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Theoretical Study of Photochromic Compounds, Part 2: Thermal Mechanism for Byproduct Formation and Fatigue Resistance of Diarylethenes Used as Data Storage Materials

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ABSTRACT: Certain organic compounds possess the ability to change color under the influence of light, called photochromism. This change is due to ultrafast chemical transition from open to closed ring isomers (photocyclization), which can be used for optical data storage and photoswitching applications. These applications require minimization of the irreversible photodegradation of the material, called photofatigue. This property is related to the chemical rate of byproduct formation. We use density functional theory methods to predict the mechanism and activation barriers to the byproduct formation for 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in order to estimate its fatigue resistance. We also explain higher fatigue resistance for its methylated derivative. The methods used in this study may become a part of rational design strategy for the new photochromic materials. © 2009 Wiley Periodicals, Inc. *Int J Quantum Chem* 109: 3711–3722, 2009

Key words: electrocyclic reaction; chemical kinetics; byproduct formation; fatigue resistance

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1. Introduction

Photochromism is a nondestructive process involving light initiated rearrangement of chemical bonds accompanied by the change in color and other properties. It often results in a 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 (HT) (open isomer) (Fig. 1).

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 of P-type compounds are diarylethenes and fulgides (Fig. 2).

The thermal stability of P-type compounds makes them promising materials in designing of various optoelectronic devices such as optical memory, optical switching, displays, and nonlinear optics. For practical use, the photochromic material has to satisfy certain requirements including (1) thermal stability of both isomers; (2) fatigue resistance; (3) efficient photochromic reactivity: high sensitivity and rapid response; (4) high solubility in polymer matrices; (5) nondestructive readout capability; (6) sensitivity at diode laser wavelengths [2]. In our previous communication [3], we reported a benchmark study of the maximum absorption wavelengths, a property related to the last requirement. In this work, we focus on the second requirement, related to the low rate of the byproduct formation.

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, 4–7]. Over the years, Irie and coworkers reported on their extensive efforts to design dual-mode optical molecular switching materials both experimentally [2, 4, 5, 8–24] and theoretically [25–31]. Lehn and coworkers [7, 32–36] have also synthesized photochromic compounds as potential molecular optical switches.

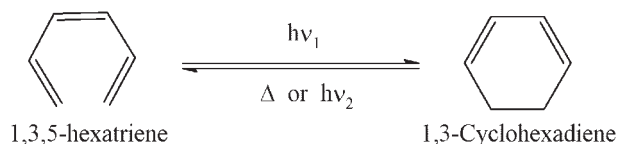


FIGURE 1. Photochromic reversible transformation of hexatriene (left) and cyclohexadiene (right).

In particular, to diarylethenes, experiments with diarylethenes have suggested that their thermal stability depends on the aryl group substitutions and it is their aromatic stabilization energies that allow conrotatory cycloreversion and hence make the closed ring isomer thermally unstable. The thermal stability of some of these compounds has been investigated as a measure of their half-life at elevated temperatures.

Irie et al. [4] also investigated the mechanism of fatigue resistance. After only a few cycles, they observed a decline in the absorbance of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (PFC-2: **1**), see Fig. 3, while the absorbance of its methylated derivative (PFC-2a: **2**) remained constant even after 800 cycles. The formation of a colored byproduct was suggested as a possible reason for the decrease in absorbance. Irie et al. 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 X-ray study revealed the molecular structure of Byproduct (Fig. 3) as two six-membered heterocyclic rings containing byproduct in another compound 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (PFC-1d: **3**), [37] and suggested two different probable schemes for their mechanistic formation based on the diradical recoupling process formulated by Celani et al. [38]. In both the cases, it was clear that the byproduct formation takes place from the closed isomer as they observed decrease in the yield of the open form.

In this work we investigated the mechanism of the byproduct formation in **1**, using the unrestricted density functional theory (DFT) formalism. We also investigated the activation barriers for the byproduct formation in two other photochromic compounds, where experimental data were available. Our study is based on the assumption that a photosystem may arrive to the ground-state potential energy surface as methylcyclopentene diradical (MCPD), as proposed by Celani et al. [38].

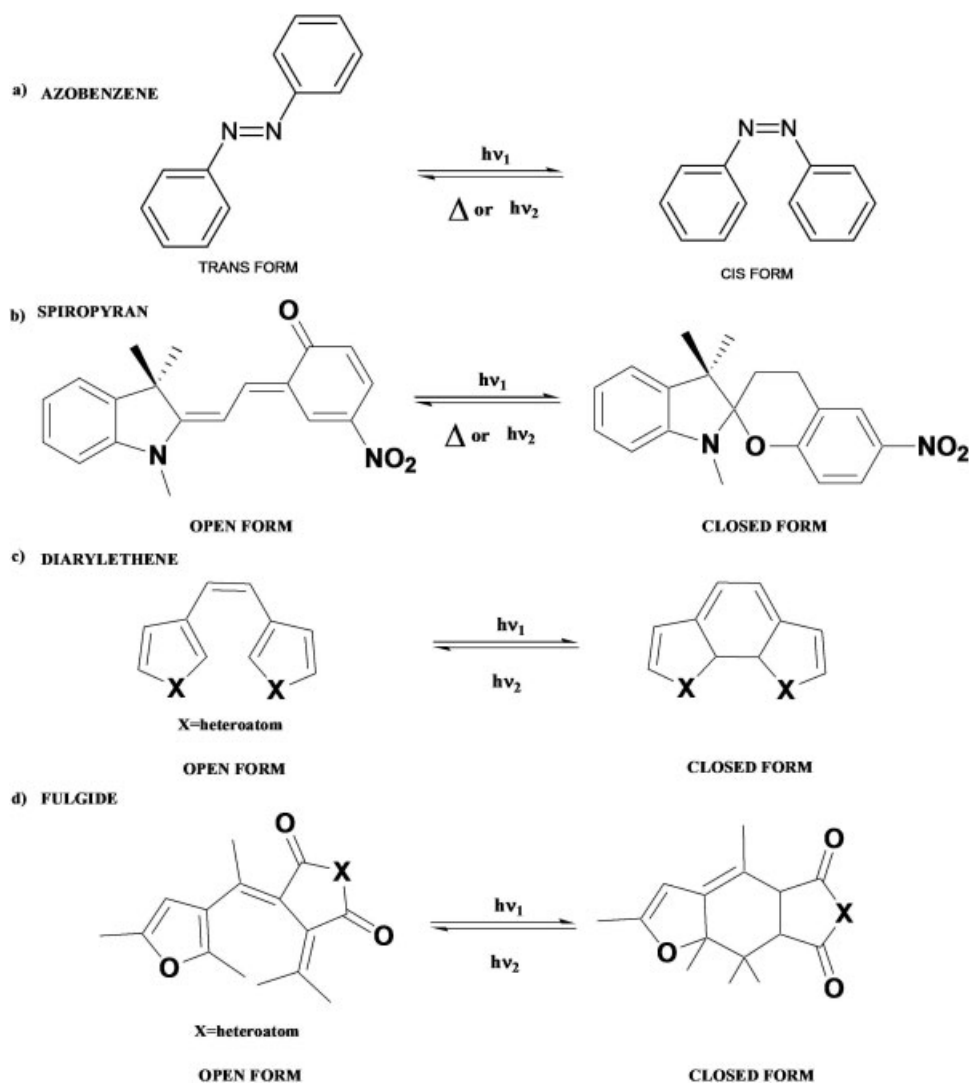


FIGURE 2. (a, b) Thermally unstable (T-type) and (c, d) thermally irreversible (P-type) photochromics.

2. Theory

Photoswitching in diarylethenes occurs through conrotatory electrocyclic mechanism. This is a unimolecular stereoselective process and can be easily understood by the Woodward-Hoffmann rules [39]. According to these rules, conrotatory and disrotatory cyclization proceeds along the pathways conserving different symmetry elements during which molecular orbitals (MOs) undergo continuous evolution. When occupied orbitals of the reactant evolve into the occupied orbitals of the product, the potential energy barrier is fairly low and the reaction is said to be thermally allowed. When the occupied orbitals of the reactant evolve into the

vacant orbitals of the product and vice versa, the reaction is said to be photochemically allowed and thermally forbidden (have a large activation barrier in the ground state). Cycloreversion in diarylethenes is an example of such a thermally forbidden reaction.

The conclusions from Woodward-Hoffmann rules have been confirmed by *ab initio* quantum chemical calculations. We published a number of studies on the photochemical conversion in the model system of CHD and cZc-HT have been published. A complete mechanistic picture of the photochemical ring opening and ring closure occurring on the $2A_1$ and $1B_2$ surface after CHD photoexcitation has been drawn by Celani et al. [38, 40] using

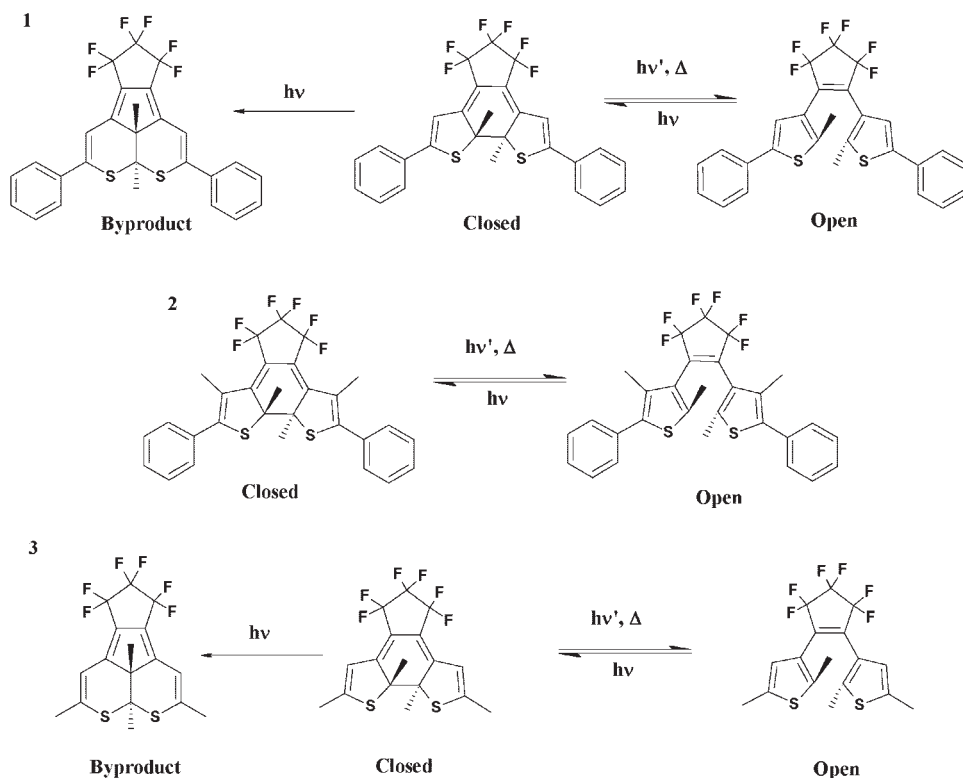


FIGURE 3. Isomeric forms of **1**, **2**, and **3**.

correlated wavefunction theory methods (CAS-SCF and CAS-SCF/MP2). Theoretical investigation of the CHD/cZc-HT photochemical interconversion has also been performed at CASPT2 [41] and MR-SCI [42] theory levels to investigate the potential energy surface, find the reaction path, and transition probabilities. Garavelli et al. [43] used the algorithm of steepest decent to compute initial relaxation directions from the tip of the conical intersection (CIX) to predict the mechanism of the product formation for the CHD/cZc-HT photochemical interconversion. Sakai and Takane [44] calculated the potential energy surfaces for the electrocyclic reactions of 1,3,5-hexatriene with different *ab initio* MO methods. The activation energies 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. Because the latter mechanism (allowed by orbital symmetry) has a lower energy barrier, the reactant and product with C_s symmetry are unstable; however, the conrotatory mechanism with a higher energy barrier leads to stable reactant and product with C_2 symmetry, and so it is the preferable pathway for ring closure. Unfortunately,

correlated wavefunction theory methods are very demanding computationally and cannot be performed on the larger molecules of practical interest. For those molecules, semiempirical and Time-Dependent Density Functional Theory (TD-DFT) studies had been reported.

Nakamura and Irie [16] carried out semiempirical calculations on three types of molecular systems (furyl, pyrrolyl, and thienyl) and concluded 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 when compared with furyl and pyrrolyl derivatives, and they concluded that the energy barrier in the case of the thienyl derivative would be the largest, which makes cycloreversion less likely.

Semiempirical Hamiltonian INDO/S in combination with coupled electronic oscillator formalism was used by Tretiak and coworkers [45, 46] to study the excited state dynamics for electrocyclic reactions in diarylethene derivatives. They were able to explain the slow conversion of the precursor for the ring opening process that corresponds to the peri-

cyclic minimum on the excited state potential surface into the ground-state products by the presence of the potential barrier separating this minimum from a CIX to the ground state [47].

Another semiempirical study was reported by Cho and Cheong [48]. They investigated the thermal stability of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride, a P-type photochromic compound. Both closed form and three open forms were optimized: one parallel and two antiparallel ones. Restricted AM1 calculations were performed to calculate the ground-state thermal stability and the energy barrier heights for cyclization and ring opening are 226 and 160 kJ/mol, respectively. For the S1 state, configuration interaction with single substitutions (CIS, MOPAC keyword excited) was used. Energy barriers of the S1 state were found to be much lower (33 kJ/mol for cyclization and 13 kJ/mol for the ring opening). Because of the low accuracy of semiempirical method, no λ_{\max} prediction was attempted.

In their pioneering TD-DFT study, Majumdar et al. investigated dithienylethene derivatives as potential nonlinear optical photoswitches. They reported the open and closed structures, stability, electronic absorption spectra, and hyperpolarizabilities [13]. Other DFT studies soon followed. Jacquemin and coworkers investigated several sets of dithienylethene derivatives and found that TD-DFT treatment gives much more accurate results than semiempirical approach [49–53]. The absorption spectra were predicted, while implicitly taking bulk solvent effects into account with polarizable continuum model (PCM). Their work however was restricted to only the closed ring isomers. Similar studies were extended to both closed and open ring isomers [54–56].

Chen et al. [54] used the TD-B3LYP/6-31G* theory level to predict the absorption spectra of closed isomers of six different diarylmalesic anhydrides. Perrier et al. [55] designed 10 photochromic diarythienyls with different conjugated substitution at the 5 and 5' position of the thiophene ring and investigated substituent effects on optical properties of both the closed ring and open ring isomers at B3LYP/6-31G theory level. For both closed and open forms, the photoreactive state was found to be the lowest excitation and to have Highest Occupied Molecular Orbital–Lowest Unoccupied Molecular Orbital (HOMO–LUMO) nature in most cases. Its λ_{\max} was predicted and correlated to the HOMO–LUMO energy gap and to the Bond Length Alternation

(BLA) parameter. Perrier et al. concluded that conjugated substituents stabilize LUMO and decrease BLA. However, in most of the cases considered, the lowest excitation has low oscillator strength and does not correspond to the brightest optical transition. No comparison with experimental data was reported.

Laurent et al. [56] investigated six oxazole-diarylethenes (both closed and open forms) using TD-PBE0/6-311+G(2d,p)/PCM//PBE0/6-311G(d,p)/PCM. The theoretical λ_{\max} for the brightest states was found to be in a good agreement with experiment. The authors concluded that the larger the experimental λ_{\max} , the larger the theory/experiment discrepancy (in nm) and introduced a linear scaling correction to predict an accurate λ_{\max} . Direct correlation was reported also between experimental λ_{\max} and the HOMO–LUMO gap for 29 dithienylazoles (closed forms only). Theoretical investigations on thermally irreversible photochromic systems have also been conducted by other groups in order to predict other ground-state properties [13, 48, 53, 57].

One has to note, however, that TD-DFT has been found to encounter difficulties in the description of potential surfaces in the vicinity of CIXs [58]. The source of these problems was traced [59] to the poor description of the reference ground state near the pericyclic minimum within the restricted Kohn–Sham (RKS) formalism. The Kohn–Sham formalism of DFT was developed for nondegenerate cases; it breaks down for systems with strong diradical character and degeneracy of the electronic levels, which happens to be the case for CIXs. 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 bond breaking [60].

A computationally inexpensive yet reliable theoretical method for property prediction would greatly assist in deriving molecular design principles for fatigue-resistant photochromics. These principles can be used in engineering the new photoswitchable materials. In the present paper, we investigate the ability of unrestricted DFT calculations to predict the thermally activated mechanism and the ground-state energy barriers to the byproduct formation in diarylethene derivatives.

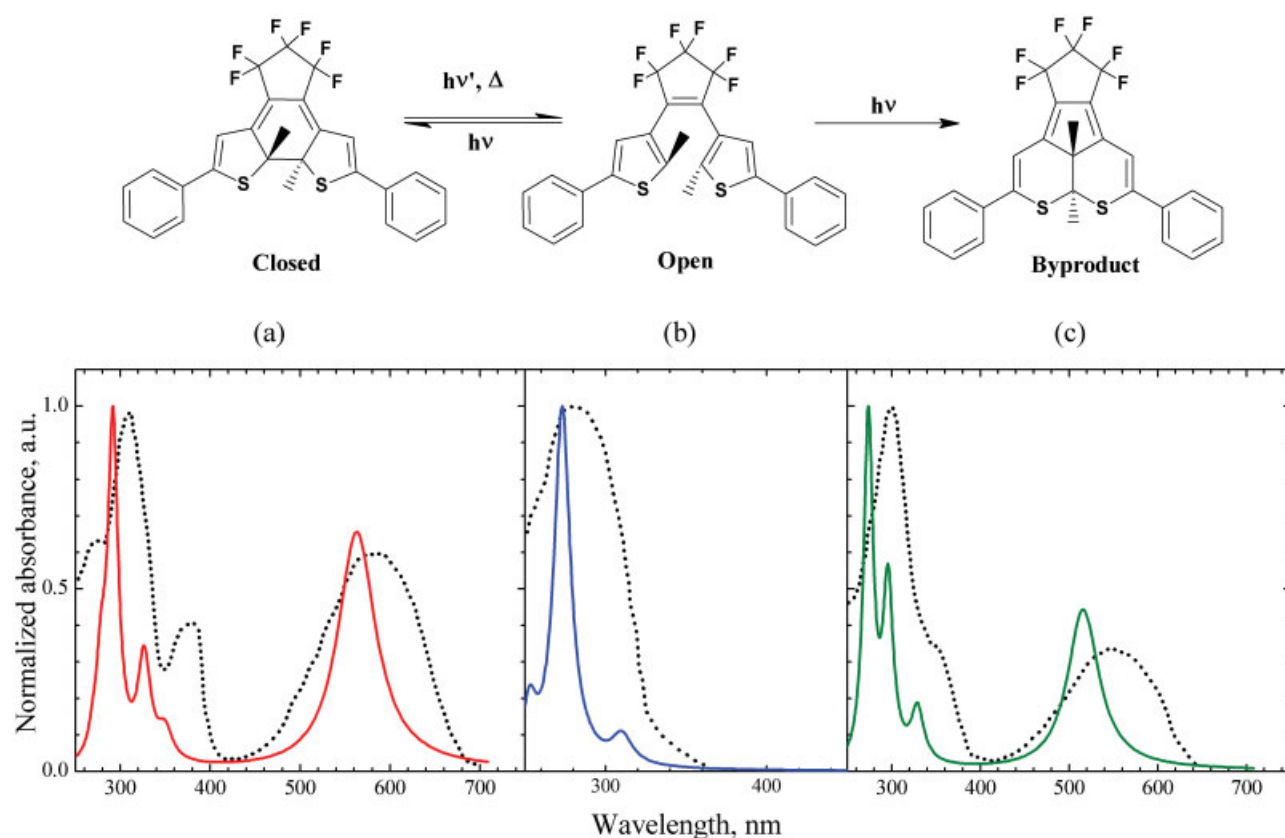


FIGURE 4. (a–c) isomers of **1** and their absorption spectra: experimental in hexane [4] (faint lines) and predicted at the TD-M05/6-31G*/PCM//M05-2X/6-31G*/PCM level of theory (bold lines). Experimental/theoretical λ_{max} (nm) for the isomers are 575/585 (Closed), 276/287 (Open), and 547/546 (Byproduct). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I

Closed ring, Open ring and Byproduct isomers of **1**: state, energy of the state (E), calculated wavelength (λ), oscillator strength (f), description of the electronic transition, and amplitude of the transition.

	State	E (eV)	λ (nm)	f	Description	Amplitude
Closed	1	2.12	585	0.4614	HOMO→LUMO	0.912
	2	3.26	380	0.0245	HOMO–1→LUMO	0.890
	3	3.54	350	0.2237	HOMO→LUMO+1	0.819
	4	3.96	313	0.6662	HOMO–2→LUMO	0.956
	5	4.02	308	0.0172	HOMO→LUMO+2	0.802
Open	1	3.73	333	0.0998	HOMO→LUMO	0.949
	2	3.98	311	0.0146	HOMO–1→LUMO	0.959
	3	4.33	287	1.3662	HOMO→LUMO+2	0.803
	4	4.39	282	0.0382	HOMO→LUMO+1	0.854
	5	4.54	273	0.2323	HOMO–2→LUMO	0.931
Byproduct	1	2.18	568	0.2768	HOMO→LUMO	0.923
	2	3.38	367	0.0511	HOMO–1→LUMO	0.925
	3	3.85	322	0.3263	HOMO→LUMO+1	0.870
	4	4.12	301	0.4428	HOMO–3→LUMO	0.960
	5	4.17	297	0.1753	HOMO–2→LUMO	0.935

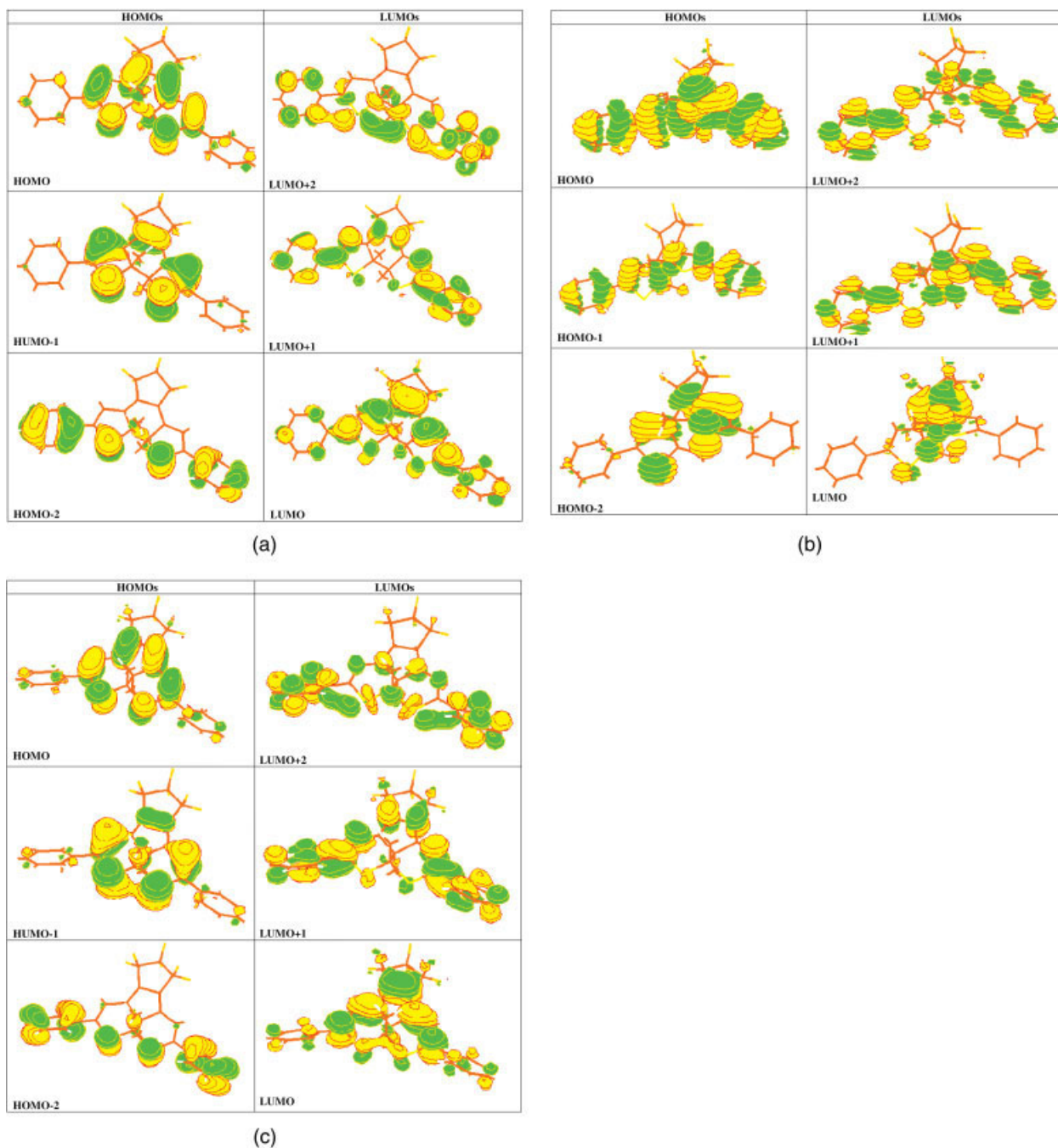


FIGURE 5. (a) Essential Kohn–Sham orbital plots for the closed isomer of **1**. (b) Essential Kohn–Sham orbital plots for the open isomer of **1**. (c) Essential Kohn–Sham orbital plots for the Byproduct isomer of **1**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3. Computational Details

Gaussian 2003 Rev. E1 program package [61] was used for all the calculations. Hybrid exchange

correlation functionals including some fraction of Hartree–Fock exchange were used (20% for B3LYP [62–64] and 56% for M05-2X [65]) in combination with the 6-31G* basis set. To obtain an unrestricted KS solution, the broken symmetry guess was gen-

erated and followed using keyword Guess (Mix, NoExtra). The stability of the Kohn–Sham orbitals was tested before and after geometry optimization using the keyword Stable = Opt. In cases where instability was found, the geometry optimization was repeated with the stable set of orbitals used as the initial guess.

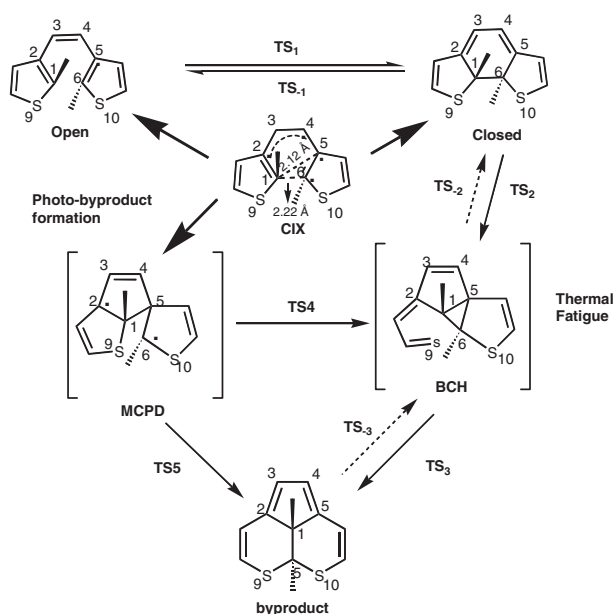
To characterize each stationary point as a minimum or a transition state and to estimate the zero-point vibrational energies (ZPE), vibrational frequencies for all optimized species were computed at all levels. The transition state search was performed by using the Synchronous Transit-Guided Quasi-Newton (STQN) method [66, 67] as implemented in the Gaussian 2003 package. This method 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. This method will converge efficiently to the actual transition state structure using an empirical estimate of the Hessian and suitable starting structures for the reactants and intermediates.

4. Results and Discussion

4.1. NATURE OF THE EXCITED STATES IN ISOMERS OF 1,2-BIS(2-METHYL-5-PHENYL-3-THIENYL)PERFLUOROCYCLOPENTENE

The absorption spectra for the three different isomers (Closed, Open, and Byproduct) of **1** (Fig. 4) were predicted using the TD-M05/6-31G*/PCM//M05-2X/6-31G*/PCM level of theory using heptane as implicit solvent. One can see that the predicted spectra are in good agreement with the experimental for all three isomers, considering that vibronic structure was not taken into account, and the spectra were broadened with Gaussian line-shapes of 0.1 eV empirical widths.

The detailed description of the electronic excitations in the open and closed forms is presented in Table I, and the KS orbitals involved in these excitations are plotted in Figure 5. The λ_{\max} is the transition with the large oscillator strength. In the case of the closed isomer or Byproduct, there are two bright states out of which the lower energy one was found to be of the HOMO→LUMO nature. This state is the one comparable with the reported experimental value (Fig. 4). In the case of the open isomer, the brightest state is of HOMO→LUMO+2 nature and hence the



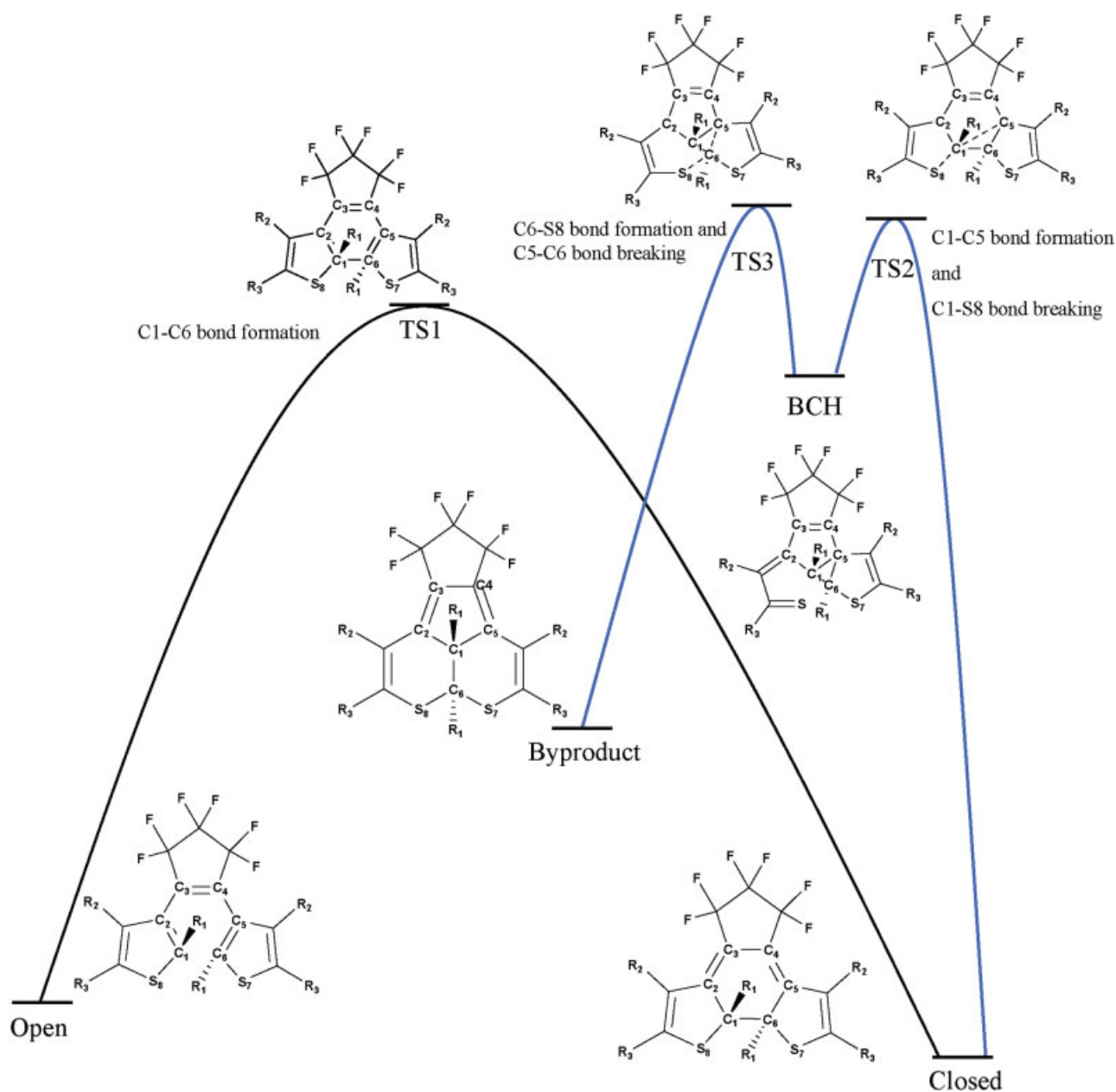
SCHEME 1. Proposed mechanistic routes for the thermal and photochemical byproduct formation in dithienylethene derivatives.

λ_{\max} is 287 nm. The byproduct also has two bright states, out of which the lower energy one was found to be of the HOMO→LUMO nature, corresponding to those states are reported in Figure 4.

From the analysis of the KS orbitals for the open isomer in Figure 5(b), one can see that the HOMO has antibonding character with respect to the new C—C bond, and the LUMO has a bonding character. Therefore, photocyclization will take place upon excitation from HOMO to LUMO. However, the optical transition proceeds to the state with large oscillator strength, which corresponds to the brightest optical band. Apparently, some vibrational relaxation from the higher lying photoabsorbing state to the lowest photoreactive state has to occur before the photocyclic transformation.

4.2. MECHANISM OF BYPRODUCT FORMATION

Celani et al. [38] investigated the prototypical electrocyclic photoreaction from cyclohexadiene (CHD) to all-cis hexatriene (cZc-HXT). They found that after excitation to the Franck–Condon region on the excited state surface, the system descends to the pericyclic minimum and funnels to the ground-state potential surface through the CIX region, where the ground and excited-state



SCHEME 2. Energy profile for thermal cycloreversion and the byproduct formation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surfaces are nearly degenerate. They suggested three possible routes for electron recoupling from the CIX region: one to the closed form, another one to the open form, and the third one to the ground-state MCPD intermediate. They stated that this intermediate is unstable and may undergo radical pairing to form bicyclohexane (BCH) or a 1,2-hydrogen shift to form methylenecyclopentene. Later Irie and coworkers [37] investigated the

byproduct formation experimentally and established that the byproduct formation takes place from the closed isomer. They suggested two different schemes to describe the formation of Byproduct corresponding to 3. One of them starts with homolytic cleavage of the C—S bond and proceeds to the BCH intermediate. Another one goes through electrocyclic CIX and also proceeds to BCH intermediate as described by Celani et al.

TABLE II

Energy barriers for thermal cycloreversion and thermal byproduct formation processes evaluated at UB3LYP/6-31G* and UM05-2X/6-31G* theory levels for 1, 2, and 3 in kcal/mol.

	Transition State	TS ₁	TS ₂	TS ₃	TS ₋₁	TS ₋₂	TS ₋₃
1	Exp	33.2					
	UM052x/6-31G*	38.2	53.4	17.3	46.7	16.5	42.7
	UM052x/6-31G*(ZPEcorr)	35.3	51.2	16.2	44.4	15.1	40.5
	UB3LYP/6-31G*	33.3	45.9		45.7	12.2	
	UB3LYP/6-31G*(ZPEcorr)	30.6	43.9		44.2	11.2	
2	UM052x/6-31G*	39.6	52.5	22.1	48.9	18.5	46.5
	UM052x/6-31G*(ZPEcorr)	36.9	49.9	21.2	47.4	17.3	44.3
	UB3LYP/6-31G*	36.0	46.7	20.0	49.7	15.2	39.9
	UB3LYP/6-31G*(ZPEcorr)	33.3	44.1	19.1	48.6	14.1	37.9
	UM052x/6-31G*	42.3	55.8	16.7	49.3	18.3	43.1
3	UM052x/6-31G*(ZPEcorr)	39.3	53.3	16.0	47.1	17.1	40.7
	UB3LYP/6-31G*	37.1	47.7	11.3	48.9	14.5	32.4
	UB3LYP/6-31G*(ZPEcorr)	34.1	45.1	10.4	47.1	13.1	30.3

We explored the ground-state potential energy surface in three diarylethene derivatives: **1**, **2**, and **3** (Fig. 3), which had their fatigue-resistant properties reported experimentally [4, 37]. In our calculations, we could identify two different intermediates to the byproduct formation, similar to the ones, described by Celani et al.: one is MCPD and another one BCH intermediate, both depicted in Scheme 1. Unlike the work of Celani, where MCPD was found unstable, in our calculations it is found to be the energy minimum. One can envision four distinctly different transition states connecting the closed form, MCPD, BCH, and the Byproduct (Scheme 1). However, extensive search of the ground-state potential energy surface using state of the art STQN algorithms did not locate transition states TS4 or TS5. We characterized, however, two other transition states: one leading to BCH from the closed form and another one connecting BCH to the final Byproduct.

On the basis of our findings, we constructed an energy diagram depicted in Scheme 2. There, TS1 corresponds to the transition state between the open and closed forms (C1—C6 bond breaking), TS2 is the transition state between the closed form and BCH (corresponds to the concurrent C1—C5 bond formation and C1—S8 bond breaking), and TS3 is the transition state from BCH to the Byproduct (corresponds to the formation of C6—S8 bond and breaking of C5—C6 bond).

Table II reports values of the energy barriers for thermal cycloreversion and the byproduct formation processes evaluated at the UM05-2X/6-31G*

theory level for compounds **1**, **2**, and **3**. The UB3LYP/6-31G* values are also given for comparison.

The TS₂ barriers for both **1** and **3** (51.2 and 53.3 kcal/mol) is slightly higher than that of **2** (49.9 kcal/mol). However, compound **2** was found to be fatigue resistant in experimental study [4, 37]. This suggests that the BCH intermediate is inaccessible by thermal reaction from the closed form, and BCH is probably reached photochemically from the excited state. In contrast, transition state TS₃ corresponds to much lower barrier of 16.2 and 16.0 kcal/mol for compounds **1** and **3**, respectively. The same transition state is much higher at a value of 21.2 kcal/mol for compound **2**. This clearly correlates with fatigue resistance properties of these compounds, suggesting transformation from BCH to be the rate limiting process. The only difference in molecular structures of **1** and **2** are the radicals R₂ (hydrogen atom vs. methyl group). Apparently, steric repulsion between this methyl group and fluorine atoms of the perfluorocyclopentene group disturbs the planarity, reduces the conjugation, and destabilizes the transition state.

Conclusions

The orbital structure of the five lowest excited states in open and closed forms of **1** was analyzed, and the vibrational relaxation from the higher lying photoabsorbing state to the lowest photoreactive state was found to be necessary for the photocyclic

transformation to occur. The mechanism of the by-product formation for the compounds **1–3** was investigated to predict the photofatigue of these molecules. We found the activation energy leading to Byproduct from the bicyclohexyl intermediate to be 5 kcal/mol higher for the methylated derivative **2** and used this fact to explain its higher fatigue resistance. This protocol may become a part of the rational design strategy for new photochromic materials used in photoswitching and optical data storage applications.

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