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

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Abstract. Certain organic compounds posess 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 thechnology 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**).
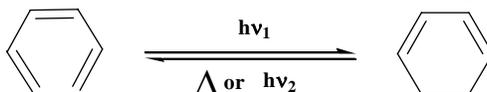
Fig. 1. Photochromic reversible transformation of hexatriene (left) and cyclohexadiene (right).

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].

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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**).
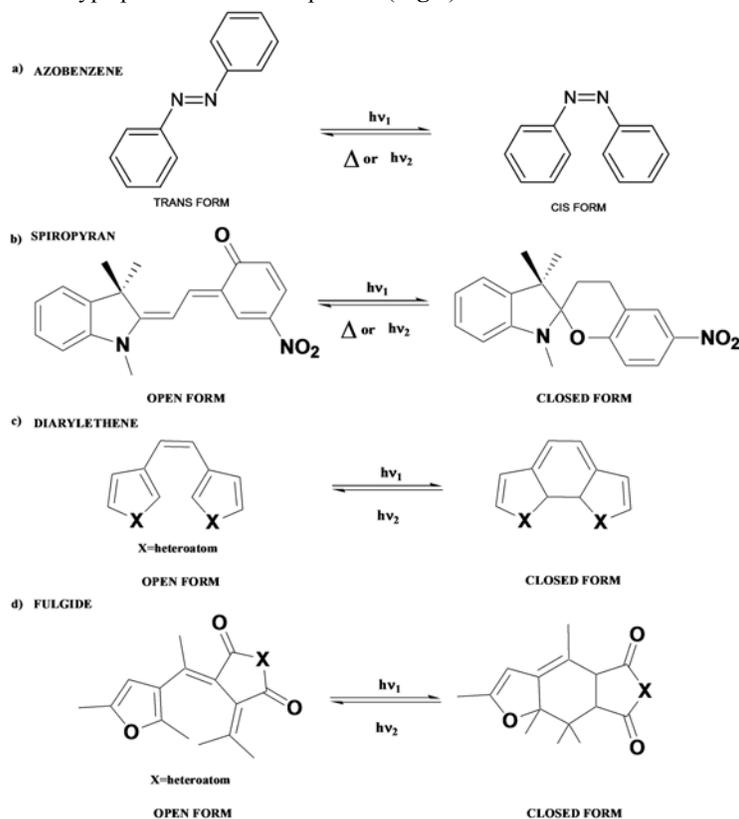
Fig.2.a,b: Thermally unstable (T-type) and **c,d:** thermally irreversible (P-type) photochromics.

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 $^2A_1$ 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 $^2A_1$ 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 $^1B_2$ 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 $^2A_1$ 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_s 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 $^2A_1/^1A_1$ 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 thienyl), 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 thienyl 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 thienyl 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 pefluorocyclopentenes 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*

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 Midi! and 6-31+G* basis sets
were used.

6: R₁=CH₃, R₂=H
7: R₁=C₂H₅, R₂=H
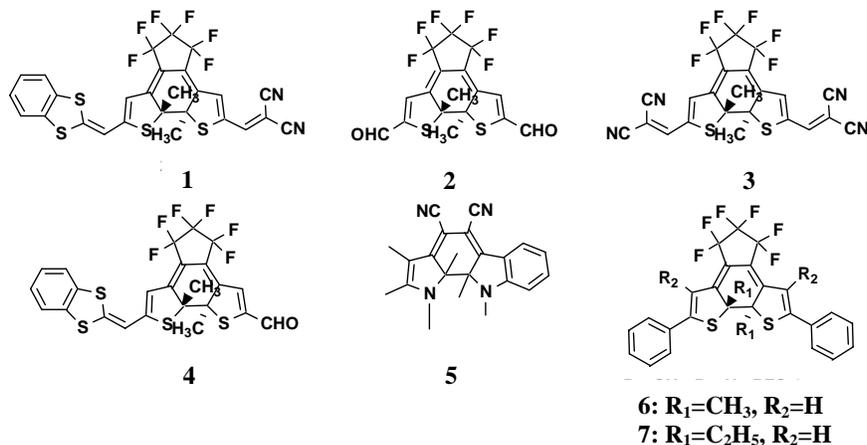
Fig. 3. Benchmark set of molecules with documented thermal stability.

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:

$$k = A \exp \frac{-E_a}{RT},$$ **(1)**

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:

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$$k = \frac{-0.693}{t_{1/2}} \qquad (2)$$

Using the Eq.(2) on the data given by Irie et al. [59] for PFC-2 ($t_{1/2}$=3.3hr at T=423K and E_a=139kJ/mol) we calculated the rate constant k= -0.21hr^{-1}. Rearranging Eq.(1), the pre-exponential factor A was found to be -2.968·10^{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)

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

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

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

References

1. Bouas-Laurent, H. and H. Durr, *Organic photochromism.* Pure and Applied Chemistry, 2001. **73**(4): p. 639-665.
2. Irie, M., *Photochromism: Memories and switches - Introduction.* Chemical Reviews, 2000. **100**(5): p. 1683-1683.

3. Irie, M., et al., *Fatigue resistant properties of photochromic dithienylethenes: by-product formation.* Chemical Communications, 1999(8): p. 747-748.
4. Kobatake, S., et al., *Photochromism of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene in a single-crystalline phase. Conrotatory thermal cycloreversion of the closed-ring isomer.* Journal of the American Chemical Society, 2000. **122**(49): p. 12135-12141.
5. Nakayama, Y., K. Hayashi, and M. Irie, *Thermally irreversible photochromic systems - reversible photocyclization of nonsymmetrical diarylethene derivatives.* Bulletin of the Chemical Society of Japan, 1991. **64**(3): p. 789-795.
6. Gilat, S.L., S.H. Kawai, and J.M. Lehn, *Light-triggered molecular devices - photochemical switching of optical and electrochemical properties in molecular wire type diarylethene species.* Chemistry-a European Journal, 1995. **1**(5): p. 275-284.
7. Hoffmann, R. and R.B. Woodward, *Selection rules for concerted cycloaddition reactions.* Journal of the American Chemical Society, 1965. **87**(9): p. 2046-&.
8. Celani, P., et al., *What happens during the picosecond lifetime of 2A(1) cyclohexa-1,3-diene - a CAS-SCF study of the cyclohexadiene hexatriene photochemical interconversion.* Journal of the American Chemical Society, 1994. **116**(22): p. 10141-10151.
9. Celani, P., et al., *Do photochemical ring-openings occur in the spectroscopic state? B-1(2) pathways for the cyclohexadiene/hexatriene photochemical interconversion.* Journal of Physical Chemistry, 1996. **100**(50): p. 19364-19366.
10. Sakai, S. and S. Takane, *Theoretical studies of the electrocyclic reaction mechanisms of hexatriene to cyclohexadiene.* Journal of Physical Chemistry A, 1999. **103**(15): p. 2878-2882.
11. Garavelli, M., et al., *Reaction path of a sub-200 fs photochemical electrocyclic reaction.* Journal of Physical Chemistry A, 2001. **105**(18): p. 4458-4469.
12. Tamura, H., et al., *A theoretical study of cyclohexadiene/hexatriene photochemical interconversion: multireference configuration interaction potential energy surfaces and transition probabilities for the radiationless decays.* Chemical Physics Letters, 2005. **401**(4-6): p. 487-491.
13. Garavelli, M., et al., *Relaxation paths from a conical intersection: The mechanism of product formation in the cyclohexadiene/hexatriene photochemical interconversion.* Journal of Physical Chemistry A, 1997. **101**(11): p. 2023-2032.
14. Asano, Y., et al., *Theoretical study on the photochromic cycloreversion reactions of dithienylethenes; on the role of the conical intersections.* Journal of the American Chemical Society, 2004. **126**(38): p. 12112-12120.
15. Nakamura, S. and M. Irie, *Thermally irreversible photochromic systems - a theoretical-study.* Journal of Organic Chemistry, 1988. **53**(26): p. 6136-6138.
16. Majumdar, D., et al., *Photoswitch and nonlinear optical switch: Theoretical studies on 1,2-bis-(3-thienyl)-ethene derivatives.* Journal of Chemical Physics, 1999. **111**(13): p. 5866-5872.
17. Irie, M., *Photochromism of diarylethene single crystals and single molecules.* Molecular Crystals and Liquid Crystals, 2005. **430**: p. 1-+.
18. Irie, M. and M. Mohri, *Thermally irreversible photochromic systems - reversible photocyclization of diarylethene derivatives.* Journal of Organic Chemistry, 1988. **53**(4): p. 803-808.
19. Kobatake, S., Y. Matsumoto, and M. Irie, *Conformational control of photochromic reactivity in a diarylethene single crystal.* Angewandte Chemie-International Edition, 2005. **44**(14): p. 2148-2151.
20. Kobatake, S., et al., *Single-crystalline photochromism of diarylethenes: reactivity-structure relationship.* Chemical Communications, 2002(23): p. 2804-2805.

21. Kobatake, S., et al., *Photochromism of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene in a single crystalline phase.* Journal of the American Chemical Society, 1999. **121**(11): p. 2380-2386.

22. Matsuda, K. and M. Irie, *Diarylethene as a photo switching unit.* Journal of Photochemistry and Photobiology C-Photochemistry Reviews, 2004. **5**(2): p. 169-182.

23. Morimitsu, K., S. Kobatake, and M. Irie, *Control of cycloreversion quantum yields of diarylethenes by introduction of substituents at the reactive carbons.* Molecular Crystals and Liquid Crystals, 2005. **431**: p. 451-454.

24. Saita, K., et al., *Raman spectroscopic study on isomers of photochromic 1,2-bis(2,5-dimethy1-3-thienyl) perfluorocyclopentene in crystal and stability of the closed-ring forms in the open-ring forms.* Chemical Physics Letters, 2008. **454**(1-3): p. 42-48.

25. Uchida, K. and M. Irie, *Photochromic reactions of bis(2-thienyl) perfluorocyclopentenes.* Journal of Information Recording, 1998. **24**(1-2): p. 101-104.

26. Uchida, K., et al., *Substituent effect on the photochromic reactivity of bis(2-thienyl)perfluorocyclopentenes.* Tetrahedron, 2001. **57**(21): p. 4559-4565.

27. Yamada, T., S. Kobatake, and M. Irie, *Single-crystalline photochromism of diarylethene mixtures.* Bulletin of the Chemical Society of Japan, 2002. **75**(1): p. 167-173.

28. Yamada, T., et al., *X-ray crystallographic study on single-crystalline photochromism of bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene.* Journal of the American Chemical Society, 2000. **122**(8): p. 1589-1592.

29. Yamada, T., et al., *Crystal structure-reactivity correlation in single-crystalline photochromism of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.* Journal of Organic Chemistry, 2001. **66**(18): p. 6164-6168.

30. Yamaguchi, T., S. Takami, and M. Irie, *Photochromic properties of 1,2-bis (6-substitute-2-methyl-1-benzofuran-3-yl) ethene derivatives.* Journal of Photochemistry and Photobiology a-Chemistry, 2008. **193**(2-3): p. 146-152.

31. Yamaguchi, T., K. Uchida, and M. Irie, *Photochromic properties of diarylethene derivatives having benzofuran and benzothiophene rings based on regioisomers.* Bulletin of the Chemical Society of Japan, 2008. **81**(5): p. 644-652.

32. Abe, Y., et al., *MNDO-PM3 MO studies on the thermal enantiomerization of 1 ',3 ',3 '-trimethyl-6-nitrospiro[2H-l-benzopyran-2,2 '-indoline].* Molecular Crystals and Liquid Crystals, 2000. **345**: p. 419-424.

33. Asano, Y., et al., *Theoretical study on novel quantum yields of dithienylethenes cyclization reactions in crystals.* Journal of Molecular Structure-Theochem, 2003. **625**: p. 227-234.

34. Guillaumont, D., et al., *An ab initio MO study of the photochromic reaction of dithienylethenes.* Journal of Physical Chemistry A, 2002. **106**(31): p. 7222-7227.

35. Uchida, K., et al., *Theoretical study of an intermediate, a factor determining the quantum yield in photochromism of diarylethene derivatives.* Journal of Molecular Structure-Theochem, 2002. **579**: p. 115-120.

36. Yoshioka, Y. and M. Irie, *Ab initio study of 3-furyl fulgide .1. Molecular structures and relative stabilities of three isomers.* Electronic Journal of Theoretical Chemistry, 1996. **1**: p. 183-190.

37. Yoshioka, Y. and M. Irie, *Ab initio study of 3-furyl fulgide .2. Substituent effects on photochemical reactions.* Electronic Journal of Theoretical Chemistry, 1996. **1**: p. 191-198.

38. Gilat, S.L., S.H. Kawai, and J.M. Lehn, *Light-triggered electrical and optical switching devices.* Journal of the Chemical Society-Chemical Communications, 1993(18): p. 1439-1442.

39. Gilat, S.L., S.H. Kawai, and J.M. Lehn, *Light-triggered electrical and optical switches.* Molecular Crystals and Liquid Crystals Science and Technology Section a-Molecular Crystals and Liquid Crystals, 1994. **246**: p. 323-326.

40. Kawai, S.H., S.L. Gilat, and J.M. Lehn, *Dual-mode optical-electrical molecular switching device.* Journal of the Chemical Society-Chemical Communications, 1994(8): p. 1011-1013.

41.Kawai, S.H., et al., *A dual-mode molecular switching device - bisphenolic diarylethenes with integrated photochromic and electrochromic properties.* Chemistry-a European Journal, 1995. **1**(5): p. 285-293.

42.Tsivgoulis, G.M. and J.M. Lehn, *Photonic molecular devices - reversibly photoswitchable fluorophores for nondestructive readout for optical memory.* Angewandte Chemie-International Edition in English, 1995. **34**(10): p. 1119-1122.

43.Cho, H.G. and B.S. Cheong, *Theoretical investigation of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride: A thermally irreversible photochromic system.* Bulletin of the Korean Chemical Society, 1998. **19**(3): p. 308-313.

44.Williams, R.V., et al., *A DFT study of the thermal, orbital symmetry forbidden, cyclophanediene to dihydropyrene electrocyclic reaction. Predictions to improve the dimethyldihydropyrene photoswitches.* Journal of the American Chemical Society, 2005. **127**(46): p. 16207-16214.

45.Levine, B.G., et al., *Conical intersections and double excitations in time-dependent density functional theory.* Molecular Physics, 2006. **104**(5-7): p. 1039-1051.

46.Gunnarsson, O. and B.I. Lundqvist, *Exchange and Correlation in Atoms, Molecules, and Solids by Spin-Density Functional Formalism.* Physical Review B, 1976. **13**(10): p. 4274-4298.

47.Frisch, M.J., et al., *Gaussian 2003*. 2004, Gaussian, Inc.: Wallingford CT.

48.Davis, L.P., et al., *MNDO Calculations for Compounds Containing Aluminum and Boron.* Journal of Computational Chemistry, 1981. **2**(4): p. 433-445.

49.Dewar, M.J.S., M.L. McKee, and H.S. Rzepa, *MNDO Parameters for 3rd Period Elements.* Journal of the American Chemical Society, 1978. **100**(11): p. 3607-3607.

50.Dewar, M.J.S. and C.H. Reynolds, *An Improved Set of MNDO Parameters for Sulfur.* Journal of Computational Chemistry, 1986. **7**(2): p. 140-143.

51.Dewar, M.J.S., et al., *The development and use of quantum-mechanical molecular-models .76. AM1 - a new general-purpose quantum-mechanical molecular-model.* Journal of the American Chemical Society, 1985. **107**(13): p. 3902-3909.

52.Bartolotti, L.J.F.K., *Reviews in Computational Chemistry*, ed. B.D. Lipkowitz KB. 1996, New York: VCH Publishers.

53.Parr, R.G.Y., Weitao T., *Density Functional Theory of Atoms and Molecules*. 1989, New York: Oxford University Press.

54.Becke, A.D., *Density-functional thermochemistry .3. The role of exact exchange.* Journal of Chemical Physics, 1993. **98**(7): p. 5648-5652.

55.Lee, C.T., W.T. Yang, and R.G. Parr, *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron-density.* Physical Review B, 1988. **37**(2): p. 785-789.

56.Perdew, J.P. and Y. Wang, *Accurate and simple analytic representation of the electron-gas correlation-energy.* Physical Review B, 1992. **45**(23): p. 13244-13249.

57.Boese, A.D. and J.M.L. Martin, *Development of density functionals for thermochemical kinetics.* Journal of Chemical Physics, 2004. **121**(8): p. 3405-3416.

58.Zhao, Y., N.E. Schultz, and D.G. Truhlar, *Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions.* Journal of Chemical Theory and Computation, 2006. **2**(2): p. 364-382.

59.Irie, M., et al., *Photochromism of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in a single-crystalline phase.* Journal of the American Chemical Society, 2000. **122**(20): p. 4871-4876.