Modeling Absorption Spectra of Optically Switchable Azobenzenes

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Abstract

Azobenzenes have the unique ability to undergo reversible isomerization between two geometrical isomers (the straight *trans* form and the bent *cis*) when exposed to certain wavelengths of light, which provide energy for the change. Thus, when embedded in liquid crystal matrices, azobenzene derivatives can function as optically triggered switches regulating, for example, membrane permeability to gases. An optimal azobenzene for this application would have an energy barrier low enough to facilitate changes from *trans* to *cis* and back again, but high enough so that such changes would remain stable. In order to identify such suitable azobenzenes, a series of azobenzene derivatives were modeled using computer software. The resulting data were compared, and it was found that nitro groups lowered both thermal and photochemical barriers, while aminoester groups increased the thermal relaxation barriers. Thus, it seems feasible to engineer azobenzene derivatives specifically for use as optical switches in these doped membranes.

Introduction

Azobenzene and its derivatives exhibit a unique ability to undergo isomerization when exposed to energy in the form of light. When subjected to irradiation with the correct wavelength of UV light, the straight *trans* configuration will transmute into the bent *cis* configuration; the reverse is true upon exposure to visible light (Fig. 1). This property, along with the concurrent rapid, easily reversible changes it comes with, allows azobenzenes to change the optical properties of liquid crystal systems to which they are added as dopants, or "guests".[1] Azobenzene isomerization can change physical properties as well: the *trans* isomer's para terminal groups are separated by 9.0 Å, while the same atoms in the *cis* isomer are only 5.5 Å apart.[2] Thus, azobenzene and its derivatives have many applications in regards to both liquid crystal systems and digital data storage.

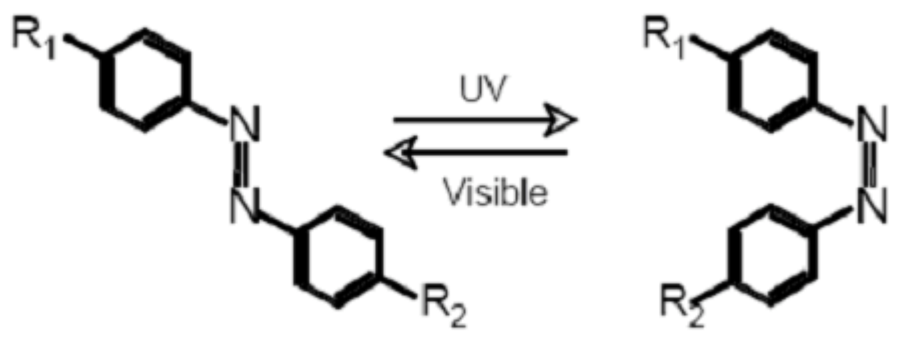


Fig. 1: Photochemically induced isomerization of azobenzene derivatives. R_1 and R_2 are terminal groups. The *trans* configuration is shown on the left; the *cis* configuration on the right.

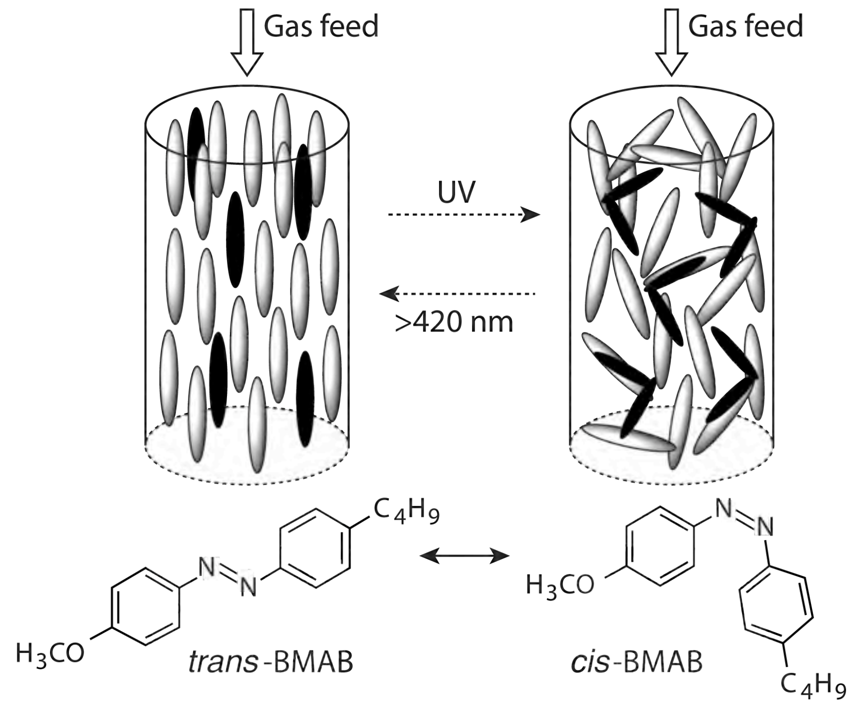


Fig. 2: Isomerization reaction of an azobenzene derivative disrupts an ordered liquid crystal matrix (on left) and reduces the permeability of its host membrane to gases.

Currently, much research at the Laboratory for Laser Energetics has been directed towards the use of these azobenzenes as optical switching devices in conjunction with liquid crystal membranes. Such membranes are constructed with pores filled with azobenzene-doped liquid crystal matrices. Such matrices can act as photochemical switches that moderate the permeability of their host membrane to gases (Fig. 2). In the trans configuration, the matrix is well ordered, and thus, gases can easily pass through the membrane. Under UV light, however, the transition from the *trans* isomer to the *cis* isomer disrupts the matrix, and membrane permeability drops dramatically[3].

These optically switchable membranes have a variety of applications in optics and photonics, but require azobenzene molecules with specific properties. The desired azobenzenes must have energy barriers low enough to facilitate change from the *trans* to the *cis* configuration (C to A, Fig. 3), but high enough to minimize spontaneous relaxation

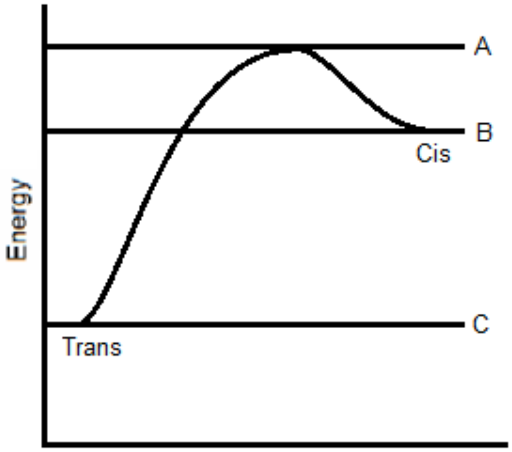


Fig. 3: Energy barriers in azobenzenes. To switch from the *trans* state to the *cis*, the isomerization barrier (C to A) must be overcome; as this requires UV light, this is called the photochemical barrier. Because the *cis* state is at a higher energy level than the *trans*, the reverse energy barrier (B to A) is lower, and can be overcome by visible light or thermal motion – hence, the name thermal barrier.

from the *cis* isomer to the *trans* due to thermal excitation (B to A, Fig. 3; this is more important for applications at higher temperatures). This project used computational chemistry to model a series of azobenzenes in an attempt to determine whether certain functional groups reliably alter energy barriers, and if so, what their effects are.

To do this computational modeling, the programs Spartan (Wavefunction, Inc) and Gaussian03 (Gaussian, Inc) were used. Spartan was used both as a molecular mechanical modeling tool and to calculate thermal relaxation barriers from the *cis* state to the *trans* state. Gaussian03 used molecular mechanical output from Spartan, along with its DFT (density-functional theory) capability, to calculate the photochemical barriers from the *trans* state to the *cis* state. The results indicated that nitro and dimethyl amino groups lowered both thermal and photochemical energy barriers, while aminoester groups raised thermal energy barriers (no significant effects on photochemical barriers).

Previous Research

Computational chemistry is a well-established method of predicting the properties of molecules, without the need to synthesize and evaluate them in order to determine their suitability for applications. There are three main categories of excited state computations: *ab initio* methods, such as Hartree-Fock and single-configuration interaction (CIS), semi-empirical methods, such as ZINDO, and DFT (Density-Functional Theory) and TDDFT (Time-Dependent DFT). Density-functional theory and its derivatives are recent developments that use 3-D electron density functions in their calculations rather than a many-electron wave function (Fig. 4).[6] The TDDFT modification to this method uses density functions to map the development of a perturbed system over time. The molecular system is perturbed with a light impulse containing all frequencies, and the maximum absorption wavelengths can subsequently be computed.

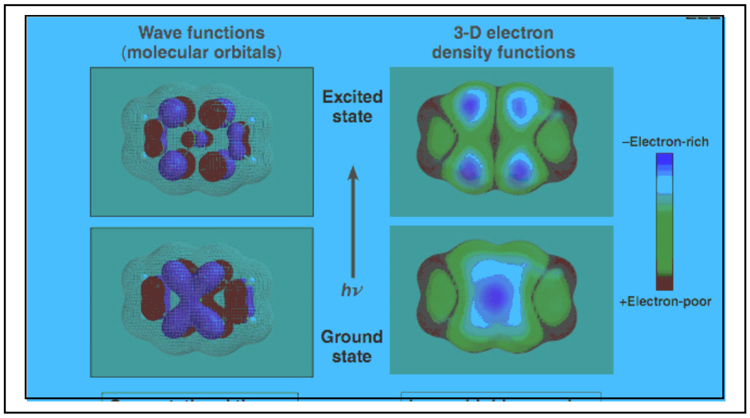


Fig. 4: Wave functions vs. density functions. Density functions require a significantly lower computational cost.

Several previous studies have been done through the high school summer research program at the Laboratory for Laser Energetics, focusing on optimal methods of excited state computations. One previous study showed that TDDFT was a relatively accurate tool for measuring absorption spectra of azobenzenes, reporting a mean absolute error of 47.1 nm.[7] A later study showed that TDDFT was more accurate than ZINDO when modeling azobenzene derivatives.[8]

Methodology

TDDFT and ground state energy calculations for the *trans* state were performed using Gaussian03[9], and ground state calculations for the *cis* state were performed using Spartan (Wavefunction, Inc). The process used in these calculations is detailed in Fig. 5.

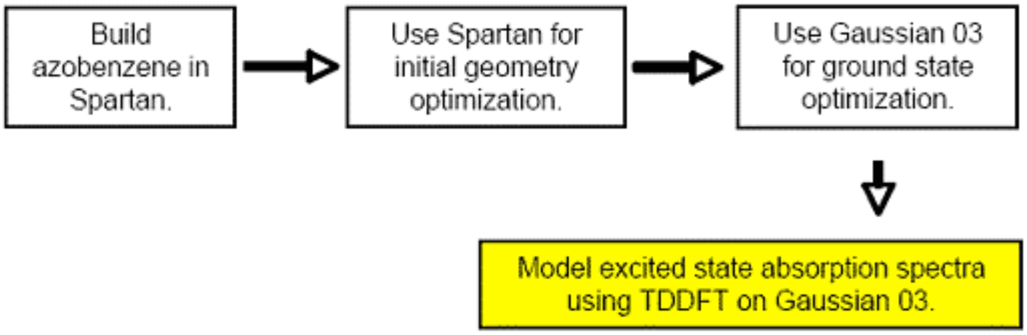


Fig. 5: Methodology used to predict excited state absorption spectra.

Spartan is a computational chemistry software package that includes tools for the visualization of molecules, as well as initial geometry optimizations. This program generates approximate Cartesian coordinates that can be subsequently fed into Gaussian03 for a more accurate geometry optimization through the use of DFT. These coordinates are then used as Gaussian03 input files themselves; the program uses the coordinates to calculate the excited state absorption spectra using TDDFT.

Previous studies were referenced in order to choose a basis set. A previous study by Marshall *et al*. determined that the 6-311G(3d, 2p) basis set was most appropriate for ground state geometry optimizations of azobenzene derivatives; therefore, this basis set was used for ground state optimization during this study.[4] Several other studies used a different basis set [6-311G+(3d, 2p), the "+" meaning that single diffuse functions have been added in order to increase accuracy] to model excited-state absorption spectra; thus, for purposes of comparison, this basis set was used in this study as well.

There are three broad categories of DFT methods, which use combinations of exchange and correlation functionals: exchange-only, pure, and hybrid functionals. Exchange-only and pure functionals use solely Hartree-Fock and DFT exchange-correlation, respectively; meanwhile, hybrid functionals are mixtures of Hartree-Fock and DFT exchange-correlation. The hybrid method B3LYP, which uses the LYP (Lee, Yang, Parr) expression for non-local correlation and VWN (Vosko, Wilk, Nusair) functional III for local correlation, was determined by a previous study to be the best method for modeling azobenzene derivatives, and as such, this method was used here.[8, 9]

The series of azobenzenes examined was based upon previous research done by Wang[8] and Marshall *et al.*[3] The series consisted of nine azobenzenes studied by Wang, and two studied by Marshall *et al.* The full series can be seen in Table 1.[3, 8] A full list of thermal and photochemical barriers is given in Table 2.

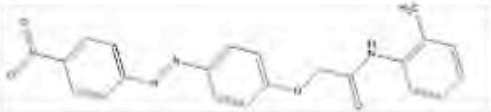
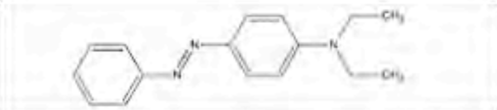
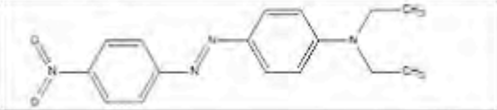
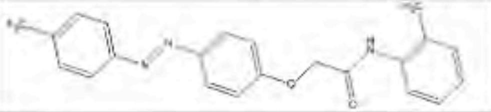
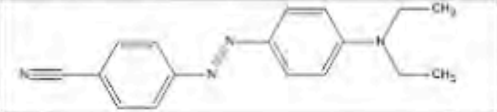
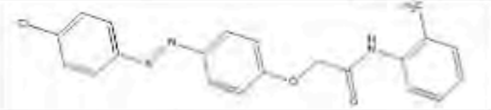
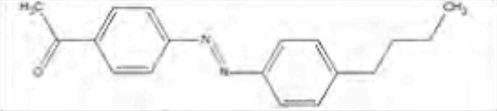
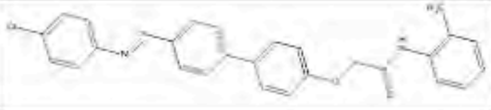
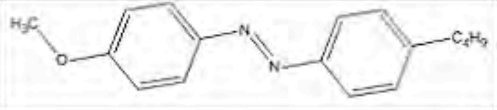
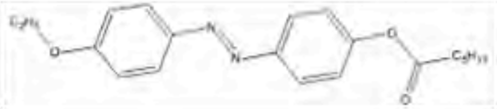
1		**6**	
2		**7**	
3		**8**	
4		**9**	
5		**10**	
		11	

Table 1. Azobenzenes 1-9 were previously examined by Wang, and azobenzenes 10 and 11 were previously used by Marshall *et al.*

Functional Group 1	Functional Group 2	*Cis-trans* thermal barrier (kcal/mol)	*Trans-cis* photochemical barrier (eV)
None	None	14.276	4.862
None	-DA	14.213	2.923
-CN	-DA	13.959	2.715
-NO_2	-DA	12.944	2.144
-NO_2	-AE	17.284	2.831
-CN	-AE	21.221	3.403
-CF_3	-AE	21.142	3.318
-Cl	-AE	21.169	3.333
-Cl	-C_6H_4-AE	21.012	3.093
-$COCH_3$	-C_4H_9	13.986	3.361
-OCH_3	-C_4H_9	14.105	3.527
-OC_2H_5	-$OCOC_5H_{11}$	14.138	3.475

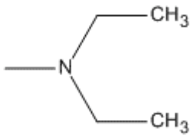
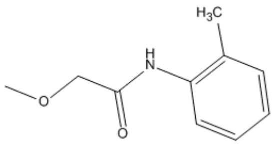
Functional group	Assigned code
Dimethyl amino  	DA
Aminoester  	AE

Table 2: *Cis-trans* thermal barriers and *trans-cis* photochemical barriers for the tested series of azobenzenes. The first row denotes an unmodified azobenzene (no functional groups); the ordering of functional groups is arbitrary.

Results

It was found that nitro groups lowered both thermal and photochemical energy barriers, while aminoester groups raised thermal energy barriers. A combination of nitro and aminoester groups produced an optimal result, raising the thermal barrier while simultaneously lowering the photochemical barrier. For comparison purposes, Table 2 also shows the base values for an unmodified azobenzene.

From the data collected, it can be seen that aminoester groups, dimethyl amino groups, and nitro groups had significant, systematic effects on energy barriers between states. Of these, aminoester groups had the greatest effect on thermal barriers, raising them on average by 6.445 kcal/mol. Nitro groups had the greatest effect on photochemical barriers, lowering them on average by 0.751 eV. These results are summarized in Table 3.

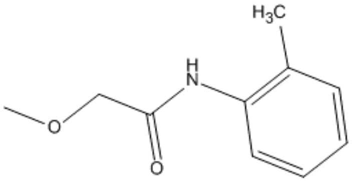
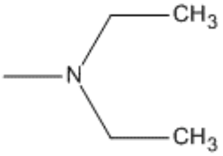
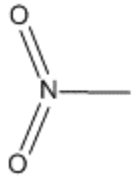
Functional group	*Cis-trans* thermal barrier difference (avg. with − avg. without	*Trans-cis* photochemical barrier difference (avg. with − avg. without)
Aminoester group 	6.445 kcal/mol, σ=1.71	0.172 eV, σ=0.53
Dimethyl amino group 	-4.235 kcal/mol, σ=3.30	-0.699 eV, σ=0.39
Nitro group 	-2.092 kcal/mol, σ=4.11	-0.751 eV, σ=0.43

Table 3: Average thermal and photochemical barrier differences for different functional groups.

For membrane doping, azobenzenes with low photochemical barriers but high thermal barriers are optimal. Nitro groups satisfy the first requirement, as azobenzenes containing them were shown to have greatly lower photochemical barriers, but as they also lowered thermal barriers, they are alone insufficient for the creation of azobenzenes for membrane doping. Aminoester groups show the same weakness: they raise thermal barriers significantly, but also slightly raise photochemical barriers. However, one azobenzene tested included both functional groups, and showed itself to be the best azobenzene of the series: not only did it raise the thermal barrier (from a base of 14.276 kcal/mol to 17.284 kcal/mol), but it also lowered photochemical barriers (from 4.862 eV to 2.831 eV) as compared to unmodified azobenzene.

Discussion/Conclusion

This study indicates that various functional groups can influence energy barriers in predictable ways. Specifically, azobenzenes modified with aminoester groups exhibit higher thermal barriers, while those modified with dimethyl amino and nitro groups had lower photochemical barriers (these two functional groups also lowered thermal barriers). An optimal azobenzene was seen to possess both an aminoester and a nitro group. This suggests that azobenzene dopants may in future be predictably developed and synthesized to fit certain needs. However, this is only a very preliminary study of feasibility. Future research would entail both selecting azobenzene series specifically by functional group, and detailed analysis using more computational chemistry packages. Also, Spartan and Gaussian03 often provided conflicting geometry optimizations when calculating values for *cis*-phase azobenzene derivatives. Because of this, future work may also focus on these inaccuracies, along with their resolution.

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