

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231647337>

Theoretical Study of Photochromic Compounds: Part 3. Prediction of Thermal Stability

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · MAY 2011

Impact Factor: 4.77 · DOI: 10.1021/jp200980v

CITATIONS

37

READS

43

2 AUTHORS:



Pansy D. Patel

University of Kansas

13 PUBLICATIONS 234 CITATIONS

SEE PROFILE



Artem E. Masunov

University of Central Florida

147 PUBLICATIONS 2,539 CITATIONS

SEE PROFILE

Theoretical Study of Photochromic Compounds: Part 3. Prediction of Thermal Stability

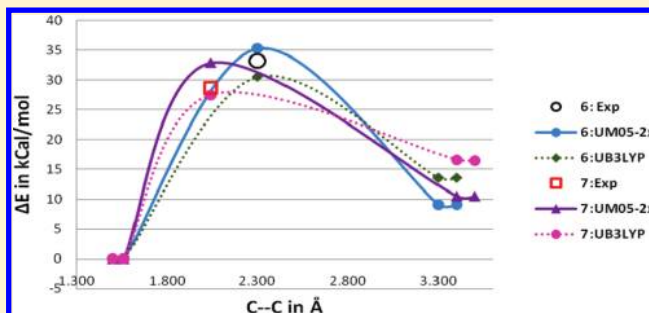
Pansy D. Patel^{†,‡} and Artëm E. Masunov^{*,§,⊥,¶,‡}

[†]Department of Chemistry, Yale University, New Haven, Connecticut 06511, United States

[‡]Gaussian Inc, Wallingford, Connecticut 06492, United States

[§]NanoScience Technology Center, [⊥]Department of Chemistry, [¶]Department of Physics, [‡]Florida Solar Energy Center, 12424 Research Parkway, Suite 400, University of Central Florida, Orlando, Florida 32826, United States

ABSTRACT: Diarylethene derivatives are known to be photochromic, that is, upon irradiation they change their color because of ultrafast photocyclization. Their proposed use as nonvolatile data storage materials requires the cycloreversion process to be very slow in the dark. We apply density functional theory (DFT) methods to predict kinetics of thermal cycloreversion. The cycloreversion occurs through symmetry forbidden conrotatory electrocyclic mechanism with transition state of strong diradical character and requires the use of unrestricted broken-symmetry DFT formalism. Our results suggest that B3LYP and M05-2X are the best functionals to describe kinetics in these compounds (accurate to within 3–4 kcal/mol from the experimental values). The methods validated in this study show great promise as tools in rational design of the improved photochromic materials.



1. INTRODUCTION

Photochromism is a light-initiated, nondestructive process resulting in reversible transformation between two isomeric forms. In the case of photochromic compounds undergoing electrocyclic reactions, the two isomers correspond to closed and open conformers (Figure 1a). Diarylethenes (DA) (Figure 1b) with heterocyclic aryl groups are a class of thermally irreversible (P-type) photochromic compounds, which means that the reversible cycloreversion occurs in the dark.¹

The ability to repeat about 10^4 coloration/decoloration cycles, termed as fatigue resistance, is significant for its photochromic performance. This property has been studied experimentally,^{2,3} and a mechanism based on some theoretical work was proposed for 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene by Higashiguchi et al.² Recently, we performed state-of-the-art theoretical calculations to investigate the mechanism of thermal fatigue in photochromic compounds.⁴ Our results suggest the existence of a bicyclohexyl (BCH) intermediate during the transformation process between the closed form and the byproduct.

Fatigue resistance and thermal stability of both closed and open isomers are indispensable properties for applications of DAs for optoelectronic devices. According to Irie and Mohri, the molecular design principle of thermally irreversible DAs is the heterocyclic aryl group.^{5,6} In particular to DAs, experiments have suggested that the thermal stability depends on the aryl group substitutions, and it is their aromatic stabilization energies which allow conrotatory cycloreversion and, hence, which make the closed ring isomer thermally unstable. It was found that in the case of low aromatic stabilization aryl groups like furan,

thiophene, selenophene, or thiazole rings, the closed isomers are thermally stable and do not return to the open-ring form isomers even at 80 °C. In the case of pyrrole, indole, or phenyl rings having high aromatic stabilization energies, the closed isomers are thermally unstable.^{5,6}

Over the past three decades, Irie and co-workers have extensively worked on designing dual-mode optical molecular switches both experimentally^{3,6–21} and theoretically.^{22–28} Lehn et al. have also synthesized photochromic compound as potential molecular optical switches and have investigated the thermal stability as a measure of their half-life time at elevated temperatures.^{29–34} In the present work, we have employed unrestricted density functional theory (DFT) formalism to investigate the activation barriers for cycloreversion of a set of seven photochromic compounds, where experimental data were available.

2. THEORY

In diarylethenes, the closed to open unimolecular cycloreversion photochromic process occurs through conrotatory electrocyclic mechanism and forms a symmetry forbidden diradical transition state along the reactive C–C bond. This stereoselective process can be easily understood by the Woodward–Hoffmann rules.³⁵ During conrotatory cyclization, the molecular orbitals (MOs) undergo continuous evolution to conserve symmetry, the occupied orbitals of the reactant evolve into the vacant orbitals

Received: January 29, 2011

Revised: March 10, 2011

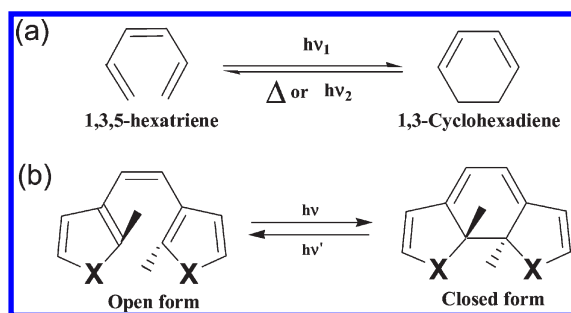


Figure 1. Photochromic reversible transformation of (a) hexatriene and cyclohexadiene and (b) diarylethene compounds ($X = S, O, Se$).

of the product, and vice versa. This is the case of photochemically allowed and thermally forbidden (large activation barrier in the ground state) cyclization reaction.

Photochemical conversion in the model system of cyclohexadiene (CHD) and 1,3,5-hexatriene (cZc-HT) has been studied extensively by various research groups using ab-initio methods like CAS-SCF and CAS-SCF/MP2,^{36,37} CASPT2,³⁸ and MR-SCI³⁹ theory levels to investigate the potential energy surface and to find the reaction path and the transition probabilities. Because of constraints like large computational demands, the correlated wave function theory methods cannot be performed on the larger molecules of practical interest. Nakamura and Irie have performed semiempirical calculations on furyl, pyrrolyl, and thienyl molecular systems to study the effect of aryl ring on thermal stability and have concluded that the energy barrier in the case of the thienyl derivative was the largest, which makes the cycloreversion reaction less likely.¹³ For those molecules, semiempirical and time-dependent density functional theory (TD-DFT) studies had been reported. The thermal stability of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride was studied using semiempirical Austin Model 1 (AM1) methods by Cho and Cheong.⁴⁰ The first excited state was calculated using configuration interaction with single substitutions (CIS, MOPAC keyword “excited”).

Using semiempirical Hamiltonian INDO/S in combination with coupled electronic oscillator (CEO) formalism,^{41,42} Ern et al. explained that the precursor for the slow conversion for ring-opening process in DA derivatives corresponds to the pericyclic minimum on the excited-state potential surface into the ground-state products by the presence of the potential barrier separating this minimum from the conical intersection to the ground state.⁴³ Majumdar et al. used time-dependent density functional theory (TD-DFT) and reported the open and closed structures, stability, electronic absorption spectra, and hyperpolarizabilities for DA derivatives.⁴⁴

The source of these problems was traced⁴⁵ to 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 nondegenerate cases. The transition state in the case of cycloreversion/cyclization of diarylethenes has a strong diradical character, and RKS formalism fails to describe it. However, static (also called left–right) electron correlation can be taken into account by introducing different orbitals for different spin. This approach, often referred to as broken symmetry or unrestricted Kohn–Sham formalism (UKS), is known to yield a qualitatively correct description of the bond breaking.⁴⁶ In the present paper, we investigate the accuracy of unrestricted DFT calculations in

prediction of the ground-state energy barriers to cycloreversion and byproduct formation in diarylethene derivatives.

3. COMPUTATIONAL DETAILS

Complete geometry optimizations and harmonic frequency calculations of the reactants, products, and transition states of the benchmark set of diarylethene derivatives (Figure 2) were performed using Gaussian 2003 Rev. E program package.⁴⁷ The transition-state search was performed by using Opt=TS keyword using Berny algorithm⁴⁸ to optimize to a transition state rather than a local minimum. Each stationary point was characterized by the number of imaginary frequencies (NImag = 1 for transition state and NImag = 0 for the local minimum) and by zero point vibrational energies (ZPE). To follow unrestricted Kohn–Sham solution, the broken-symmetry guess was generated and followed using keyword Guess (mix, always). This allows the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) to be mixed, and this removes the α, β spatial symmetries and also generates a new initial guess at each step of the optimization. Different levels of density functional theory (DFT)⁴⁹ were used. Hybrid exchange–correlation functionals including various fractions of Hartree–Fock (HF) exchange were used (20% for B3LYP,^{50–52} 42% for BMK,⁵³ and 56% for M05-2X⁵⁴) in combination with MIDI! and 6-31G* basis sets. The stability of the Kohn–Sham orbitals was tested before and after geometry optimization using the keyword Stable=Opt. If cases where instability was found, the geometry optimization was repeated with the stable set of orbitals used as the initial guess.

4. RESULTS AND DISCUSSION

4.1. Kinetics of Thermal Cycloreversion. For this study, we selected a benchmark set of diarylethene perfluorocyclopentenes (Figure 3) for which thermal cycloreversion kinetics data is available from the literature.^{3,9,31,55,56} Experiments have suggested that thermal stability of the diarylethenes depends on the specific aryl substituents. Their aromatic stabilization energies allow conrotatory cycloreversion and hence make the closed ring isomer thermally unstable. The half-lives for the thermal opening process at elevated temperatures were reported in the literature.^{3,5,9,31,55,56} The electrocyclic cycloreversion is unimolecular reaction. Therefore, for a given half-life ($t_{1/2}$), the rate constant is

$$k = \frac{\ln 2}{t_{1/2}} \quad (1)$$

Using eq 1 with the data published by Irie et al.⁵⁵ for **6** ($t_{1/2} = 3.3$ h at $T = 423$ K and $E_a = 139$ kJ/mol), we calculated the rate constant to be $k = -0.21$ h^{−1}. To estimate the activation barrier for these systems, we used Arrhenius equation

$$k = A \exp \frac{-E_a}{RT} \quad (2)$$

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. From **6** data at two temperatures, we calculate the pre-exponential factor A to be $-2.968 \cdot 10^{16}$. Since the cycloreversion process is a unimolecular process, we assumed the value of A to be similar for all the molecules in Figure 2, and we used

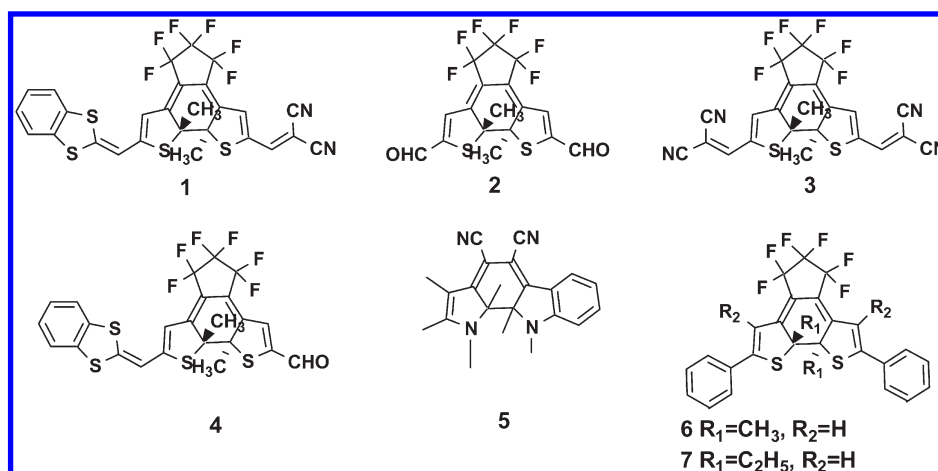


Figure 2. Benchmark set of molecules with documented thermal stability.

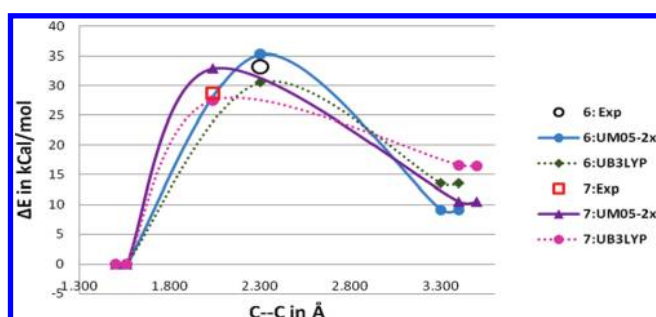


Figure 3. Comparison of the UM05-2X/6-31G* and UB3LYP/6-31G* calculated activation thermal energy barriers for cycloreversion in molecules 6 and 7 with experimental values.

Table 1. Experimental Activation Barriers^a for Thermal Cycloreversion Process from Closed to Open Isomers (1–7) Using the Arrhenius Equation

molecule	$t_{1/2}$ (min)	K (min ⁻¹)	E_a (kJ/mol)	E_a (kcal/mol)
1	573	−0.07	112.3	26.8
2	3.3	−12.60	98.0	23.4
3	16 300	−0.003	121.5	29.0
4	186	−0.224	109.2	26.1
5		−0.023	115.5	27.6
6	198	−0.210	139.0	33.2
7			120.0	28.7

^a 1–4: ref 31; 5: ref 56; 6: ref 3; 7: ref 9.

this value for the pre-exponential factor to calculate the experimental activation energy for other molecules whose $t_{1/2}$ was reported (Table 1),^{3,9,31,56} and we used those values to benchmark the theoretical predictions (Table 2).

4.2. Transition States to Cycloreversion Reaction. The transition states (TS) in thermally forbidden cycloreversion reactions are expected to have a strong diradical character. The Kohn–Sham or molecular orbital description of singlet diradical uses different orbitals for electrons of opposite spin (a pair of SOMO, singly occupied molecular orbital). The single determinant with a pair of SOMO is not an eigenvector of the spin operator. Instead, it is an equal mix of singlet and triplet spin states characterized by the average value of S^2 operator to be

close to 1 for all DFT functionals studied (not shown). However, AM1 and HF determinants remained unrestricted along the reaction path from the open to the closed form, while UKS solution was found to collapse to the restricted determinant soon after the system moved away from the TS. This discontinuity on the potential surface presented the main technical difficulty and required a new unrestricted guess on each optimization step with Guess(Always,Mix) keyword. To avoid this difficulty, we initially combined Unrestricted Hartree–Fock (UHF) or Unrestricted Austin Model 1 (UAM1) geometry with single-point energy evaluation at DFT level of theory. However, UHF geometry was found to be unsatisfactory at equilibrium (diradical-like) and was not considered further.

There are two distinct (and opposite) types of DFT errors for the description of transition states. The first type is the tendency of functionals to overstabilize transition states of radical reactions, and another is the static correlation error. Because of approximate treatment of the static electron correlation, density functionals tend to destabilize a strongly correlated system, which is why recourse must be made to the broken-symmetry wave functions that give incorrect spin densities but more correct energies for diradicals. The broken-symmetry dilemma⁵⁷ (correct spin density or correct energy) has a long history starting from the DFT description of the atomic terms.⁵⁸ This dilemma, however, is hardly an issue for the systems where bond dissociation occurs. It was firmly established that only broken-symmetry Kohn–Sham determinant can describe the homolytic bond breaking qualitatively correct, while the restricted formalism fails dramatically. Various methods to correct for spin-contamination were suggested.^{59–67} When the density functional designed for kinetics is constructed, its adjustable parameters are calibrated to reproduce the activation energies of the bond breaking in the training set consisting mostly of the small radical systems in their doublet state. Restricted formalism is not applicable for these systems, restricted open-shell method often suffers from the convergence problems, and unrestricted broken-symmetry approach remains the only choice. No spin-contamination correction is made during this calibration procedure, and higher spin-state mixing is simply ignored. Therefore, the same procedure should be used to calculate the activation barriers in the systems of interest if one would like to avoid systematic errors.

As one can see from the Table 2, the unrestricted KS methods (UB3LYP, UBMK, or UM05-2X) give lower energy for the

Table 2. Activation Barriers for Thermal Cycloreversion Process from Closed to Open Isomers (in kcal/mol)

	molecule							MAE ^b	rmsd ^c
	1	2	3	4	5	6	7		
exp ^a	26.8	23.4	29.0	26.1	27.6	33.2	28.7		
UB3LYP/Midi!	29.9	29.1	32.0	29.4	34.5	35.4	31.6	3.9	4.2
UB3LYP/Midi!(ZPE correction)	27.8	27.6	29.7	27.8	31.1	32.8	29.5	1.7	2.2
UB3LYP/Midi!(thermal correction)	27.7	27.5	29.8	27.7	31.6	32.8	29.5	1.8	2.3
UB3LYP/6-31G*	28.8	21.8	36.1	29.4	32.6	33.3	29.9	2.9	3.6
UB3LYP/6-31G*(ZPE correction)	26.8	19.8	35.1	27.6	29.3	30.6	27.5	2.4	3.0
UB3LYP/6-31G*(thermal correction)	26.8	19.9	34.7	27.5	29.8	30.8	27.6	2.3	2.9
UBMK/Midi!	37.1	32.4	38.7	35.8	40.5	43.5	41.5	10.7	10.8
UBMK/Midi!ZPE correction)	34.9	31.2	36.9	33.7	36.1	42.9	39.7	8.7	8.7
UBMK/Midi!(thermal correction)	36.7	30.9	36.5	33.7	37.1	42.5	39.7	8.9	9.0
UBMK/6-31G*	34.7	28.3	37.5	34.6	38.4	40.6	38.0	8.2	8.3
UBMK/6-31G*(ZPE correction)	32.6	26.0	34.5	33.0	34.8	38.4	34.9	5.6	5.8
UBMK/6-31G*(thermal correction)	32.5	26.6	34.6	32.8	35.4	38.4	35.3	5.8	6.0
UM052x/6-31G*	31.4	25.1	34.5	31.5	39.3	38.2	35.8	5.8	6.5
UM052x/6-31G*(ZPE correction)	29.3	22.8	32.1	29.4	35.6	35.3	32.9	3.4	4.0
UM052x/6-31G*(thermal correction)	29.2	22.8	30.0	29.3	36.2	35.1	32.6	3.1	4.0
RB3LYP/6-31G*/UB3LYP/6-31G*	31.3	24.1	34.2	30.4	38.9	37.4	34.2	5.1	5.9
RB3LYP/6-31G*/UB3LYP/6-31G*(ZPE correction)	29.8	22.6	33.2	29.0	35.8	35.2	32.1	3.5	4.1
RB3LYP/6-31G*/UB3LYP/6-31G*(thermal correction)	30.6	22.6	32.9	28.5	36.3	35.3	32.2	3.6	4.3
RM052x/6-31G*/UM052x/6-31G*	35.1	28.7	37.7	33.8	45.6	42.9	40.3	9.9	10.6
RM052x/6-31G*/UM052x/6-31G* (ZPE correction)	33.6	27.1	36.0	32.2	42.5	40.5	37.9	7.8	8.5
RM052x/6-31G*/UM052x/6-31G* (thermal correction)	33.4	27.1	35.3	29.3	42.9	40.8	38.3	7.5	8.4

^a 1–4: ref 31; 5: ref 56; 6: ref 3; 7: ref 9. ^b MAE: mean absolute error. ^c rmsd: root mean square deviation.

transition state than the restricted ones (RB3LYP or RM05-2X) and are closer to the experimental values in all cases. The root mean square deviations are 3, 4, and 6 kcal/mol for UB3LYP, UM05-2X, and UBMK, respectively. Both BMK and M05-2X are hybrid meta-exchange-correlation functionals designed for calculations of both thermochemistry and thermochemical kinetics. However, BMK gave a relatively poor result which is somewhat surprising. This can be explained by the fact that organic molecules were excluded from the training set during the calibration of BMK.⁵³ In contrast, M05-2X was shown to perform considerably better than other functionals for a wide range of organic reactions and molecular properties.⁵⁴ The systematic plot of the comparison of the calculated activation energy barrier for thermal cycloreversion process in two of the benchmark molecules 6 and 7 with their corresponding experimental barriers (Figure 3) suggested that UM05-2X functional overestimates the experimental barriers by ~2–4 kcal/mol. On the other hand, UB3LYP method underestimates the barrier. As a part of our ongoing investigation, we found that M05-2X also results in improved predictions of the excited-state potential surfaces.⁴⁵ For these reasons, we use M05-2X functional in the rest of this study.

5. CONCLUSIONS

The kinetics of cycloreversion was studied for the benchmark set of seven diarylethene derivatives using density functional theory methods. The activation energies were calculated from the published experimental data on the basis of 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 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 formalism and the use of zero-point energy correction were important to achieve better agreement with experiment. Our results suggest that B3LYP and M05-2X functionals predict the activation barrier for the cycloreversion reaction within 3–4 kcal/mol from experimental value, while BMK overestimates it by 6 kcal/mol on average. The M05-2X hybrid functional is currently being used to predict the quantum yield for a set of diarylethene derivatives.

AUTHOR INFORMATION

Corresponding Author

*E-mail: amasunov@knights.ucf.edu.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation Grants No. CCF 0740344 and CHE 0832622. 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

- (1) Bouas-Laurent, H.; Durr, H. Organic photochromism. *Pure Appl. Chem.* **2001**, 73 (4), 639–665.
- (2) Higashiguchi, K.; Matsuda, K.; Kobatake, S.; Yamada, T.; Kawai, T.; Irie, M. Fatigue mechanism of photochromic 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene. *Bull. Chem. Soc. Jpn.* **2000**, 73 (10), 2389–2394.

- (3) Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. Fatigue resistant properties of photochromic dithienylethenes: by-product formation. *Chem. Commun.* **1999**, 8, 747–748.
- (4) Patel, P. D.; Mikhailov, I. A.; Belfield, K. D.; Masunov, A. E. Theoretical Study of Photochromic Compounds, Part 2: Thermal Mechanism for Byproduct Formation and Fatigue Resistance of Diarylethenes Used as Data Storage Materials. *Int. J. Quantum Chem.* **2009**, 109, 3711–3722.
- (5) Irie, M. Photochromism: Memories and switches - Introduction. *Chem. Rev.* **2000**, 100 (5), 1683–1683.
- (6) Irie, M.; Mohri, M. Thermally Irreversible Photochromic Systems - Reversible Photocyclization of Diarylethene Derivatives. *J. Org. Chem.* **1988**, 53 (4), 803–808.
- (7) Irie, M. Photochromism of diarylethene single crystals and single molecules. *Mol. Cryst. Liq. Cryst.* **2005**, 430, 1 ff.
- (8) Kobatake, S.; Matsumoto, Y.; Irie, M. Conformational control of photochromic reactivity in a diarylethene single crystal. *Angew. Chem., Int. Ed.* **2005**, 44 (14), 2148–2151.
- (9) Kobatake, S.; Shibata, K.; Uchida, K.; Irie, M. 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. *J. Am. Chem. Soc.* **2000**, 122 (49), 12135–12141.
- (10) Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. Single-crystalline photochromism of diarylethenes: reactivity-structure relationship. *Chem. Commun.* **2002**, 23, 2804–2805.
- (11) Kobatake, S.; Yamada, T.; Uchida, K.; Kato, N.; Irie, M. Photochromism of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene in a single crystalline phase. *J. Am. Chem. Soc.* **1999**, 121 (11), 2380–2386.
- (12) Matsuda, K.; Irie, M. Diarylethene as a photo switching unit. *J. Photochem. Photobiol., C: Photochem. Rev.* **2004**, 5 (2), 169–182.
- (13) Nakamura, S.; Irie, M. Thermally Irreversible Photochromic Systems - A Theoretical-Study. *J. Org. Chem.* **1988**, 53 (26), 6136–6138.
- (14) Saita, K.; Kobatake, S.; Fukaminato, T.; Nanbu, S.; Irie, M.; Sekiya, H. Raman spectroscopic study on isomers of photochromic 1,2-bis(2,5-dimethyl-3-thienyl) perfluorocyclopentene in crystal and stability of the closed-ring forms in the open-ring forms. *Chem. Phys. Lett.* **2008**, 454 (1–3), 42–48.
- (15) Uchida, K.; Kido, Y.; Yamaguchi, T.; Irie, M. Thermally irreversible photochromic systems. Reversible photocyclization of 2-(1-benzothiophen-3-yl)-3-(2 or 3-thienyl)maleimide derivatives. *Bull. Chem. Soc. Jpn.* **1998**, 71 (5), 1101–1108.
- (16) Uchida, K.; Nakamura, S.; Irie, M. Thermally Irreversible Photochromic Systems - Substituent Effect on the Absorption Wavelength of 11,12-Dicyano-5A,5B-Dihydro-5A,5B-dimethylbenzo(1,2-B:6,5-B')bis[1]benzo Thiophene. *Bull. Chem. Soc. Jpn.* **1992**, 65 (2), 430–435.
- (17) Uchida, K.; Nakayama, Y.; Irie, M. Thermally Irreversible Photochromic Systems - Reversible Photocyclization of 1,2-Bis(benzo[b]thiophen-3-yl)ethene Derivatives. *Bull. Chem. Soc. Jpn.* **1990**, 63 (5), 1311–1315.
- (18) Yamada, T.; Kobatake, S.; Irie, M. Single-crystalline photochromism of diarylethene mixtures. *Bull. Chem. Soc. Jpn.* **2002**, 75 (1), 167–173.
- (19) Yamada, T.; Muto, K.; Kobatake, S.; Irie, M. Crystal structure-reactivity correlation in single-crystalline photochromism of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene. *J. Org. Chem.* **2001**, 66 (18), 6164–6168.
- (20) Yamaguchi, T.; Takami, S.; Irie, M. Photochromic properties of 1,2-bis(6-substitute-2-methyl-1-benzofuran-3-yl) ethene derivatives. *J. Photochem. Photobiol., A: Chem.* **2008**, 193 (2–3), 146–152.
- (21) Yamaguchi, T.; Uchida, K.; Irie, M. Photochromic properties of diarylethene derivatives having benzofuran and benzothiophene rings based on regioisomers. *Bull. Chem. Soc. Jpn.* **2008**, 81 (5), 644–652.
- (22) Abe, Y.; Okada, S.; Horii, T.; Nakao, R.; Irie, M. MNDO-PM3MO studies on the thermal enantiomerization of 1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline]. *Mol. Cryst. Liq. Cryst.* **2000**, 345, 419–424.
- (23) Asano, Y.; Murakami, A.; Kobayashi, T.; Goldberg, A.; Guillaumont, D.; Yabushita, S.; Irie, M.; Nakamura, S. Theoretical study on the photochromic cycloreversion reactions of dithienylethenes; on the role of the conical intersections. *J. Am. Chem. Soc.* **2004**, 126 (38), 12112–12120.
- (24) Asano, Y.; Murakami, A.; Kobayashi, T.; Kobatake, S.; Irie, M.; Yabushita, S.; Nakamura, S. Theoretical study on novel quantum yields of dithienylethenes cyclization reactions in crystals. *J. Mol. Struct.: THEOCHEM* **2003**, 625, 227–234.
- (25) Guillaumont, D.; Kobayashi, T.; Kanda, K.; Miyasaka, H.; Uchida, K.; Kobatake, S.; Shibata, K.; Nakamura, S.; Irie, M. An ab initio MO study of the photochromic reaction of dithienylethenes. *J. Phys. Chem. A* **2002**, 106 (31), 7222–7227.
- (26) Uchida, K.; Guillaumont, D.; Tsuchida, E.; Mochizuki, G.; Irie, M.; Murakami, A.; Nakamura, S. Theoretical study of an intermediate, a factor determining the quantum yield in photochromism of diarylethene derivatives. *J. Mol. Struct.: THEOCHEM* **2002**, 579, 115–120.
- (27) Yoshioka, Y.; Irie, M. Ab initio study of 3-furyl fulgide. 1. Molecular structures and relative stabilities of three isomers. *Electron. J. Theor. Chem.* **1996**, 1, 183–190.
- (28) Yoshioka, Y.; Irie, M. Ab initio study of 3-furyl fulgide. 2. Substituent effects on photochemical reactions. *Electron. J. Theor. Chem.* **1996**, 1, 191–198.
- (29) Gilat, S. L.; Kawai, S. H.; Lehn, J. M. Light-Triggered Electrical and Optical Switching Devices. *J. Chem. Soc., Chem. Commun.* **1993**, No. 18, 1439–1442.
- (30) Gilat, S. L.; Kawai, S. H.; Lehn, J. M. Light-Triggered Electrical and Optical Switching Devices. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A: Mol. Cryst. Liq. Cryst.* **1994**, 246, 323–326.
- (31) Gilat, S. L.; Kawai, S. H.; Lehn, J. M. Light-Triggered Molecular Devices - Photochemical Switching of Optical and Electrochemical Properties in Molecular Wire Type Diarylethene Species. *Chem.—Eur. J.* **1995**, 1 (5), 275–284.
- (32) Kawai, S. H.; Gilat, S. L.; Lehn, J. M. Dual-Mode Optical-Electrical Molecular Switching Device. *J. Chem. Soc., Chem. Commun.* **1994**, 8, 1011–1013.
- (33) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J. M.; Dual-Mode, A Molecular Switching Device - Bisphenolic Diarylethenes with Integrated Photochromic and Electrochromic Properties. *Chem.—Eur. J.* **1995**, 1 (5), 285–293.
- (34) Tsigoulis, G. M.; Lehn, J. M. Photonic Molecular Devices - Reversibly Photoswitchable Fluorophores for Nondestructive Readout for Optical Memory. *Angew. Chem., Int. Ed. Engl.* **1995**, 34 (10), 1119–1122.
- (35) Hoffmann, R.; Woodward, R. B. Selection Rules for Concerted Cycloaddition Reactions. *J. Am. Chem. Soc.* **1965**, 87, (9), 2046 ff.
- (36) Celani, P.; Ottani, S.; Olivucci, M.; Bernardi, F.; Robb, M. A. What Happens During The Picosecond Lifetime of 2A(1) Cyclohexa-1,3-diene - A CAS-SCF Study of The Cyclohexadiene Hexatriene Photochemical Interconversion. *J. Am. Chem. Soc.* **1994**, 116 (22), 10141–10151.
- (37) Celani, P.; Bernardi, F.; Robb, M. A.; Olivucci, M. Do photochemical ring-openings occur in the spectroscopic state? B-1(2) pathways for the cyclohexadiene/hexatriene photochemical interconversion. *J. Phys. Chem.* **1996**, 100 (50), 19364–19366.
- (38) Garavelli, M.; Page, C. S.; Celani, P.; Olivucci, M.; Schmid, W. E.; Trushin, S. A.; Fuss, W. Reaction path of a sub-200 fs photochemical electrocyclic reaction. *J. Phys. Chem. A* **2001**, 105 (18), 4458–4469.
- (39) Tamura, H.; Nanbu, S.; Nakamura, H.; Ishida, T. A theoretical study of cyclohexadiene/hexatriene photochemical interconversion: multireference configuration interaction potential energy surfaces and transition probabilities for the radiationless decays. *Chem. Phys. Lett.* **2005**, 401 (4–6), 487–491.
- (40) Cho, H. G.; Cheong, B. S. Theoretical investigation of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride: A thermally irreversible photochromic system. *Bull. Kor. Chem. Soc.* **1998**, 19 (3), 308–313.

- (41) Ern, J.; Bens, A.; Martin, H. D.; Mukamel, S.; Schmid, D.; Tretiak, S.; Tsiper, E.; Krysch, C. Femtosecond Reaction Dynamics of a Photochromic Dithienylethene Derivative. *J. Lumin.* **2000**, *87–9*, 742–744.
- (42) Ern, J.; Bens, A. T.; Martin, H. D.; Mukamel, S.; Tretiak, S.; Tsyganenko, K.; Kuldova, K.; Trommsdorff, H. P.; Krysch, C. Reaction dynamics of a photochromic fluorescing dithienylethene. *J. Phys. Chem. A* **2001**, *105* (10), 1741–1749.
- (43) Ern, J.; Bens, A. T.; Martin, H. D.; Mukamel, S.; Schmid, D.; Tretiak, S.; Tsiper, E.; Krysch, C. Reaction dynamics of photochromic dithienylethene derivatives. *Chem. Phys.* **1999**, *246* (1–3), 115–125.
- (44) Majumdar, D.; Lee, H. M.; Kim, J.; Kim, K. S.; Mhin, B. J. Photoswitch and nonlinear optical switch: Theoretical studies on 1,2-bis-(3-thienyl)-ethene derivatives. *J. Chem. Phys.* **1999**, *111* (13), 5866–5872.
- (45) Mikhailov, I. A.; Belfield, K. D.; Masunov, A. E. DFT-based Methods in the Design of Two-Photon Operated Molecular Switches. *J. Phys. Chem. A* **2009**, *113*, 7080–7089.
- (46) Gunnarsson, O.; Lundqvist, B. I. Exchange and Correlation in Atoms, Molecules, and Solids by Spin-Density Functional Formalism. *Phys. Rev. B* **1976**, *13* (10), 4274–4298.
- (47) Frisch, M. J.; Trucks, G.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian03*, rev. E; Gaussian, Inc.: Wallingford, CT, 2003.
- (48) Schlegel, H. B. Optimization of Equilibrium Geometries and Transition Structures. *J. Comput. Chem.* **1982**, *3*, 214–218.
- (49) Parr, R. G. Y.; Weitao, T. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- (50) Becke, A. D. Density-Functional Thermochemistry. 3. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652.
- (51) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti Correlation Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1988**, *37* (2), 785–789.
- (52) Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation-Energy. *Phys. Rev. B* **1992**, *45* (23), 13244–13249.
- (53) Boese, A. D.; Martin, J. M. L. Development of density functionals for thermochemical kinetics. *J. Chem. Phys.* **2004**, *121* (8), 3405–3416.
- (54) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions. *J. Chem. Theory Comput.* **2006**, *2* (2), 364–382.
- (55) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. Photochromism of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in a single-crystalline phase. *J. Am. Chem. Soc.* **2000**, *122* (20), 4871–4876.
- (56) Nakayama, Y.; Hayashi, K.; Irie, M. Thermally Irreversible Photochromic Systems - Reversible Photocyclization of Nonsymmetrical Diarylethene Derivatives. *Bull. Chem. Soc. Jpn.* **1991**, *64* (3), 789–795.
- (57) Perdew, J. P.; Savin, A.; Burke, K. Escaping The Symmetry Dilemma Through a Pair-Density Interpretation of Spin-Density Functional Theory. *Phys. Rev. A* **1995**, *51* (6), 4531–4541.
- (58) Ziegler, T.; Rauk, A.; Baerends, E. J. Calculation of Multiplet Energies by Hartree-Fock-Slater Method. *Theor. Chim. Acta* **1977**, *43* (3), 261–271.
- (59) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110* (13), 6158–6170.
- (60) Baker, J.; Pulay, P. Assessment of the OLYP and O3LYP density functionals for first-row transition metals. *J. Comput. Chem.* **2003**, *24* (10), 1184–1191.
- (61) Barone, V.; Adamo, C. First-row transition-metal hydrides: A challenging playground for new theoretical approaches. *Int. J. Quantum Chem.* **1997**, *61* (3), 443–451.
- (62) Barone, V.; Adamo, C.; Mele, F. Comparison of conventional and hybrid density functional approaches. Cationic hydrides of first-row transition metals as a case study. *Chem. Phys. Lett.* **1996**, *249* (3–4), 290–296.
- (63) Diaconu, C. V.; Cho, A. E.; Doll, J. D.; Freeman, D. L. Broken-symmetry unrestricted hybrid density functional calculations on nickel dimer and nickel hydride. *J. Chem. Phys.* **2004**, *121* (20), 10026–10040.
- (64) Goel, S.; Masunov, A. E. Potential energy curves and electronic structure of 3d transition metal hydrides and their cations. *J. Chem. Phys.* **2008**, *129* (21), 14.
- (65) Riley, K. E.; Merz, K. M. Assessment of density functional theory methods for the computation of heats of formation and ionization potentials of systems containing third row transition metals. *J. Phys. Chem. A* **2007**, *111* (27), 6044–6053.
- (66) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. Density functionals for inorganometallic and organometallic chemistry. *J. Phys. Chem. A* **2005**, *109* (49), 11127–11143.
- (67) Ziegler, T.; Li, J. Bond-Energies for Cationic Bare Metal-hydrides of the First Transition Series - A Challenge to Density-Functional Theory. *Can. J. Chem., Rev. Can. Chim.* **1994**, *72* (3), 783–789.