Prediction of Thermal Stability of Photochromic Materials Used for Optical Switching and Data Storage Applications

Pansy D. Patel,1,2 Ivan A. Mikhailov,1,4 and Artëm E. Masunov*1,2,3

1Nanoscience Technology Center, 2Department of Chemistry, 3Department of Physics, 12424 Research Parkway, Suite 400, University of Central Florida, Orlando, FL 32826 USA, 4St. Petersburg Nuclear Physics Institute, Gatchina, St. Petersburg 188300, Russia
amasunov@mail.ucf.edu

Abstract. Certain organic compounds possess the ability to change color under the influence of light, called photochromism. This change is often due to ultrafast chemical transition from open to closed ring isomers (photocyclization). Information technology applications of these photochromics require the reverse transformation to be very slow in the dark. We have applied Density Functional Theory (DFT) methods to predict kinetics of this cycloreversion. This cycloreversion occurs through symmetry forbidden conrotatory electrocyclic mechanism with transition state of strong diradical character, and requires the unrestricted broken-symmetry DFT formalism. Our results suggest that B3LYP functional describes the activation barrier for the cycloreversion process with about 1-2 kcal/mol error, while M052x functional gives an error of about 2-3 kcal/mol compared to the experimental values.

Keywords: Ring opening, cycloreversion, electrocyclic reaction, chemical kinetics

1 Introduction

Photochromism is a non-destructive process involving light initiated rearrangement of chemical bonds accompanied by the change in color and other properties. It often results in reversible transformation of a chemical species from open to closed ring isomers. The simplest example of photochromism is 1,2-cyclohexadiene (CHD) (closed isomer) and 1,3,5-hexatriene (cZc-HT) (open isomer) (Fig.1).

Fig. 1. Photochromic reversible transformation of hexatriene (left) and cyclohexadiene (right).

The two isomers differ from one another not only in the absorption spectra but also in various physical and chemical properties such as geometrical structure, refractive index, dielectric constant and oxidation-reduction potential [1].
Photochromic compounds can be broadly classified into thermally reversible compounds (T-type or thermally unstable) and thermally irreversible (P-type or thermally stable) compounds. Typical examples of T-type compounds are Azobenzene and Spiropyran; and Diarylethenes and Fulgides belong to thermally irreversible P-type photochromic compounds (Fig. 2).

The thermal stability of P-type compounds makes them promising materials in design of various optoelectronic devices such as optical memory, optical switching, displays and nonlinear optics. In order to be practically useful, the photochromic material has to satisfy certain requirements, such as: 1. Thermal stability of both isomers; 2. Fatigue resistance; 3. Efficient photochromic reactivity: high sensitivity, rapid response; 4. High solubility in polymer matrices; 5. Non-destructive readout capability; 6. Sensitivity at diode laser wave lengths [2]. In the present contribution we focus on the first requirement, which is met by a high activation energy to cycloreversion. Dithienyl perfluorocyclopentenes are an important class of thermally irreversible (P-type) photochromic compounds, which have been extensively investigated to estimate the above mentioned properties and their potential application.
as optical switches [2-6]. Cycloreversion process occurs through conrotatory

electrocyclic mechanism involving symmetry forbidden diradical intermediate. This is

a unimolecular stereoselective process and can be easily understood by the
Woodward-Hoffmann rules and the Frontier Molecular Orbital (FMO) theory [7]. To
understand the reaction mechanism of pericyclic reactions, Woodward and Hoffmann
showed that by examining the interaction of the Frontier molecular orbitals (i.e. the
highest occupied, HOMO and lowest unoccupied, LUMO) both the regio- and
stereospecificity could be accounted for. They suggested that in a photochemical
reaction, an electron in the HOMO of the reactant is promoted to an excited state
leading to a reversal of terminal symmetry relationships and reversal of
stereospecificity. Reactions that take the opposite course are symmetry forbidden and
require a lot more energy to take place if they take place at all. These rules have
known to be supported by quantum chemical calculations. Computational studies
have been done extensively on the model system of cyclohexadiene (CHD) to 1,3,5-
hexatriene (cZc-HT) photochemical interconversion. A complete mechanistic picture
of the photochemical ring opening occurring on the $^2\text{A}_1$ surface after CHD
photoexcitation has been drawn by Celani et al. using computationally expensive ab

initio CAS-SCF and CAS-SCF/MP2 method [8]. Their results on the $^2\text{A}_1$

potential energy surface suggested that the cZc-HT must be the only primary photoproduct of
the direct irradiation of CHD form the conical intersection, which also agreed with the
experimental data. They also described the $^1\text{B}_2$ pathways for the same process and

proposed that although the photochemical ring opening of CHD occurs (in

femtoseconds) in the spectroscopic state, the associated photochemical ring closure
reaction of cZc-HT is initiated upon decay of $^2\text{A}_1$ cZc-HT to the ground state
picoseconds after the initial excitation [9]. Sakai et al. calculated the potential energy
surfaces for the electrocyclic reactions of 1,3,5-hexatriene with different

ab initio molecular orbital methods [10]. The transition states of two electrocyclic reaction
pathways (conrotatory, 47.62 kcal/mol and disrotatory, 37.24 kcal/mol) for hexa-
1,3,5-triene were reported at CASPT2/6-311+G** level. Since the latter mechanism
allowed by orbital symmetry has a lower energy barrier, the reactant and product with
C$_4$ symmetry are unstable; while the conrotatory mechanism with a higher energy
barrier leads to stable reactant and product with C$_2$ symmetry, so it is the preferable
pathway for ring closure.

Theoretical investigation of the CHD/cZc-HT photochemical interconversion have
also been performed with CASPT2 [11] and MR-SCI [12] theory levels to explain the
reaction path and to suggest the potential energy surface and transition probabilities
respectively. Garavelli et al. employed the algorithm of steepest decent path to
compute initial relaxation directions (IRD) from the tip of the conical intersection to
predict the mechanism of the product formation for the CHD/cZc-HT photochemical
interconversion [13]. A systematic search for the IRD in the region of the $^2\text{A}_1$/1$\text{A}_1$
conical intersection yields three relaxation paths. The first two paths, which start in
the strict vicinity of the intersection, are nearly equivalent energetically and lead to
production of CHD and cZc-HT, respectively. The third path, which begins at a much
larger distance, lies higher in energy and ends at a methylenecyclopentene diradical
(MCPD) minimum. CASSCF and CASPT2 calculations with various basis sets and
different active space definitions have been performed to study the photochromic
cycloreversion reaction in dithienylethenes (Fig.2c; X=S) using [14].

Nakamura and Irie [15] carried out semiempirical calculations on the three types of
molecular systems (furyl, pyrrolyl, and thiienyl), and have decided that the energy
difference between the ring closed and open forms controls the ease of their
conversion as well as thermal stability. They observed that in the case of the thiienyl
derivative, the ground-state energy difference between the open and closed forms is
the lowest, compared to furyl and pyrrolyl derivatives and concluded that the energy
barrier in the case of the thiienyl derivative would be the largest, which makes
cycloreversion reaction less likely. Later, Majumdar et al. performed DFT and TD-
DFT calculations on selective dithienylethenes and their derivatives to study their
structures, photophysics, and different molecular properties at the ground and
vertically excited states [16]. They reported that dithienylethenes derivatives of
maleic anhydrides and perfluorocyclopentenes are more effective photoswitches.
Based on their calculations using DFT and restricted FOCI methods, they suggested
the use of such molecules as nonlinear optical materials. Over the years Irie and co-
workers have done extensive work on design of the dual-mode optical molecular
switching materials both experimentally [2-4, 15-31] and theoretically [14, 32-37].
Lehn et al. have also synthesized some potential molecular optical switches [6, 38-
42]. Theoretical investigations on thermally irreversible photochromic systems have
also been conducted by other groups, using semi-empirical, ab initio and DFT
methods [16, 43, 44].

TD-DFT has been found to have problems in description of excited state potential
surfaces in the vicinity of conical intersections [45]. These problems are probably
routed in the poor description of the reference ground state near pericyclic minimum
within restricted Kohn-Sham (RKS) formalism. The Kohn-Sham formalism of DFT
was developed for non-degenerate cases; it breaks down for systems with strong
diradical character and degeneracy of the electronic levels, which is exactly the case
for conical intersections. However, static (also known as left-right) electron
correlation can be taken into account by introducing different orbitals for different
spin. This approach, known as unrestricted Kohn-Sham formalism (UKS) is known to
yield qualitatively correct description of the bond breaking [46].

From the detailed analysis of all the previous experimental and theoretical data
on photochromic compounds, it is clear that computationally inexpensive yet reliable
theoretical method for property prediction would greatly assist in devising the
molecular design principles for thermally irreversible photochromics. These
principles can then be used in synthesis of the new photoswitchable materials. In the
present paper we report the results of DFT calculations to predict the thermal stability
property.

2 Computational Details

For this study we selected benchmark set of diarylethene perfluorocyclopentenes
(Fig.3) for which thermal cycloreversion kinetics data is available in the literature.
GAUSSIAN03 package [47] was used to perform semi-empirical AM1 [48-51], ab
Prediction of Thermal Stability of Photochromic Materials Used for Optical Switching and Data Storage Applications

\( \textit{initio} \) Hartree-Fock (HF) and Density Functional theory (DFT) [52, 53] calculations. Hybrid DFT functionals such as B3LYP [54-56], BMK [57] and M052x [58] with various fractions of Hartree-Fock exchange and the 6-31+G* basis sets were used.

![Chemical structures](image)

**Fig. 3.** Benchmark set of molecules with documented thermal stability.

To characterize each stationary point as a minimum or a transition state and to estimate the zero point vibrational energies (ZPE) and vibrational frequencies for all optimized species were computed at all levels.

### 3 Results and Discussion

Experiments have suggested that thermal stability of the diarylethenes depends on the aryl groups and their aromatic stabilization energies allow conrotatory cycloreversion and hence makes the closed ring isomer thermally unstable [2-4, 6].

The thermal stabilities of the closed forms of some of the typical photochromic compounds have been studied experimentally [3-6] (Fig. 3). They report the half-lives for the thermal opening process at elevated temperatures. The activation barrier was then calculated for these systems using the Arrhenius equation:

\[
k = A \exp \left( \frac{-E_a}{RT} \right)
\]

where \( k \) is the rate constant, \( A \) is the pre exponential factor, \( E_a \) is the activation energy, \( R \) is the universal gas constant and \( T \) is the temperature. The electrocyclic cycloreversion process is a unimolecular reaction therefore for a given half-life (\( t_{1/2} \)) we can calculate the rate constant as:
Using the Eq.(2) on the data given by Irie et al. [59] for PFC-2 (\(t_{1/2}=3.3\text{hr at } T=423\text{K and } E_a=139\text{kJ/mol}) we calculated the rate constant \(k=-0.21\text{hr}^{-1}\). Rearranging Eq.(1), the pre-exponential factor \(A\) was found to be \(-2.968 \cdot 10^{16}\). Since cycloreversion occurs through the same transition state irrespective of substituents, the value of \(A\) is expected be similar for all the molecules in Fig.3. Using this value for \(A\) we calculated the experimental activation energy for other molecules whose \(t_{1/2}\) was determined experimentally [3-6], and compared those values to the theoretical predictions in Table 1.

Table 1. Activation barriers for thermal cycloreversion process from open to closed isomers (in kcal/mol) and mean values of the spin operator at TS geometry \(<S^2>=0\) for pure singlet and \(<S^2>=1\) for pure triplet.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>26.1</td>
<td>26.8</td>
<td>23.4</td>
<td>29.1</td>
<td>27.6</td>
<td>33.2</td>
<td>28.7</td>
</tr>
<tr>
<td>UAM1</td>
<td>30.1</td>
<td>29.5</td>
<td>29.8</td>
<td>29.9</td>
<td>24.3</td>
<td>27.1</td>
<td>24.8</td>
</tr>
<tr>
<td>UHF/Midi!</td>
<td>30.2</td>
<td>27.9</td>
<td>28.2</td>
<td>30.2</td>
<td>28.2</td>
<td>30.0</td>
<td>27.7</td>
</tr>
<tr>
<td>(&lt;S^2&gt;) value (UHF level)</td>
<td>2.80</td>
<td>2.44</td>
<td>3.09</td>
<td>2.48</td>
<td>2.34</td>
<td>3.28</td>
<td>3.28</td>
</tr>
<tr>
<td>UB3LYP/Midi!/UAM1</td>
<td>28.9</td>
<td>24.6</td>
<td>22.4</td>
<td>28.6</td>
<td>38.2</td>
<td>30.0</td>
<td>27.8</td>
</tr>
<tr>
<td>RM05-2x/Midi!/UAM1</td>
<td>33.6</td>
<td>29.8</td>
<td>26.6</td>
<td>36.2</td>
<td>45.8</td>
<td>43.1</td>
<td>52.7</td>
</tr>
<tr>
<td>UM05-2x/Midi!/UAM1</td>
<td>30.7</td>
<td>27.5</td>
<td>26.2</td>
<td>32.1</td>
<td>39.6</td>
<td>33.1</td>
<td>32.3</td>
</tr>
<tr>
<td>RB3LYP/Midi!/UHF/Midi!</td>
<td>31.7</td>
<td>29.3</td>
<td>26.3</td>
<td>33.9</td>
<td>38.7</td>
<td>37.3</td>
<td>33.6</td>
</tr>
<tr>
<td>UB3LYP/Midi!/UHF/Midi!</td>
<td>30.1</td>
<td>27.1</td>
<td>25.2</td>
<td>31.4</td>
<td>33.4</td>
<td>33.3</td>
<td>30.0</td>
</tr>
<tr>
<td>RRMK/Midi!/UHF/Midi!</td>
<td>38.0</td>
<td>35.3</td>
<td>31.8</td>
<td>40.5</td>
<td>45.4</td>
<td>44.8</td>
<td>42.1</td>
</tr>
<tr>
<td>R3LYP/Midi!</td>
<td>37.8</td>
<td>35.2</td>
<td>31.8</td>
<td>40.5</td>
<td>39.8</td>
<td>44.5</td>
<td>42.1</td>
</tr>
<tr>
<td>UB3LYP/Midi!</td>
<td>29.4</td>
<td>29.9</td>
<td>25.2</td>
<td>32.0</td>
<td>34.5</td>
<td>35.4</td>
<td>31.6</td>
</tr>
<tr>
<td>UB3LYP/Midi! (+ZPE)</td>
<td>27.8</td>
<td>27.8</td>
<td>23.2</td>
<td>29.7</td>
<td>31.1</td>
<td>32.8</td>
<td>29.6</td>
</tr>
<tr>
<td>(&lt;S^2&gt;) value (UB3LYP level)</td>
<td>0.62</td>
<td>0.77</td>
<td>0.70</td>
<td>0.75</td>
<td>1.04</td>
<td>0.85</td>
<td>0.83</td>
</tr>
<tr>
<td>UBMK/Midi!</td>
<td>35.8</td>
<td>37.1</td>
<td>34.1</td>
<td>38.7</td>
<td>40.5</td>
<td>43.5</td>
<td>41.6</td>
</tr>
<tr>
<td>UBMK/Midi! (+ZPE)</td>
<td>33.7</td>
<td>34.9</td>
<td>32.0</td>
<td>36.9</td>
<td>36.2</td>
<td>42.9</td>
<td>39.7</td>
</tr>
<tr>
<td>(&lt;S^2&gt;) value (UBMK level)</td>
<td>0.61</td>
<td>0.72</td>
<td>0.65</td>
<td>0.70</td>
<td>1.00</td>
<td>0.77</td>
<td>0.75</td>
</tr>
<tr>
<td>UM05-2x/6-31G*</td>
<td>31.5</td>
<td>31.4</td>
<td>26.6</td>
<td>34.5</td>
<td>39.3</td>
<td>38.2</td>
<td>35.8</td>
</tr>
<tr>
<td>UM05-2x/6-31G* (+ZPE)</td>
<td>29.4</td>
<td>29.3</td>
<td>24.4</td>
<td>32.1</td>
<td>35.6</td>
<td>35.3</td>
<td>32.9</td>
</tr>
<tr>
<td>(&lt;S^2&gt;) value (UM052x level)</td>
<td>0.71</td>
<td>0.80</td>
<td>0.77</td>
<td>0.79</td>
<td>1.08</td>
<td>0.90</td>
<td>0.89</td>
</tr>
</tbody>
</table>

While the HF and AM1 determinants remain unrestricted along the entire path from the open to closed form, the UKS solution collapses to the restricted determinant soon after the geometry deviates from the TS. This discontinuity on the potential surface presented the main technical difficulty and required to generate new unrestricted guess on each optimization step with Guess(Always,Mix) keyword. In order to avoid this difficulty we used UHF and UAM1 geometry of the transition state. However, the compound method UB3LYP//UHF was found to have poor agreement with experimental data. As one can see from the Table 1 the unrestricted
Prediction of Thermal Stability of Photochromic Materials Used for Optical Switching and Data Storage Applications

KS methods (UB3LYP, UBMK or UM052x) give lower energy for the transition state than the restricted ones (RB3LYP or RM052x). These UKS activation energies are closer to the experimental values in all cases. Zero point energy correction improves the agreement with experiment in all cases. The UB3LYP+ZPE method gives the deviation from the experimental data of about 1-2 kcal/mol exception that of 5. The higher deviation for this molecule (3.5 kcal/mol) could be explained by the higher spin contamination of $<S^2>=1.04$. The UM052x functional, designed for kinetic calculations, also gives low deviation of about 2-3 kcal/mol. However the UBMK method, which was also designed to describe chemical kinetics, strongly overestimates the activation barrier due to the fact organic molecules were excluded from the training set used in BMK parameterization.

4 Conclusions

The kinetics of cycloreversion was studied for the benchmark set of seven diarylethene derivatives. The activation energies were calculated from the published experimental data, based on the assumption of equal pre-exponential factors in the Arrhenius equation. The geometries of the closed and open isomers, as well as transition states between them were optimized with AM1, HF, B3LYP, BMK, and M05-2x methods using Midi! And 6-31G* basis sets. The predicted activation energies were compared with experimental ones. The use of unrestricted Slater determinant and zero-point energy correction were found important to achieve better agreement with experimental data. Our results suggest that B3LYP and M05-2x functionals overestimate the activation barrier for the cycloreversion reaction by about 1-2 kcal/mol and 2-3 kcal/mol respectively, while BMK consistently overestimates it by 7-9 kcal/mol. We recommend B3LYP/Midi! and M05-2x/6-31G* theory levels for prediction of the thermal stability of the photochromic compounds.

5 Acknowledgements

This work was supported in part by the National Science Foundation Grant No. CCF 0740344. The authors are thankful to DOE NERSC, UCF I2Lab, and UCF Institute for Simulations and Training (IST) HPC Stokes facility for the generous donation of the computer time.

References

Prediction of Thermal Stability of Photochromic Materials Used for Optical Switching and Data Storage Applications


