# Calculated UV/VIS Spectra of Two Geometric Isomers

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# Comparing calculated electronic spectra of two similar molecules

- In this example, we are looking at two isomers of a modified azobenzene.
- The azobenzene modification is a two-carbon atom bridge between the two phenyl groups (ortho to where the azo group bonds).
- We then take the cis and trans configurations (of the azo group double bonded nitrogen's) and perform a geometry optimization of the two  molecules.
- This is then followed by a TDDFT calculation to obtain the first 6 excited states of the molecules and the resulting estimated electronic spectra.
- The DFT method used is  the B3LYP functional with the triple zeta basis set def2-TZVP.
- The purpose of this is see if we can calculate the excited state energy levels,and get at least similar results to experiment.
- The intent is to demonstrate that we can do similar calculations on molecular qubit candidate molecules to provide their electronic structure and behavior.

# Original References

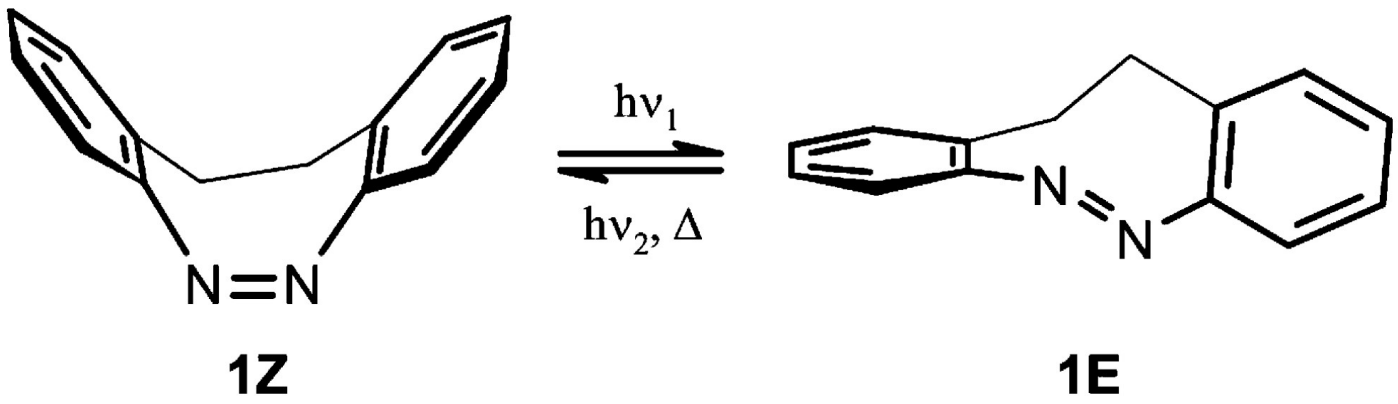
- The experimental work on the two isomers was reported in

  **J. AM. CHEM. SOC.** 9 VOL. 131, NO. 43, 2009 **15595**

- The paper title was "**Highly Efficient Reversible *Z*-*E* Photoisomerization of a Bridged Azobenzene with Visible Light through Resolved S1(n$\pi^*$) Absorption Bands**"
- These molecules are of interest in that they can potentially act as a two position molecular photo-switch. They are not a molecular qubit. But this example illustrates how we can calculate properties that can be of interest in molecular qubits also.
- The link https://www.orcasoftware.de/tutorials_orca/spec/UVVis.html# will take you to a page where they use ORCA to do the spectral calculation usng the same DFT functional and basis set as used here employing Spartan-20. They also additionally do the exercise with a higher level of DFT than used here.

# Isomer Pair as a Molecular Photoswitch

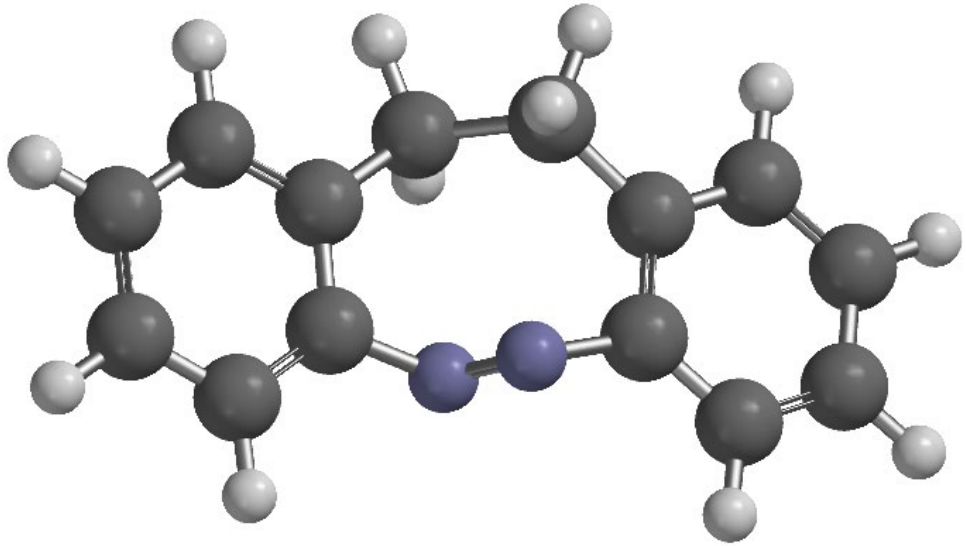
***Scheme 1***




**1Z** **1E**


Photon 1 excites the Z-isomer to the E-isomer configuration.
Photon 2 can convert E-isomer to the lower energy state Z-isomer.
The E-isomer can also revert to the lower energy Z-isomer thermally.
Experimentally, the two isomers are observed to have two different colors- yellow and red.

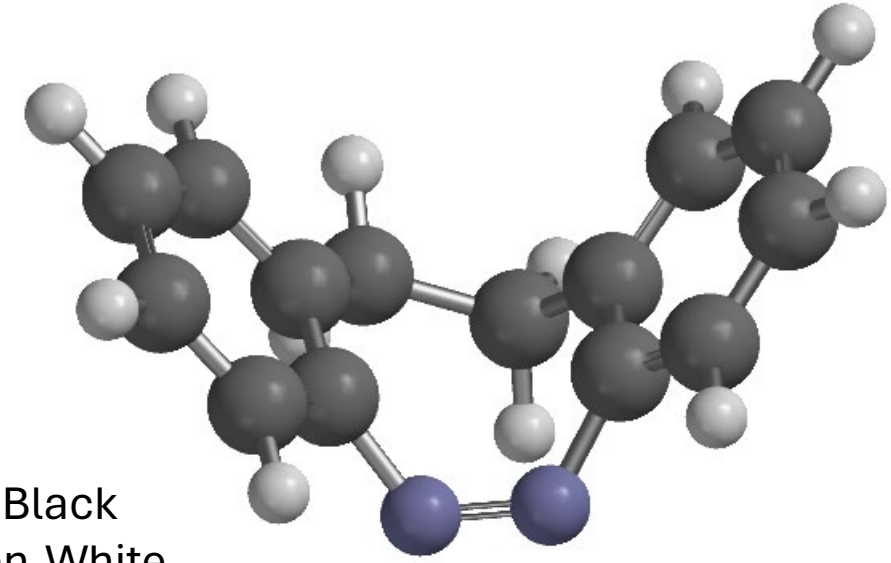
# E and Z Isomer Molecular Structure Models



E-Isomer (trans)

Carbon-Black
Hydrogen-White
Nitrogen-Blue

Models generated using Spartan-20



Z-Isomer (cis)

# Geometry Optimization Job

- Processing $rem in input file
- … JOBTYPE OPT
- … TIDY_SYM TRUE
- … EXCHANGE B3LYP
- … CORRELATION none (built-in)
- … BASIS DEF2-TZVP
- … THRESH 13
- … SMALL_PROD_XCMAT 10

… MAXSCF 500
… VARTHRESH 2 (default DFT)
… INCDFT TRUE (default DFT)
… GEOM_OPT_HESSIAN READ (main opt)
… EXTERNAL_HESSIAN 1
… GUI GUI_SPARTAN
… TERSE_OUTPUT TRUE
NAlpha2: 110
NElect 110
Mult 1

# TDDFT/TDA Calculation

- Direct TDDFT/TDA calculation will be performed
- Exchange: 0.2000 Hartree-Fock + 0.0800 Slater + 0.7200 B88
- Correlation: 0.1900 VWN1RPA + 0.8100 LYP
- Using SG-1 standard quadrature grid
- Singlet excitation energies requested
- CIS energy converged when residual is below 10e- 6

# TDDFT Excitation Energies (Z-Isomer)

Excited state 1:
Excitation energy (eV) = 2.8583
Wavelength (nm) = 433.7670
Total energy for state 1: -
-650.29039449 au
Multiplicity: Singlet
Trans. Mom.:
0.0611 X 0.2149 Y -0.0969 Z
Strength : 0.0041530359
X: D( 55) --> V( 1) amplitude = 0.9693

Excited state 2:
Excitation energy (eV) = 3.9707
Wavelength (nm) = 312.2479
Total energy for state 2: -
-650.24951529 au
Multiplicity: Singlet
Trans. Mom.:
-0.5736 X 0.3513 Y 0.1716 Z
Strength : 0.0468731196
X: D( 54) --> V( 1) amplitude = 0.9806

Excited state 3:
Excitation energy (eV) = 4.3060
Wavelength (nm) = 287.9333
Total energy for state 3:
-650.23719302 au
Multiplicity: Singlet
Trans. Mom.:
0.0794 X 0.1940 Y -0.0791 Z
Strength : 0.0052934380
X: D( 53) --> V( 1) amplitude = 0.9560

Excited state 4:
Excitation energy (eV) = 4.3588
Wavelength (nm) = 284.4434
Total energy for state 4:
-650.23525155 au
Multiplicity: Singlet
Trans. Mom.:
0.0902 X 0.0311 Y -0.0676 Z
Strength : 0.0014597263
X: D( 52) --> V( 1) amplitude = 0.9219
X: D( 55) --> V( 2) amplitude = -0.3256

Excited state 5:
Excitation energy (eV) = 4.5536
Wavelength (nm) = 272.2754
Total energy for state 5:
-650.22809293 au
Multiplicity: Singlet
Trans. Mom.:
0.3071 X -0.1805 Y -0.0901 Z
Strength : 0.0150619165
X: D( 52) --> V( 1) amplitude = 0.3111
X: D( 55) --> V( 2) amplitude = 0.9209

Excited state 6:
Excitation energy (eV) = 4.6198
Wavelength (nm) = 268.3763
Total energy for state 6:
-650.22566169 au
Multiplicity: Singlet
Trans. Mom.:
0.0683 X -0.0154 Y 0.2597 Z
Strength : 0.0081892247
X: D( 51) --> V( 1) amplitude = -0.9422

Time for Single Excitation Calculation:
25249.95s (cpu), 3685.70s (wall)

# TDDFT Excitation Energies (E-Isomer)

Excited state 1:
Excitation energy (eV) = 2.6233
Wavelength (nm) = 472.6285
Total energy for state 1:
-650.28286403 au
Multiplicity: Singlet
Trans. Mom.:
0.2527 X -0.0261 Y -0.0000 Z
Strength : 0.0041470082
X: D( 55) --> V( 1) amplitude = 0.9708

Excited state 2:
Excitation energy (eV) = 3.8169
Wavelength (nm) = 324.8302
Total energy for state 2:
-650.23900013 au
Multiplicity: Singlet
Trans. Mom.:
-0.0000 X -0.0000 Y 0.0629 Z
Strength : 0.0003698468
X: D( 54) --> V( 1) amplitude = 0.9893

Excited state 3:
Excitation energy (eV) = 3.9461
Wavelength (nm) = 314.1937
Total energy for state 3:
-650.23425162 au
Multiplicity: Singlet
Trans. Mom.:
0.3639 X -0.0117 Y -0.0000 Z

Strength : 0.0128128833
X: D( 51) --> V( 1) amplitude = -0.3344
X: D( 53) --> V( 1) amplitude = 0.9178

Excited state 4:
Excitation energy (eV) = 4.2821
Wavelength (nm) = 289.5376
Total energy for state 4:
-650.22190247 au
Multiplicity: Singlet
Trans. Mom.:
0.0000 X -0.0000 Y -0.1339 Z
Strength : 0.0018822199
X: D( 52) --> V( 1) amplitude = 0.9928

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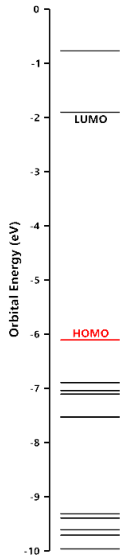
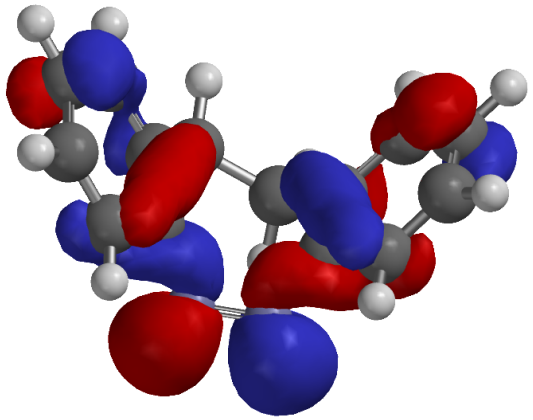
Time for Single Excitation Calculation:
18926.59s (cpu), 2698.13s (wall)

Excited state 5:
Excitation energy (eV) = 4.2896
Wavelength (nm) = 289.0346
Total energy for state 5:
-650.22162866 au
Multiplicity: Singlet
Trans. Mom.:
-0.2493 X 0.0087 Y -0.0000 Z
Strength : 0.0065392647
X: D( 51) --> V( 1) amplitude = 0.9167
X: D( 53) --> V( 1) amplitude = 0.3652

Excited state 6:
Excitation energy (eV) = 4.8384
Wavelength (nm) = 256.2491
Total energy for state 6:
-650.20145966 au
Multiplicity: Singlet
Trans. Mom.:
-0.0688 X 0.0172 Y 0.0000 Z
Strength : 0.0005965382
X: D( 55) --> V( 2) amplitude = 0.9682

# Z-Isomer MO’s



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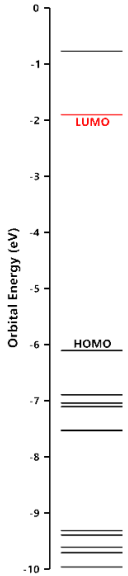
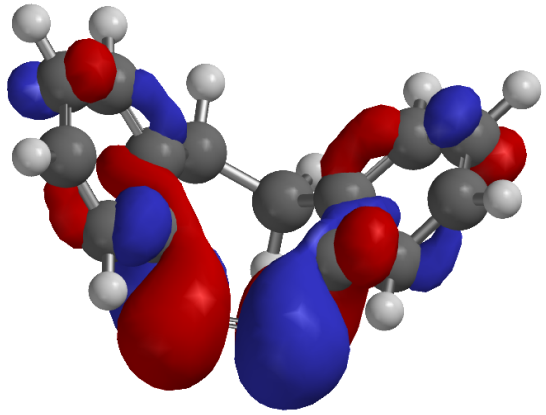
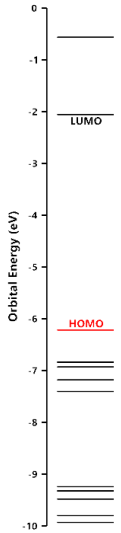
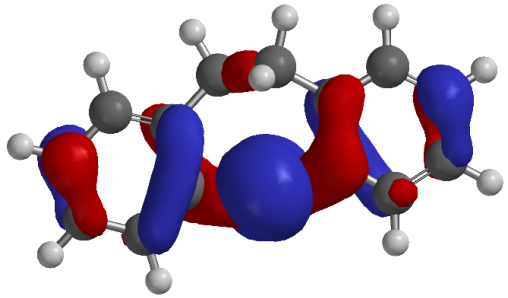


LUMO

# E-Isomer MO’s



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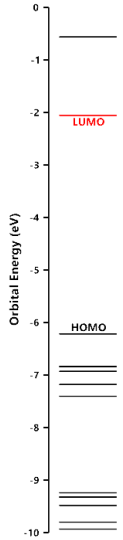
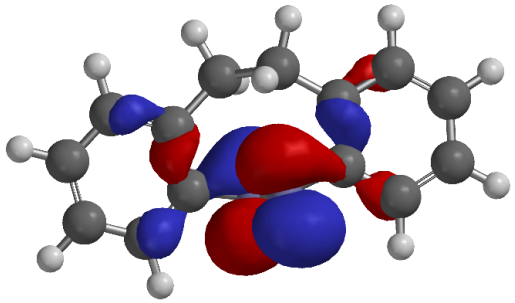
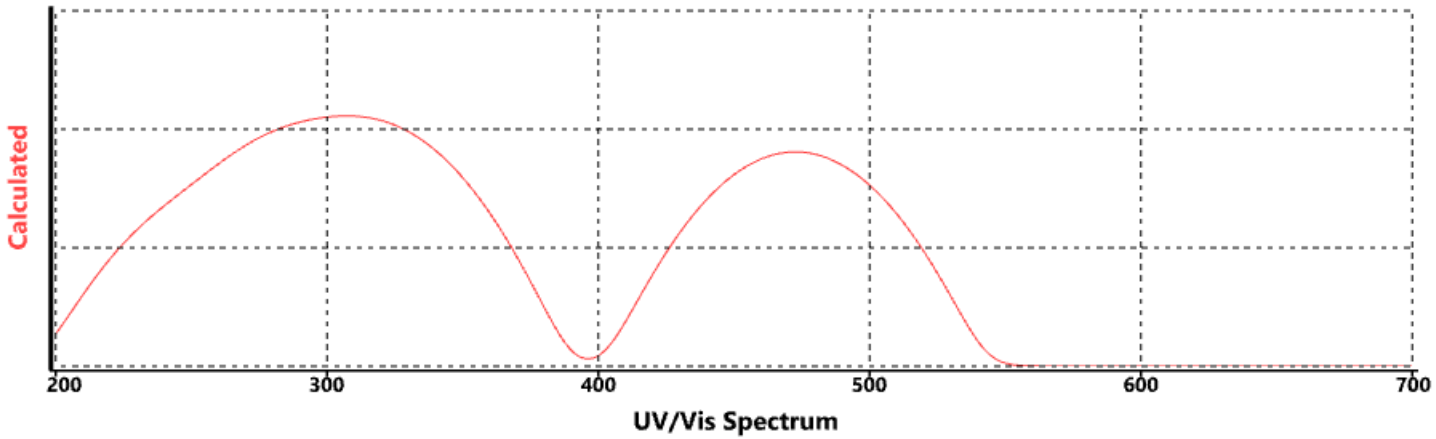


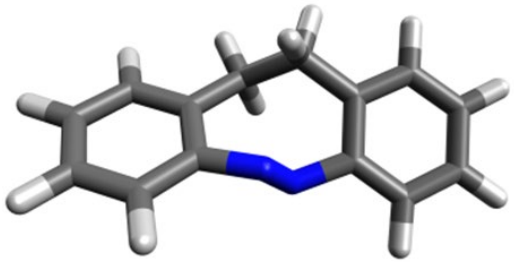



LUMO

# Calculated UV-VIS Spectrum

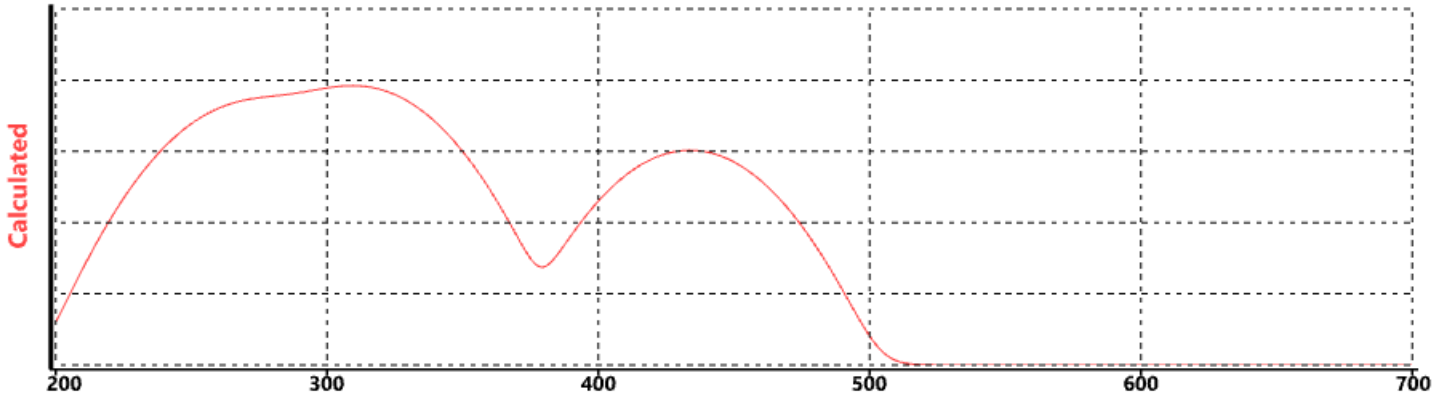
E-Isomer

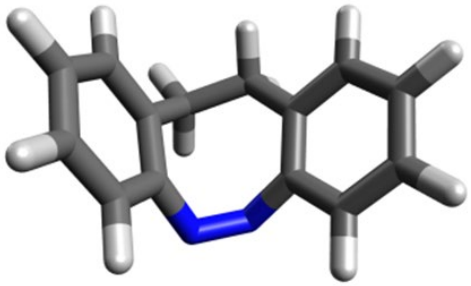


E

Z-Isomer



Z