Density Functional Theory Study of Photodegradation and Fatigue-Resistance of Photochromic Materials for Optical Switching and Data Storage Applications

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

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

Abstract. Photochromic compounds are promising materials for optoelectronic and photonic applications because of their ability to undergo change in color under UV/Vis illumination due to reversible chemical transition from open to closed ring isomers (photocyclization). The by-produc formation may lead to irreversible photodegradation of the material, called fatigue. We use Density Functional Theory methods to predict the rate for the by-product formation for 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (PFC-2) in order to estimate its fatigue resistance. We propose a mechanism of the photofatigue for PFC-2 and explain higher fatigue resistance for its derivative. The method can become a part of rational design strategy for the new photochromic materials.

Keywords: theoretical photochemistry, reaction mechanism.

1 Introduction

Photochromism is the ability to change color under the influence of light. It involves reversible phtoisomerization with rearrangement of chemical bonds between the open and closed ring isomers, exemplified by dithienylethenes (**Fig.1**):

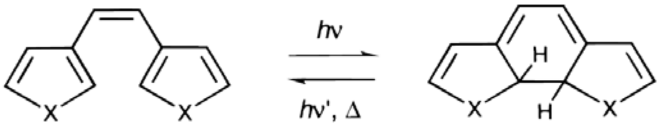


Fig. 1. Photochromic reversible transformation of dithienylethenes (X=O,NH,S).

Some photochromic compounds are perspective materials for optical disks and nonvolatile optical memory application. The requirements to these compounds include: 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 [1]. The present contribution is focused on the second requirement.

Concurrently with the photochromic rearrangement, irreversible photochemical reactions may also occur. This limits the number of cycles of photochromic reactions and is often referred to as photochemical fatigue. A successful candidate for photoswitching applications should be able to undergo the reversible reaction more than 10^4 cycles. Another example of implementation is optical data storage. While devices of the write–one–read–many type do not need a large number of lifecycles, fatigue resistance is crucial for a desirable write–many–read–many storage device.

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 [2]. To explain 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.

Many computational studies have been done on the simplest model system for photoinitiated interconversion, cyclohexadiene(CHD)/1,3,5-hexatriene(cZc-HT). A complete mechanistic picture of the photochemical ring opening occurring on the $2A_1$ surface after CHD photoexcitation has been done by Celani et. al. using expensive *ab initio* CAS-SCF and CAS-SCF/MP2 method [3]. 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 [4]. Sakai et al. calculated the potential energy surfaces for the electrocyclic reactions of 1,3,5-hexatriene at different *ab initio* molecular orbital methods [5]. 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 MP2//CAS/6-311+G** level. Since the latter mechanism allowed by orbital symmetry has a lower energy barrier, the reactant and product with Cs symmetry are unstable; while the conrotatory mechanism with a higher energy barrier leads to stable reactant and product with C2 symmetry, so it is the preferable pathway for ring closure.

Theoretical investigation of the CHD/cZc-HT photochemical interconversion have also been performed at MS-CASPT2[6] and MRSCI[7] methods as well 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 [8]. A systematic search for the IRD in the region of the $1A_1/2A_1$ 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.

Similar theoretical calculations have been performed to study the photochromic cycloreversion reaction in dithienylethenes (Figure 2c; X=S) using CASSCF and MS-CASPT2 method at variable basis sets and different active space definitions [9]. 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 [10]. 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.

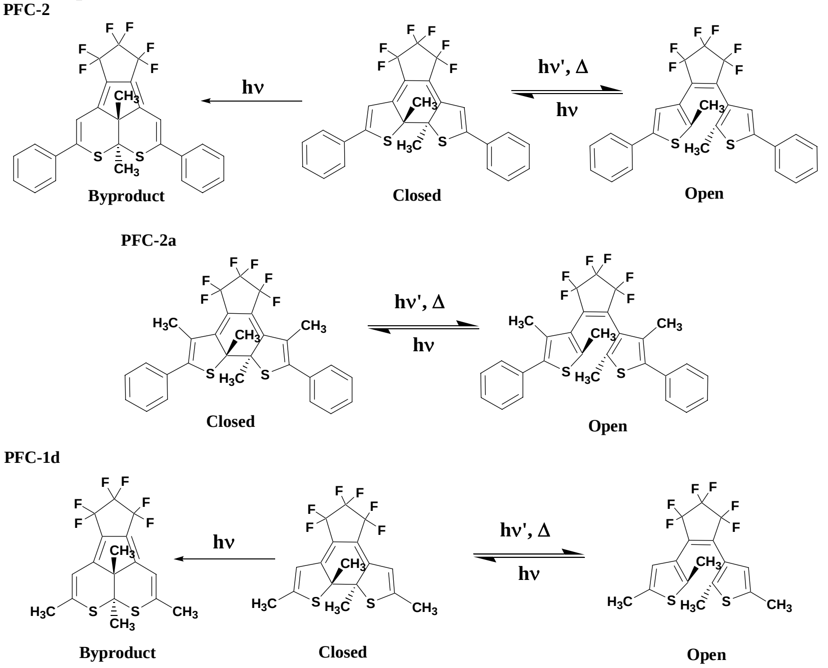


Fig. 2. Isomeric forms of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (PFC-2), 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (PFC-2a) and 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene(PFC-1d)

Over the years Irie and his co-workers have done extensive designing of the dual-mode optical molecular switching devices both experimentally [1, 10-28] and theoretically [9, 29-34]. Lehn et al. have also synthesized some potential molecular optical switches [35-40]. Irie et al. also investigated the mechanism of fatigue resistance [12]. He observed the decline in the absorbance of 1,2-bis(2-methyl-5-

phenyl-3-thienyl)perfluorocyclopentene (PFC-2) after only a few cycles while the absorbance of its methylated derivative PFC-2a remained constant even after 800 cycles (**Fig.2**). The formation of a colored by-product was suggested as the possible reason for the decrease in absorbance.

They suggested that the methyl substituents at the 4- and 4′-positions are considered to prevent rearrangement of the thiophene rings to the six-membered condensed ring. The authors later also isolated similar two six-membered heterocyclic ring containing byproduct in another compound 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene [41], and suggested two different probable schemes for the mechanistic formation based on the diradical recoupling process formulated by Celani et al. [3]. In both the cases it was clear that the byproduct formations takes place from the closed isomer since they observed decrease in the yield of the open form.

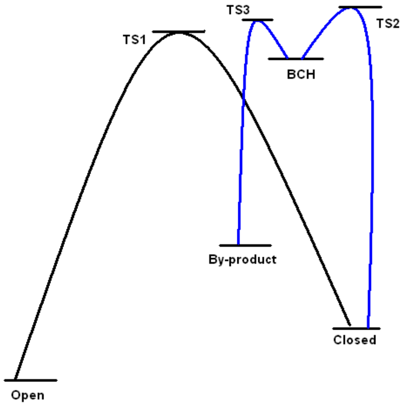
In the present paper we carried out DFT calculations to predict the mechanism for by-product formation in 2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (PFC-2). Our hypothesis for the formation of the by-product is based on a third route mechanism of the formation of a MCPD diradical from the conical intersection proposed by Celani et al. [3].

2 Computational Details

Density Functional theory (DFT) [42, 43] calculations have been performed using the GAUSSIAN03 package [44]. The transition state search was performed by employing the *Synchronous Transit-Guided Quasi-Newton* (STQN) method [45, 46] incorporated in the GAUSSIAN03 package. It uses a linear synchronous transit or quadratic synchronous transit approach to get closer to the quadratic region around the transition state and then uses a quasi-Newton or eigenvector-following algorithm to complete the optimization. It performs optimizations by default using redundant internal coordinates. This method will converge efficiently to the actual transition structure using an empirical estimate of the Hessian and suitable starting structures. 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

Celani et al. [3] investigated the prototypical electrocyclic photoreaction from cyclohexadiene (CHD) to all-cis hexatriene (cZc-HXT). They found that after the excitation to the Franck-Condon region on the excited state surface, the system decends to the pericyclic minimum, and funnels to the ground state potential surface through the conical intersection (CIX) region, where the ground and excited state surfaces are nearly degenerate. Form the CIX region they suggested three possible routes for electron recoupling process: Route1 to the closed CHD, Route2 to the open cZc-HXT and Route3 to the ground-state methylcyclopentene diradical (MCPD) intermediate. They stated that the MCPD intermediate is unstable which may undergo ground state reactivity to form methylenecyclopentene via 1,2-H shift or bicyclohexane (BCH) via radical pairing. Later Irie et al proposed two different schemes to describe the formation of byproduct in 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, based on the recoupling process suggested above. Following the same lead, we hypothesized a possible scheme to investigate the fatigue resistant of PFC-2 and PFC-2a (**Fig.2**). From our calculations we can define two different routes to form the by-product: thermal and photochemical. The thermal by-product pathway involves the bicyclohexane (BCH) ring formation as a stable intermediate; while the photochemical by-product formation pathway may involve the MCPD intermediate. An energy profile diagram depicting the transition state scheme for the by-product formation (**Scheme 1**) was construsted from the above hypothesis.



Scheme 1. Energy profile for thermal cycloreversion and the by-product formation

In the **Scheme 1**, the TS1 corresponds to the transition state between the open and closed forms. TS2 and TS3 are the transition states between the thermal pathway from the closed form to BCH and from BCH to the byproduct respectively.

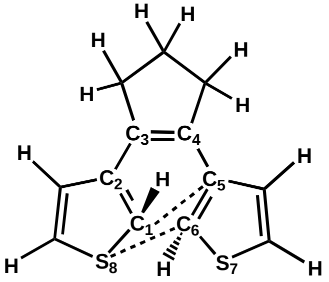


Fig. 3. Simpler prototype for STQN search calculations

The two transition state structures TS2 and TS3 from open and closed forms were evaluated employing the STQN method by using the QST2 method on a simple prototype of the perflourocyclopentene (**Fig.3**). These transition states correspond to simultaneous bond formation and breaking for the formation of the by-product from either of the isomers. The transition state TS2 corresponds to the concurrent C1-C5 bond formation and C1-S8 bond breaking leading to the BCH intermediate at a barrier of 51.2 kcal/mol at M052x/6-31G* level. The formation of C6-S8 bond and breaking of C5-C6 bond corresponds to the TS3 transition state between the BCH intermediate and the by-product at a barrier of 16.2kcal/mol at M052x/6-31G* level. **Table 1** gives the values of the energy barriers for thermal cycloreversion and the by-product formation processes evaluated at B3LYP and M052x level of energies for PFC-2, PFC2-a and PFC-1d.

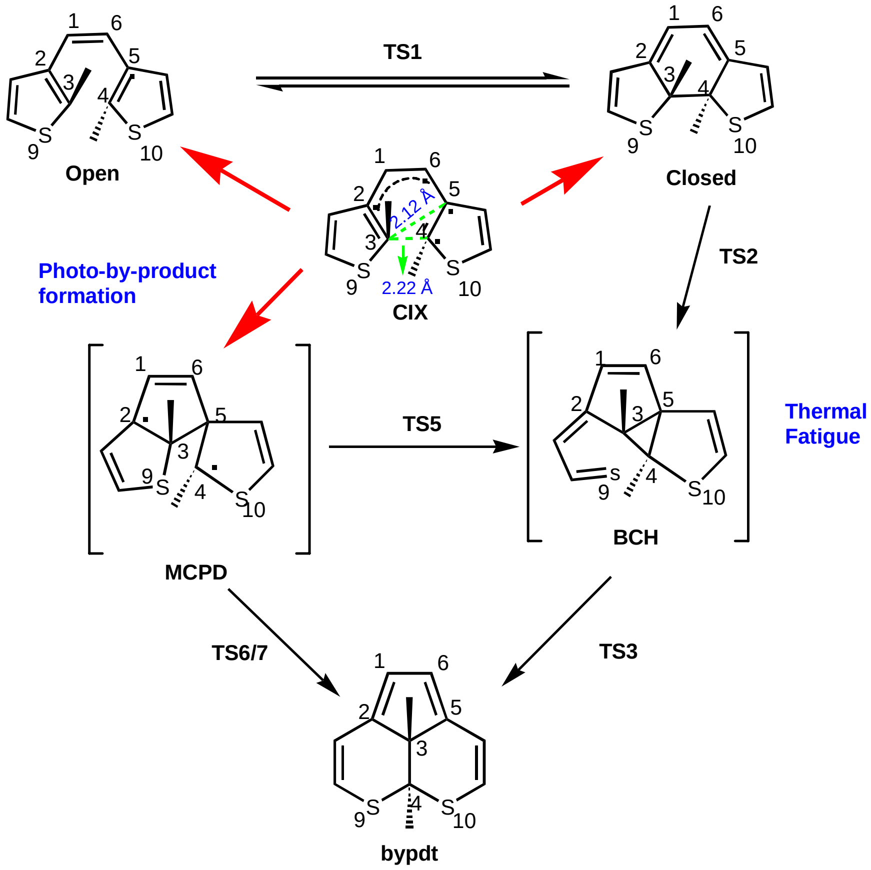
Table 1. Energy barriers for thermal cycloreversion and thermal by-product formation processes evaluated at UB3LYP and UM052x level of energies for PFC-2, PFC-2a and PFC-1d in kcal/mol.

	PFC-2			PFC-2a			PFC-1d		
Barrier	TS1	TS2	TS3	TS1	TS2	TS3	TS1	TS2	TS3
Experiment	33.2								
UM052x/6-31G*	38.2	53.4	17.3	39.6	52.5	22.1	42.3	55.8	16.7
UM052x/6-31G*(ZPE corr)	35.3	51.2	16.2	36.9	49.9	21.2	39.3	53.3	16.0
UB3LYP/MidiX	35.4	57.6		39.3	57.5	15.0	39.5	59.4	6.3
UB3LYP/MidiX(ZPE corr)	32.8	55.1		36.5	54.8	14.2	36.3	56.7	5.5
UB3LYP/6-31G*	33.3	45.9		36.0	46.7	20.0	37.1	47.7	11.3
UB3LYP/6-31G*(ZPE corr)	30.6	43.9		33.3	44.1	19.1	34.1	45.1	10.4

Scheme 2 depicts the thermal as well photochemical formation of the byproduct. According to the experimental procedures of Irie et al.,[12, 41] the formation of the byproduct is a photochemical process. This involves the presence of the conical intersection (CIX).

4 Conclusions

The mechanism and kinetics of the by-product formation for 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (PFC-2) is investigated using Density Functional Theory methods to predict the fatigue resistance of this molecule. We propose a mechanism leading from the conical intersection to the biradical intermediate, and then through the sinchronious transition state to the by-product. The activation energies corresponding to this transition state explains higher fatigue resistance for the methylated derivative PFC-2a. This protocol may become a part of the rational design strategy for the new photochromic materials used in phhtoswitching and optical data storage applications.



Scheme 2. Proposed mechanistic routes for thermal and photochemical byproduct formation in dithioethylene derivatives

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References

1. Irie, M., *Photochromism: Memories and switches - Introduction.* Chemical Reviews, 2000. **100**(5): p. 1683-1683.
2. Hoffmann, R. and R.B. Woodward, *Selection rules for concerted cycloaddition reactions.* Journal of the American Chemical Society, 1965. **87**(9): p. 2046-&.
3. 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.
4. 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.
5. 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.
6. 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.
7. 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.
8. 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.
9. 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.
10. 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.
11. Irie, M., *Photochromism of diarylethene single crystals and single molecules.* Molecular Crystals and Liquid Crystals, 2005. **430**: p. 1-+.
12. Irie, M., et al., *Fatigue resistant properties of photochromic dithienylethenes: by-product formation.* Chemical Communications, 1999(8): p. 747-748.
13. Irie, M. and M. Mohri, *Thermally irreversible photochromic systems - reversible photocyclization of diarylethene derivatives.* Journal of Organic Chemistry, 1988. **53**(4): p. 803-808.
14. 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.
15. 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.
16. Kobatake, S., et al., *Single-crystalline photochromism of diarylethenes: reactivity-structure relationship.* Chemical Communications, 2002(23): p. 2804-2805.
17. 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.
18. 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.

19. 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.
20. Nakamura, S. and M. Irie, *Thermally irreversible photochromic systems - a theoretical-study.* Journal of Organic Chemistry, 1988. **53**(26): p. 6136-6138.
21. 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.
22. Uchida, K. and M. Irie, *Photochromic reactions of bis(2-thienyl) perfluorocyclopentenes.* Journal of Information Recording, 1998. **24**(1-2): p. 101-104.
23. Uchida, K., et al., *Substituent effect on the photochromic reactivity of bis(2-thienyl)perfluorocyclopentenes.* Tetrahedron, 2001. **57**(21): p. 4559-4565.
24. 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.
25. 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.
26. 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.
27. 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.
28. 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.
29. 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.
30. 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.
31. 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.
32. 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.
33. 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.
34. 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.
35. 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.
36. 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.
37. 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.
38. 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.

39. 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.
40. 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.
41. Higashiguchi, K., et al., *Fatigue mechanism of photochromic 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene.* Bulletin of the Chemical Society of Japan, 2000. **73**(10): p. 2389-2394.
42. Bartolotti, L.J.F.K., *Reviews in Computational Chemistry*, ed. B.D. Lipkowitz KB. 1996, New York: VCH Publishers.
43. Parr, R.G.Y., Weitao T., *Density Functional Theory of Atoms and Molecules*. 1989, New York: Oxford University Press.
44. Frisch, M.J., et al., *Gaussian 2003*. 2004, Gaussian, Inc.: Wallingford CT.
45. Peng, C.Y., et al., *Using redundant internal coordinates to optimize equilibrium geometries and transition states.* Journal of Computational Chemistry, 1996. **17**(1): p. 49-56.
46. Peng, C.Y. and H.B. Schlegel, *Combining Synchronous Transit and Quasi-Newton Methods to Find Transition-States.* Israel Journal of Chemistry, 1993. **33**(4): p. 449-454.