Gaussian 03 input file. Using Gaussian 03, the ground states were first optimized by DFT. DFT optimizes the geometry by varying the coefficients of a selected basis set and the atom coordinates until a minimum energy is reached. Then the excited state absorption spectra were modeled using TDDFT. With TDDFT, an impulse potential containing all frequencies disturbs the molecular ground state so the absorption spectrum can be generated.

In order to accurately model the ground state and excited state absorption spectra, appropriate basis sets needed to be chosen. Basis sets determine the linear combination of spatially dependent elemental functions. In previous work it was established that out of the eighty-one Gaussian03 basis sets 6-311G(3d, 2p) was the most appropriate for the ground state geometry optimization of nickel dithiolenes [8]. This same basis set was applied to the azobenzene derivatives in hopes that it would later model azobenzene substituted nickel dithiolenes. For the excited state absorption spectra, the 6-311+G(d, 2p) basis set was chosen. Both the DFT and TDDFT calculations modeled the azobenzenes in cyclohexane solutions.

#### **4. Maximum Absorbance Wavelengths**

This study tested the accuracy to which TDDFT predicts the spectral properties of azobenzene derivatives. Five derivatives were chosen based on the experimental study conducted by Rau, Iacobescu and Meltzer [9]. The maximum absorbance wavelengths calculated by TDDFT were compared against experimental values (see Table 1). Each azobenzene derivative provided three maximum absorbance wavelengths. A reasonably good correlation was obtained between the theoretical and experimental values.

No.	Name	Experimental [9]	Theory
1	6"-methyl-4'-nitro-4-(N-phenylacetamidoxy)-azobenzene	249	336
		369	383
		422	494
2	6"-methyl-4'-cyano-4-(N-phenylacetamidoxy)-azobenzene	249	316
		353	368
		414	483
3	6"-methyl-4'-trifluoromethyl-4-(N-phenylacetamidoxy)-azobenzene	286	303
		349	356
		406	475
4	6"-methyl-4'-chloro-4-(N-phenylacetamidoxy)-azobenzene	247	294
		348	358
		402	465
5	4-(o-methyl-N-phenylacetamidoxy)-4'-[p-methyl-phenylazo] biphenyl	262	312
		332	388
		412	476

*All absorptions calculated using 6-311G(d,2p)*

Table 1: The maximum absorbance wavelengths calculated by TDDFT compared against experimental values from the literature (Ref 9).

When plotted against one another (Fig. 4), a Pearson correlation coefficient of  $R^2 = 0.95$  was found. When the wavelengths were converted into eV, there was a mean absolute error of 0.48 eV. An error of 0.4 eV is generally acceptable for azobenzene derivatives.

### 5. Free Energy Convergence Problems

Several azobenzene substituted nickel dithiolenes were also tested using the above-mentioned basis sets. However, the attempts to model the molecules using TDDFT were unsuccessful. The free energy of the molecules began to loop infinitely. This was attributed to the incorrect choice of basis sets. A large combination of spatially dependent elementary

functions substantially increases the computation time, and often leads no energy convergence. But too few functions would lead to poor accuracy.

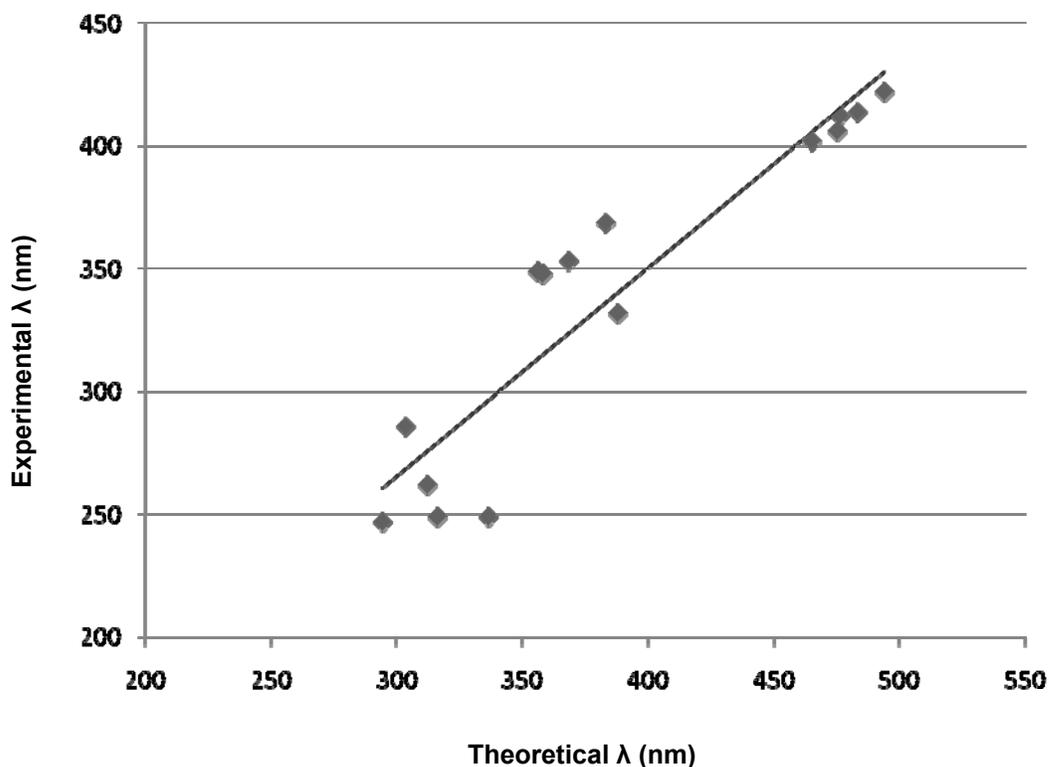


Fig. 4: Theoretical absorbance wavelengths calculated by TDDFT for the five substituted azobenzenes plotted against the experimental data for the same compounds. A Pearson correlation coefficient of  $R^2 = 0.95$  was found for this data.

Rather than discard basis sets marked as having the least convergence error, the azobenzene substituted nickel dithiolenes were modeled in a gaseous phase rather than in cyclohexane. This also resulted in free energy convergence problems that were attributed to the complexity of the azobenzene terminal groups. Computations ran between three to five days for each molecule. Although this is the typical computation time for nickel dithiolenes, it proved extremely inefficient considering that all molecules failed.

## 6. Discussion/Conclusions

The spectral properties of photochemically switchable azobenzene derivatives have been accurately modeled [9]. TDDFT was applied to the design of near IR photoswitchable nickel dithiolene dyes with terminal azobenzene groups. TDDFT can model highly complex molecules accurately, efficiently, and cost-effectively. Free energy convergence problems prevented modeling of both the core and the terminal groups at the same time. The absorbance spectra of the azobenzene derivatives were modeled independently of the dithiolene core. A reasonably good correlation was obtained between absorbance values calculated by TDDFT and experimental data for five azobenzene derivatives. Further research would entail finding appropriate basis sets to model the excited states for azobenzene substituted nickel dithiolene dyes.

## 7. Acknowledgements

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