

Computational Modeling of Optically Switchable Azobenzenes

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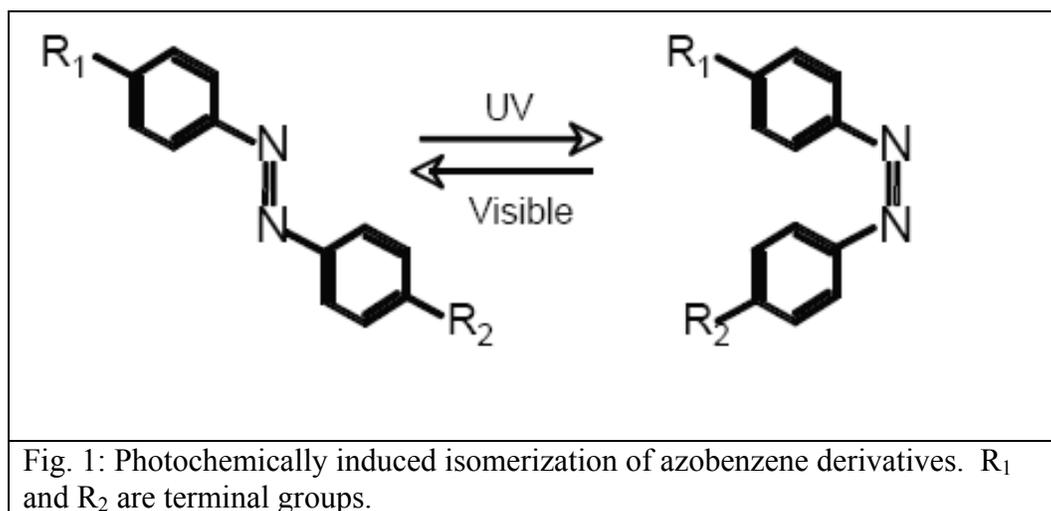
Abstract

Azobenzenes have a unique ability to undergo reversible isomerization between two geometrical isomer forms (the straight *trans* and the bent *cis*) when irradiated with the correct wavelength of UV or visible light. These systems are of interest because of their numerous potential applications as reversible photoswitchable absorbers. The azobenzenes can also be used as terminal groups in nickel dithiolene metal complexes, which have applications as photoswitchable absorbers in the near infrared region. To reduce the need to synthesize a large number of materials in order to establish structure-property relationships, computational chemistry was used to model the absorption spectra of these materials as a function of molecular structure. Time-dependent density functional theory (TDDFT) was used in this study to model the absorption spectra of azobenzene derivatives, and the process was refined to produce results closer to observed spectra than previous research. An alternative method, Zerner's intermediate neglect of differential overlap (ZINDO), was also investigated and the results were compared with those obtained with TDDFT. The TDDFT approach was found to give consistently better agreement with experimental data than the semiempirical ZINDO approach.

Introduction

Azobenzenes are noted for their ability to undergo photochemically induced isomerization. When irradiated with the correct wavelength of UV light, the rod-like *trans* isomer transforms into the bent *cis* isomer. Likewise, when irradiated with the correct wavelength of visible light, the bent *cis* isomer transforms into the rod-like *trans* isomer (Figure 1). Because of this rapid and reversible isomerization between *cis*-azobenzene and *trans*-azobenzene, azobenzene derivatives can change the optical

properties of liquid crystal “host” systems (e.g., birefringence and dichroism) when they are added to these materials as dye dopants, or “guests”.¹ Also, as the distance between the para carbon atoms in azobenzene is 9.0 Å in the trans isomer and only 5.5 Å in the cis isomer, physical properties can be changed.² Because of these chemical and physical changes, azobenzene derivatives have numerous applications in liquid crystal systems and digital data storage.^{2,3}



Nickel dithiolenes are noted for their intense absorption over a wide range of near-IR wavelengths between 600 nm and 1600 nm. The nickel dithiolene dye consists of a zerovalent planar core with dithiolene rings surrounding a nickel atom (Figure 2). Because of the zerovalent core, nickel dithiolene dyes have high solubility in nonpolar solvents such as liquid crystal hosts. As some metal dithiolenes have inherent liquid crystal phases, they are easily dissolvable in liquid crystal hosts in relatively large quantities of up to 10 wt%.¹⁶

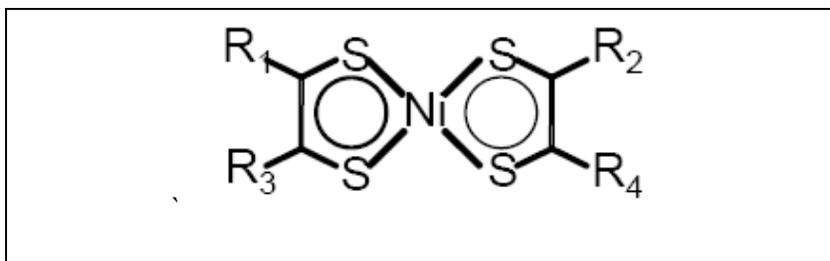


Fig. 2: Nickel dithiolene metal complex. R_1 - R_4 are terminal groups.

Due to these properties, nickel dithiolene metal complexes have numerous applications. For example, they are useful as photodetectors in fiber-optic systems at wavelengths of 1300 nm and 1550 nm, as Q-switching saturable absorbers in IR lasers at wavelengths between 950 nm and 1100 nm, and as IR sensor protection for the military. When the terminal groups are substituted with azobenzene derivatives, nickel dithiolenes are capable of producing large photochemically-induced changes in the optical properties of liquid crystal hosts when added as a dopant.⁴

However, nickel dithiolene metal complexes are expensive and time-intensive to produce, and as such, a trial-and-error procedure is extremely inefficient. Large numbers of these materials would need to be produced to establish structure-property relationships. Computational chemistry can predict these properties with minimal sacrifice in accuracy and immense savings in time and expense. Rather than synthesize large numbers of molecules to establish structure-property relationships, computational chemistry allows only the most promising molecules to be synthesized, thereby saving resources.

In this study, computational chemistry methods were refined to produce more accurate results than could be obtained previously. Two computational methods were used to predict the spectral properties of azobenzenes: time-dependent density functional theory (TDDFT) and Zerner's intermediate neglect of differential overlap (ZINDO), a

semi-empirical method. The TDDFT approach was found to give consistently more accurate results than ZINDO. The density functional theory (DFT) method B3LYP was likewise found to be consistently more accurate than the DFT method PME1PME when used with TDDFT. Several azobenzene derivatives were modeled more accurately than in previous research, but when TDDFT was applied to larger molecules, computational time increased. When TDDFT was applied to nickel dithiolene metal complexes substituted with azobenzene terminal groups, small basis sets sacrificed too much accuracy, while large basis sets caused free energy convergence errors, making it impossible to map the electron distribution.

2. Previous Research

Computational chemistry has previously been used to predict the properties of other molecules. The methods for excited state computation can be separated into three general categories: (1) ab initio methods such as Hartree-Fock and single configuration interaction (CIS); (2) semi-empirical methods such as ZINDO, and (3) DFT and TDDFT.

Ab initio methods do not use any empirical data and base calculations entirely on physical principles.⁵ As such, they are generally the most accurate methods, but have the highest computational cost, which grows exponentially with increasing complexity of molecular structure. The Hartree-Fock method is the most basic ab initio method. Electron orbitals are expressed as one-electron functions, and the multi-electron calculation is based on the sum of the single-electron functions. The Hartree-Fock method does not account for Coulombic electron repulsion but instead includes the mean field in the calculation. Because of this, the Hartree-Fock method can only give energy approximations greater than or equal to energy approximations made by the ground state

wave function.⁶ Post-Hartree-Fock ab initio methods start with the Hartree-Fock method and then proceed to correct for the Coulombic electron repulsion.

Semi-empirical methods use some empirical data to estimate unknown parameters, thereby decreasing computational cost and accuracy. Semi-empirical methods are based on Hartree-Fock methods, but some parameters are approximated or completely omitted. To correct for these approximations, semi-empirical methods fit results to best agree with empirical data or results obtained from ab initio calculations. Semi-empirical methods such as ZINDO are limited in accuracy by how similar the molecule at hand is to the molecule in the database used to parameterize the results. The ZINDO method is an extension of Intermediate Neglect of Differential Overlap (INDO) as it can cover a wider range on the periodic table.⁷

Density functional theory is a recent method that uses a 3-D electron density function rather than a many-electron wave function (Figure 3).⁸ The TDDFT modification maps the development of a perturbed system over time with density functions. The molecular system is perturbed with an impulse potential containing all frequencies, and the maximum absorption wavelengths can subsequently be computed.

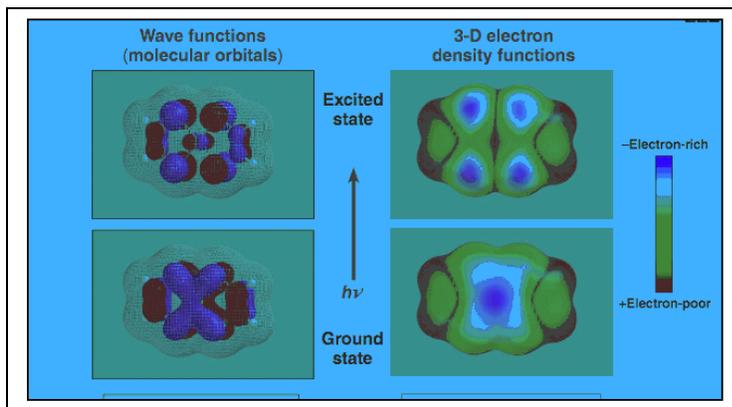


Fig. 3: Wave functions vs. density functions. Density functions require a significantly lower computational cost.

A previous study used TDDFT to predict the absorption spectra of azobenzenes, and the results were relatively accurate, with a mean absolute error of 47.1 nm.⁹ In this study we investigated alternative computational methods and refined the process used in earlier work to obtain more accurate results.

3. Methodology

All TDDFT and ground state energy calculations performed in this study used the Gaussian03 program¹⁰, but other programs were also used in the process. This process is detailed in Figure 4.

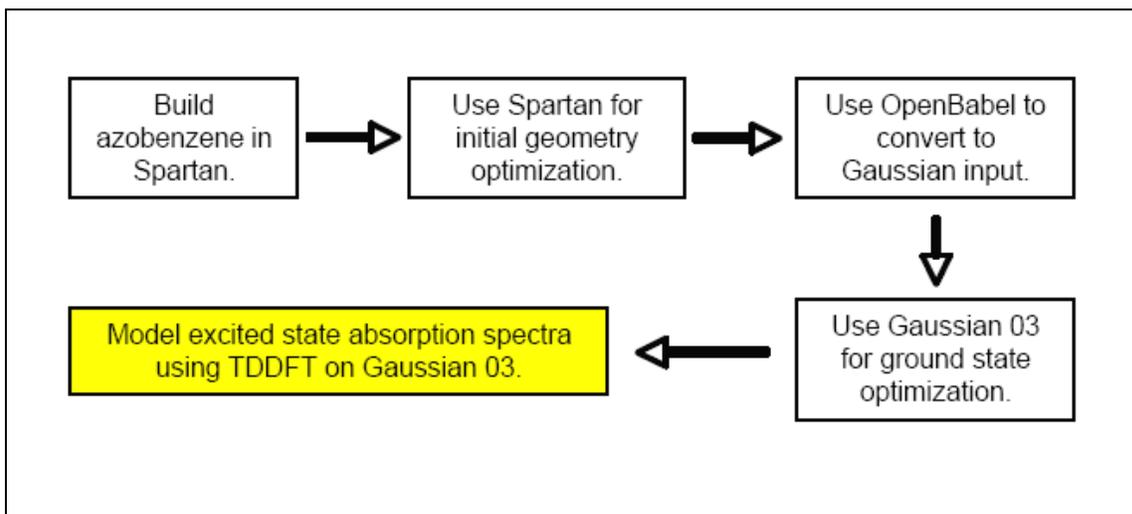


Fig. 4: Methodology used to predict excited state absorption spectra.

Spartan is a computational chemistry software package that allows for the visualization of molecules and initial geometry optimization. Spartan generates approximate Cartesian coordinates that can be converted to a Gaussian input file¹¹ using OpenBabel, a chemical language translator. The appropriate input is added to the newly converted input file, and the Gaussian03 program performs a more accurate geometry

optimization using DFT. Finally, these new coordinates are used as input for TDDFT in Gaussian03, which models the excited state absorption spectra.

In deciding which basis set should be used, previous studies were referenced.⁴ A previous study by Marshall *et al.* determined that the 6-311G(3d, 2p) basis set was the most appropriate for the ground state geometry optimization of nickel dithiolenes, and as such, this study used the same basis set for the ground state geometry optimization of azobenzenes. For modeling excited-state absorption spectra, the same basis set was used in this study as in a previous study⁹ for purposes of comparison. This is the 6-311+G(3d, 2p) basis set, in which the “+” notation indicates the addition of single diffuse functions to increase accuracy in modeling electrons farther from the nuclei of nonhydrogen atoms.

4. Selecting a DFT Method

There are three broad categories of standalone DFT methods, which make use of combinations of exchange and correlation functionals: (1) exchange-only; (2) pure; and (3) hybrid functionals. Exchange-only and pure functionals are based solely on Hartree-Fock exchange and DFT exchange-correlation, respectively. Hybrid functionals, however, are mixtures of Hartree-Fock exchange and DFT exchange-correlation. Two different hybrid DFT methods were considered for this study. PBE1PBE uses 25% electron-exchange and 75% electron-correlation weighting. PBE1PBE was used in a previous study to predict absorption maxima with a mean deviation of 47.1 nm from accepted values. An alternative DFT method, B3LYP, was considered. B3LYP uses the LYP expression for non-local correlation and the VWN functional III for local correlation.¹⁰ Five azobenzenes were selected based on a study conducted by Rau, Iacobescu and Meltzer, each of which produced three absorption maxima λ_{\max} ¹². The

calculated absorption maxima in this study, which used B3LYP, and in a previous study, which used PBE1PBE, are shown in Table 1 together with the experimental values and the molecular structures used.

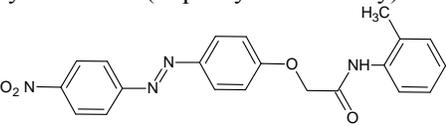
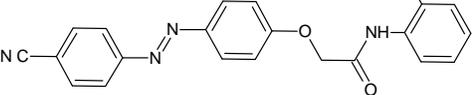
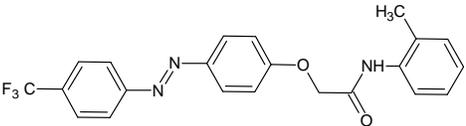
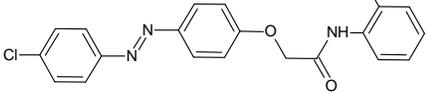
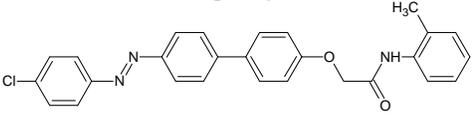
No.	Molecule	Experimental λ_{\max} (nm) ¹²	Calculated λ_{\max} (nm) (B3LYP)	Calculated λ_{\max} (nm) (PBE1PBE) ⁹
1	6''-methyl-4'-nitro-4-(N-phenylacetamidoxy)-azobenzene 	249	380	336
		369	427	383
		422	448	494
2	6''-methyl-4'-cyano-4-(N-phenylacetamidoxy)-azobenzene 	249	346	316
		353	362	368
		414	420	483
3	6''-methyl-4'-trifluoromethyl-4-(N-phenylacetamidoxy)-azobenzene 	286	341	303
		349	352	356
		406	417	475
4	6''-methyl-4'-chloro-4-(N-phenylacetamidoxy)-azobenzene 	247	333	294
		348	342	358
		402	414	465
5	4-(o-methyl-N-phenylacetamidoxy)-4'-[p-methyl-phenylazo] biphenyl 	262	313	312
		332	347	388
		412	415	476

Table 1: Wavelengths of three absorbance maxima for each of the five azobenzene derivatives modeled.

It is seen from Table 1 that the B3LYP DFT method is substantially more accurate than PBE1PBE for the longest wavelength and more accurate at the middle wavelength in four out of the five cases. At the shortest wavelength PBE1PBE comes close to the experimental value, but the errors are large in both models. Since the two longer-wavelength maxima are of greater practical interest, all further calculations in this study used B3LYP as the DFT method with TDDFT. Once sufficiently accurate results were obtained, other computational methods could be investigated, as could modeling nickel dithiolene dyes with azobenzenes substituted as terminal groups.

5. TDDFT and ZINDO

Two methods for determining the maximum absorption wavelengths were investigated in this study. As all experimental absorption maxima were for azobenzene derivatives in solution, the PCM model was used to account for solvent effects in TDDFT calculations. The PCM model separates the calculation into two parts: a solvent part and a solute part.¹³ Because this correction was incompatible with ZINDO as implemented in Gaussian 03, it was left out of ZINDO calculations. Table 2 shows the absorption maxima of ten azobenzenes predicted with both ZINDO and TDDFT. Overall, the TDDFT method was found to be consistently more accurate, being closer to experiment in seven out of the ten cases, while ZINDO gave better results for compounds 5, 9, and 10. For this comparison, only the absolute absorption maxima were considered, as experimental data for local maxima was not known for all molecules. However, experimental data of the absolute absorption maxima existed from a number of sources.^{12,14,15}

No	Structure	Accepted λ_{\max} (nm) ^{12,14,15}	Calculated λ_{\max} (nm) (TDDFT)	Calculated λ_{\max} (nm) (ZINDO)
1		369	427	446
2		353	362	338
3		349	352	341
4		348	342	333
5		332	347	336
6		415	467	311
7		468	484	359
8		486	464	450
9		342	416	341
10		420	448	445

Table 2: Absorbance maxima of ten azobenzene derivatives. Overall, TDDFT consistently predicts absorption maxima more accurately than ZINDO. (The first five structures are the same as in Table 1)

6. Free Energy Convergence Problems

While the main purpose of this study was to improve the accuracy to which azobenzenes could be modeled, nickel dithiolene metal complexes substituted with azobenzene terminal groups were nonetheless further investigated. However these complexes were never successfully modeled to any degree of accuracy. Calculations took several days to complete for each molecule, and the free energy looped infinitely and failed to converge. Because larger basis sets increase the computational cost and lead to convergence failures, smaller basis sets were used. Even with the smallest basis sets, calculations rarely converged, and results were never accurate.

7. Discussion/Conclusions

The TDDFT method can accurately, efficiently, and cost-effectively predict the spectral properties of azobenzene derivatives. TDDFT predictions with the B3LYP DFT method are more accurate than those with the PBE1PBE DFT method, and TDDFT can predict absorption maxima more accurately than ZINDO, with minimal computational cost. However, free energy convergence problems impeded the modeling of nickel dithiolene metal complexes substituted with azobenzene derivatives. Future research would include modeling these complexes using the Gaussian09 program. Also, Gaussian09 and other computational chemistry packages could be investigated for ZINDO's compatibility with the PCM correction for modeling molecules in solution. Thus, ZINDO could also be explored as a possible, more cost-efficient alternative to TDDFT in nickel dithiolene metal complexes.

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