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Rotational Isomerization of Dithienylethenes: A Study on the Mechanism Determining Quantum Yield of Cyclization Reaction

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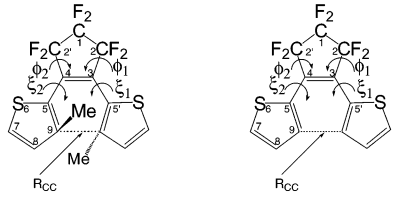
Aiming at the improvement of the photochemical performance of dithienylethenes, we present an analysis of the parameters that influence the quantum yield. We address some basic features of the ground-state potential energy surface of the photochromic dithienylethenes, showing the existence of three to five rotational conformers. Among those, only one is reactive. The energetical ordering and energy gaps between different conformers are investigated. The calculated results were compared to X-ray, proton NMR, and absorption spectra.

Introduction

Photochromic molecules have attracted much attention from both fundamental and practical points of view because of their potential for various applications. Among the many recently investigated photochromic molecules, dithienylethene (DTE) compounds have shown great promise as new materials for optoelectronic devices, owing to their thermal irreversibility and fatigue resistance. These two properties make it possible to use these molecules as memories and switches in a wide range of optoelectronic devices.[1,2] Recently, a high-density three-dimensional optical recording in a DTE single crystal was demonstrated.[3] In this case, it is possible to repeat the photon-induced coloration−decoloration cycle more than 10000 times. The single crystal of this DTE derivative shows a quantum yield (QY) for photocyclization of approximately 1.0. However, important parameters influencing the QY have not been completely clarified. Theoretical studies of dithienylethenes on the molecular level are crucial to understand the mechanism determining the QY of the photochromic reaction and to improve the reaction performance.

SCHEME 1



Molecule (1)   Model (2)

We have previously reported theoretical studies on the molecular design of dithienylethenes,[4] focusing on thermal stability,[5] absorption properties,[6] and the analysis of the QY for the cycloreversion reaction.[7] The present investigation is intended to provide a detailed description of the ground-state potential energy profile of the 1,2-bis(3-methyl-2-thienyl)-perfluorocyclopentene (molecule **1**, Scheme 1); the study takes into account its relation to the cyclization QY. This molecule is the smallest in the family of various dithienylethene derivatives, making it suitable for a detailed theoretical investigation. It undergoes the ring-closure (cyclization) reaction under the ultraviolet irradiation, while the ring-opening (cycloreversion) reaction takes place under visible light irradiation (Figure 1). The cyclization QY depends on many parameters, previously two important parameters have been reported: (i) The ratio between the antiparallel (**a-p**) and parallel (**p**) conformers (Figure 2), Uchida et al. reported the coexistence of two conformers called **a-p** with the C_2 symmetry and **p** with the C_s symmetry;[8] only the **a-p** conformer is photochromically reactive.[5] We will provide a general definition of the antiparallel (**a-p**) and parallel (**p**) conformations in the following section. (ii) The branching of the excited-state potential energy surfaces[9] is also important (Figure 3). The existence of nonreactive minimum on the excited state was suggested by Uchida et al. as an important factor in the determination of the cyclization QY.

Other derivatives were also investigated to isolate various structural effects. To get rid of the influence of the methyl group on the QY, the model molecule **1** and 2-bis(2-thienyl)perfluorocyclopentene, model **2**, will be considered (Scheme 1). To clarify further the influence of different parts of the DTE molecule on the QY, another simplified model, **3**, as well as a real molecule of 1,2-bis(3-methyl-4-phenyl-2-thienyl)perfluorocyclopentene, molecule **4**, will also be explored (Scheme 2). This paper is a natural extension of the previous works:[5−9] the details and

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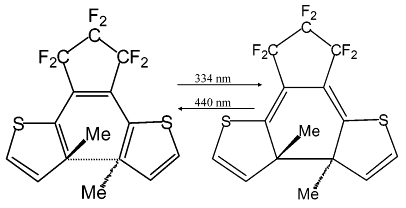


Figure 1. Photochromic reaction of 1,2-bis(3-methyl-2-thienyl)-perfluorocyclopentene, Molecule **1**.

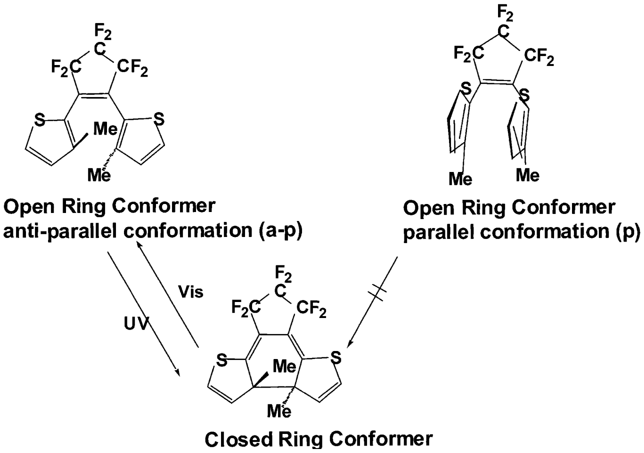


Figure 2. The cyclization reaction proceeds only from antiparallel (**a-p**) conformer with C_2 symmetry.[8]

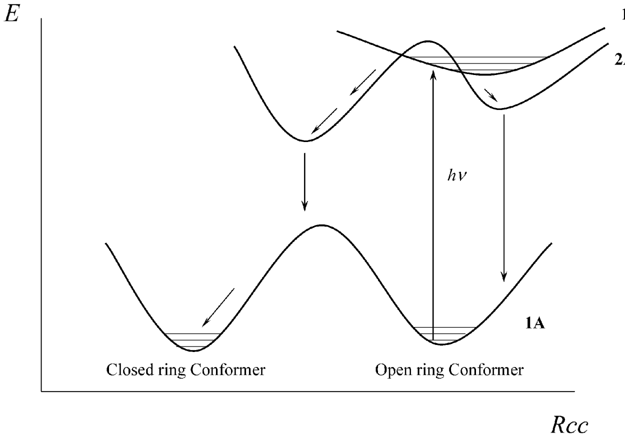
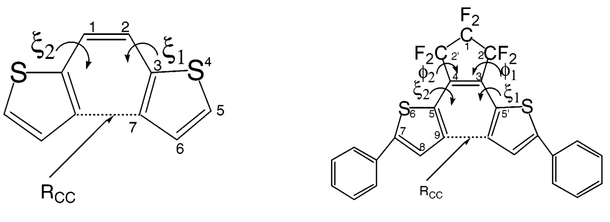


Figure 3. Schematic drawing of the ground-state and excited-state potential energy surfaces for cyclization of dithienylethenes. The cyclization reaction also depends on the branching of the excited-state potential energy surface.[9]

general features of the ground-state conformational change are presented, focusing on its relation to QY.

SCHEME 2



Model (3) Molecule (4)

Computational Details

To adopt the most plausible method of calculations, we performed the optimization procedure using different methods and compared the calculated structures with the X-ray data. The *Gaussian 98* package[10] was used for the calculations. The reported X-ray data for molecule **1**[3] was used for comparison (Tables 1 and 2). Initially, C_2 symmetry was imposed, and the relaxation to C_1 symmetry was allowed. The calculated results in the C_2 symmetry are summarized in Table 1. R_{CC} is the reaction distance between the two carbon atoms numbered 9 and 9′ (see Scheme 1 for the numbering). R_{SS} is the distance between the two sulfur atoms, and ξ is the dihedral angle between the atoms numbered 2′, 4, 5, and 6 of the cyclopentene and thiophene rings.[11]

The comparison of the calculated results with the X-ray data showed that the best agreement was obtained using density functional theory (DFT) calculated at the B3LYP/6-311G(2d,p) level. The largest error in determination of the important geometrical parameters did not exceed 2.5%. This method gives a slightly underestimated dihedral angle ξ (8% error) and a larger R_{SS} distance (4% error), while the most important parameter, the reaction distance, is in good agreement with the experimental value (1% error).

The Hartree–Fock (HF) methods overall give larger errors for the geometrical parameters than the DFT determined parameters, although the R_{SS} distance is usually better described with the HF methods. HF calculations reveal that the structure with the large dihedral angles ξ (∼100) is lower in energy than those structures with the small dihedral angles (∼40). However, the DFT methods pointed toward the more stable conformer with smaller dihedral angle ξ. The energy difference is from 5 to 10 times larger in cases of the DFT and MP2 calculations than in the case of the HF calculation. Thus, we can work with the DFT (B3LYP/6-31G) method to obtain plausible results with sufficient accuracy to satisfy our purpose, even with these large organic molecules. The Table 2 outlines the important bond distances obtained with this method in comparison with X-ray data.[3]

TABLE 1: Comparison of the Experimental Geometrical Parameters with the Calculated Ones by Different Methods for 1,2-Bis(3-methyl-2-thienyl)perfluorocyclopentene, Molecule 1

			RHF/6-31G		DFT/ B3LYP/6-31G		MP2/6-31G		DFT/B3LYP/6-311G(2d,p)	
conformers	properties	X-ray		ϵ (%)		ϵ (%)		ϵ (%)		ϵ (%)
a-p1	ξ (deg)	46	53	19	43	8	44	4	46	0.3
	R_{CC} (Å)	3.62	3.81	5	3.67	1	3.58	1	3.68	2
	R_{SS} (Å)	6.25	6.27	0.03	6.50	4	6.47	4	6.30	1
a-p2	ξ (deg)		99		128.9		112.2		119.3	
	R_{CC} (Å)		4.88		5.44		5.17		5.27	
	R_{SS} (Å)		5.02		4.08		4.48		4.26	
ΔE(**a-p1**−**a-p2**) (kcal/mol)			0.10		−4.13		−2.79		−2.63	

TABLE 2: Comparison of Geometrical Parameters between X-ray Data and B3LYP/6-31G Calculations for Molecule 1

R (Å)	X-ray[a]	calculation
C1−C2	1.49	1.55
C2−C3	1.49	1.51
C3−C4	1.34	1.37
C4−C5	1.46	1.45
C5−C6	1.73	1.83
C6−C7	1.69	1.79
C7−C8	1.33	1.36
C8−C9	1.41	1.44
C9−C5	1.37	1.38
C9−CMe	1.47	1.51
R_{CC}	3.62	3.67
R_{SS}	6.25	6.50
ξ (deg)	46	42

[a] Reference 3.

Results and Discussion

Various Conformers. Preliminary energy minimization for the ground state with imposed C_2 and C_s symmetry restrictions showed that there are two energy minima on the C_2 potential energy profile, whereas there is only one on the C_s (Figure 4). The frequency analysis indicated that two C_2 minima are transition states while that of C_s is the stable conformer. The calculated energy of the C_s minimum is more than 4 kcal/mol higher than that of the global minimum for this particular molecule.

After the symmetry restrictions were removed, four additional C_1 minima emerged as presented in Table 3. Two similar but distinct dihedral angles, ξ_1 and ξ_2, schematically shown in Scheme 1, are obtained for all the calculated conformers. These distinct dihedral angles were also observed in the X-ray experimental data. The other dihedral angles ϕ_1 and ϕ_2 (Table 3) are the dihedral angles between atoms 1, 2, 3, and 5′ and 1, 2′, 4, and 5, respectively (see Scheme 1 for the numbering). These values stress the fact that the cyclopentene ring is nonplanar and distorted at the optimized geometry. The agreement of the geometrical parameters with the X-ray data is better when the symmetry restrictions were removed. The conformers with both positive dihedral angles ξ_1 and ξ_2 are called hereafter as antiparallel (**a-p**) conformers, while those with one positive and one negative dihedral angle are denoted as parallel (**p**) conformers.

Optimization revealed the relative stability of the conformers in the following order of increasing energy (See Table 3):

$$E(\textbf{a-p1}) < E(\textbf{p1}) < E(\textbf{a-p2}) < E(\textbf{p2}) < E(\textbf{p3})$$

The energy difference between conformer **a-p1** and **p1** is very small (0.025kcal/mol); therefore, these two conformers can be equally populated in the representative canonical Boltzmann distribution.

Conformers and Cyclization Quantum Yield. According to the Woodward−Hoffmann rules,[12] the photochromic cyclization reaction should proceed only from the **a-p** conformer. Thus, a significant population of the **p** conformer will decrease the QY of the photochromic reaction. The presence of higher energy **a-p2** conformer (only 0.75 kcal/mol higher than **a-p1**, Table 3) will also decrease the QY, whereas an R_{CC} = 5.55 Å is too long to be reactive. The thermodynamic relative stability of the conformers will be dependent on the substituents. A basic understanding of the substituent effect is to be presented at the last part of this paper in a systematic way after the existence of the conformers in the experimental data is confirmed.

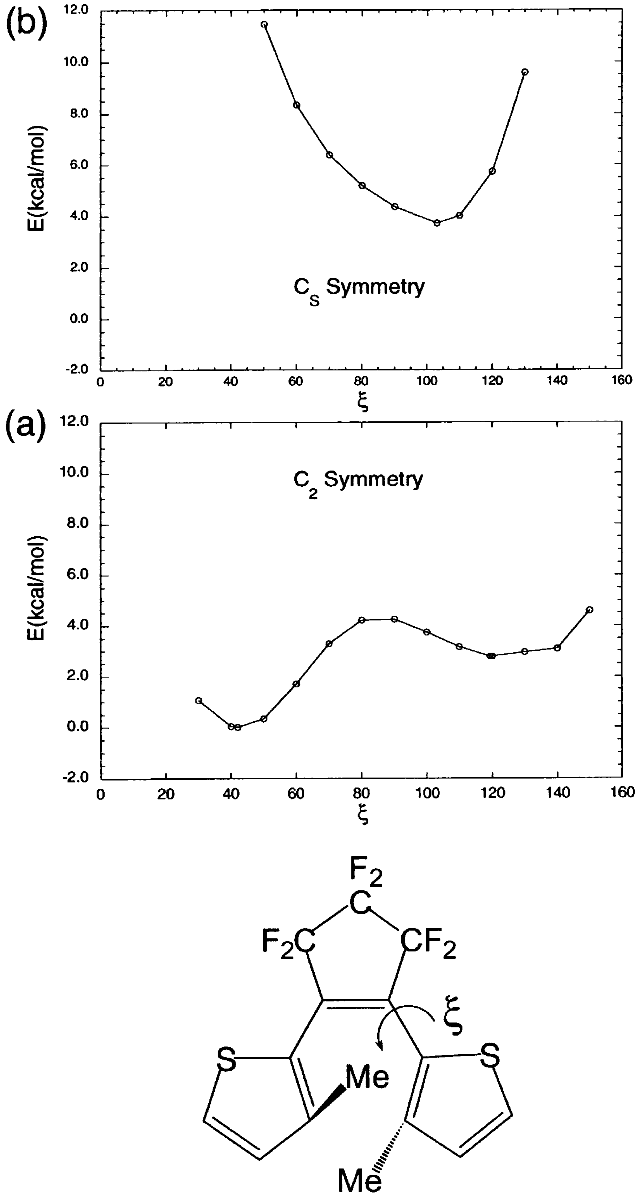


Figure 4. (a) C_2 and (b) C_s symmetrical energy profiles of 1,2-bis-(3-methyl-2-thienyl)perflouorocyclopentene, Molecule **1**.

Solvent Effect. The solvent also can change the population of conformers. The solvent effect calculated by the conductor-like solvation model (COSMO)[13] changed the energy order of the obtained conformers. The energy gap between the conformers is increased (Table 4). The increase of the energy gap is

TABLE 3: Ground-State Minima of Molecule 1

properties	X-ray **a-p** (C_2)	**a-p1** (C_1)	**a-p2** (C_1)	**p1** (C_1)	**p2** (C_1)	**p3** (C_s)
ΔE (kcal/mol)		0	0.75	0.025	1.35	4.16
ratio		43	12	41	4	0
(ξ_1,ξ_2)	(46,46)	(46,41)	(148,108)	(−48,141)	(−42,117)	(103,−103)
(φ_1,φ_2)	(−174,174)	(−177,162)	(−159,169)	(174,−155)	(−166,176)	(165,−165)
R_{CC}(Å)	3.62	3.66	5.55	4.55	4.35	4.83

TABLE 4: Solvation Effect Estimated by COSMO for Molecule 1

		a-p1	a-p2	p1	p2
vacuum	ΔE (kcal/mol)	0	0.75	0.025	1.35
$\epsilon = 1$	μ (D)	7.45	5.71	6.80	6.94
	ratio	43	12	41	4
CH$_3$Cl	ΔE (kcal/mol)	0	1.45	0.29	1.52
$\epsilon = 4.9$	μ (D)	8.98	6.79	8.15	8.31
	ratio	57	5	34	4
DMSO	ΔE (kcal/mol)	0	1.62	0.32	1.52
$\epsilon = 46.7$	μ (D)	9.50	7.15	8.59	8.49
	ratio	58	4	34	5

attributed to changes in the dipole moment. The **a-p1** has the largest dipole moment in a vacuum, CH$_3$Cl and DMSO. As a result, the stabilization energy of **a-p1** relative to the second stable conformer **p2** becomes larger as the polarity of the solvent increases, from 0.025 kcal/mol in a vacuum to 0.29 (in CH$_3$Cl) and 0.32 (in DMSO), as shown in Table 4. The almost even distribution of **a-p1** and **p1** conformers in a vacuum (**a-p1**/**p1** ~ 43:41) is shifted to a ratio of **a-p1**/**p1** of 57:34[14] in DMSO. Thus, the solvent polarity increases the **a-p1** population, which favors a high QY for cyclization.

TABLE 5: Comparison of Calculated and Experimental Values of Chemical Shift for Molecule 1[a]

	calculation		
exptl	a-p1	p1	position assignment
1.65	1.70	2.46	Me
6.87	6.78	6.79	H$_\beta$
7.51	7.64	7.46	H$_\alpha$

[a] Experimental values are taken at lowest measured temperature.

Experimental Confirmation of Conformers Distribution

^{1}H NMR Chemical Shift. Using the gauge-independent atomic orbital (GIAO) method,[15] the ^{1}H NMR chemical shift for different atomic groups have been calculated and compared with the experimental ^{1}H NMR chemical shift to confirm the structural analysis. The reference chemical shift of the tetramethylsilane (TMS) molecule was used for both the experimental and calculated shifts. The results are shown in Table 5. The experimentally obtained ^{1}H NMR spectrum in deuterium chloroform (CDCl$_3$) showed three main peaks. One singlet peak is assigned to the methyl group of the thiophene ring (Figure

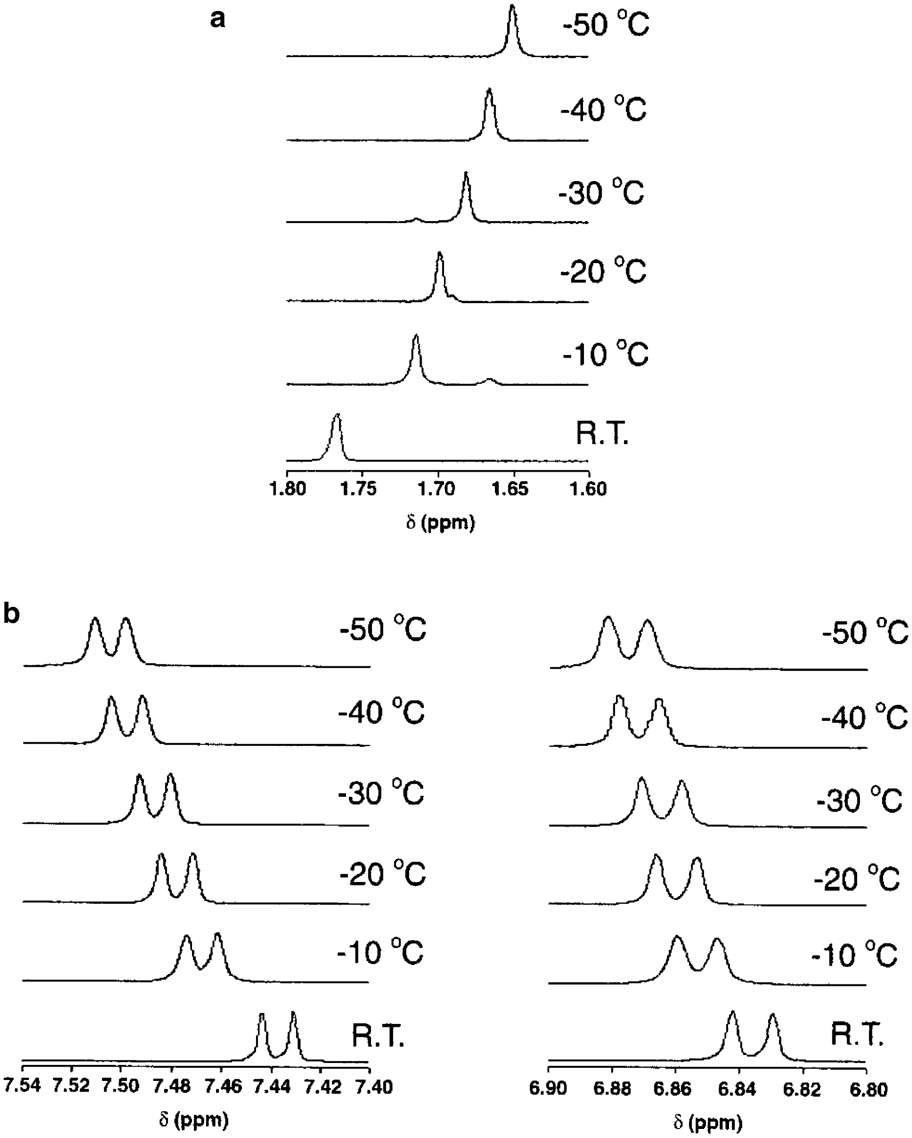


Figure 5. Experimental proton NMR temperature dependence of 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene, Molecule **1**. Chemical shift of (a) methyl group protons and (b) thiophene ring aromatic protons. ^{1}H NMR spectra in CDCl$_3$ were recorded on a JEOL GSX400 spectrometer (400 MHz). Tetramethylsilane was used as an internal standard.

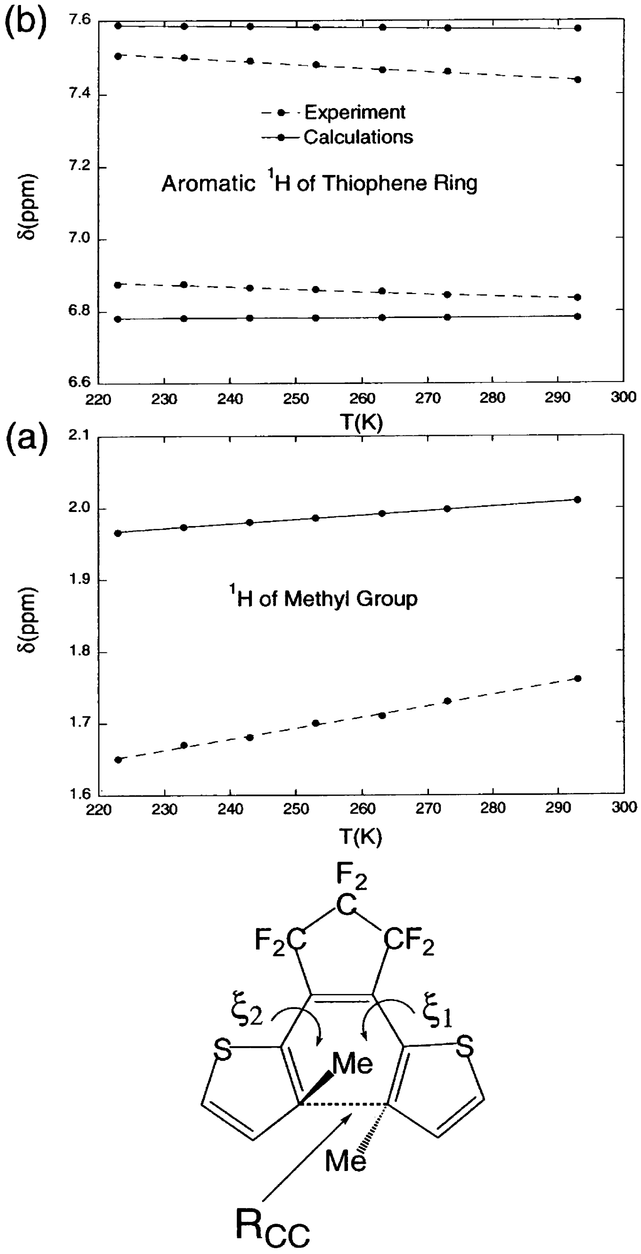


Figure 6. Comparison of calculated and experimental proton NMR chemical shift in chloroform, chemical shift of (a) methyl group protons and (b) thiophene ring aromatic protons.

5a), while the other two doublet peaks are assigned to the protons of thiophene rings (Figure 5b).

The calculation suggests the existence of four peaks. Two of them (1.70 and 2.46) are assigned to the methyl protons, while the others (~6.8 and ~7.5, 7.6) belong to the aromatic protons of the thiophene ring (Table 5). The chemical shift of the methyl group proton provides peaks largely affected by the relative position of two thiophene rings. If the methyl group faces the thiophene ring, then the ring current induces high magnetic field on the methyl protons resulted in 1.7 ppm. Conversely, when there is no thiophene-ring-induced magnetic field on the methyl protons, the chemical shift provides peaks at about 2.5 ppm. In the **a-p1** conformer, the two methyl groups are above the thiophene rings (1.7 ppm). On the other hand, in case of the **p1** conformer, there is no thiophene ring above the methyl protons and the shifts are about 2.5 ppm for those protons. The **a-p2** and **p2** conformers (not shown in Table 5) have both situations, i.e., with one methyl group above the thiophene ring and the other without it, contributing to both values of the chemical shift (see Tables 3 and 5 with Scheme 1).

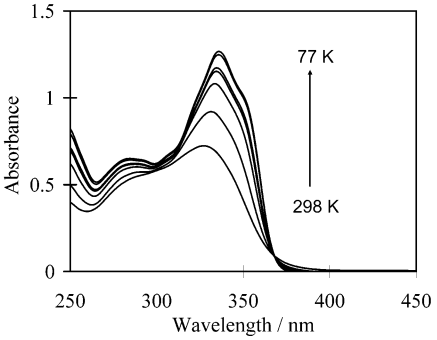


Figure 7. Experimental temperature-dependent absorption spectrum of 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene, Molecule **1** (8×10^{-6} M, in 2-methyl-THF). Absorption spectra are measured with Hitachi U-3500 spectrometer when temperature became constant in each point by using Oxford 1015 cryostat).

TABLE 6: Excitation Energies and Oscillator Strengths of Two Conformers by TDDFT of Molecule 1

isomer	λ (nm)	oscillator strength
a-p1	355	0.31
p1	377	0.26

A reason for only one peak of the methyl protons observed in the experiment, instead of two in the calculations, can be ascribed to rapid thermal interconversion between the two conformers. The merging of the two peaks of methyl protons in NMR spectrum was already reported by Uchida et al.[16]

Temperature Dependence of Chemical Shift. To confirm the existence of different conformers, we have examined the experimental temperature dependence of the chemical shift (Figure 5a,b) by taking into account solvent and entropy effects. When we compare the calculated shift with experimental data, the increased energy difference in polar solvent is important; the existence of **a-p2** and **p2** conformers are almost ruled out by the Boltzmann distribution. Conformers **a-p1** and **p1** are the main representatives in the canonical ensemble of the considered molecules in the equilibrium (Table 4).

If a correction for the entropy effect is introduced, the experimental and calculated ^{1}H NMR chemical shift becomes closer. The Gibbs free energy correction to the electronic energy[17,18] was calculated at every experimental temperature, and subsequently the averaged value of methyl proton NMR chemical shift was evaluated. The averaging was done with the corresponding Boltzmann factor for all four important conformers by using the electronic energy obtained in the presence of chloroform solvent.

Figure 6a shows the computed temperature dependence of methyl proton NMR chemical shift in comparison with the experimental one. The slope of the calculated and experimental lines shows a similar trend of shifting toward the higher magnetic field as temperature increases. The difference in the absolute values may be originating from the exclusion of the solvent effect in the calculations of ^{1}H NMR chemical shift values. Conformers **a-p2** and **p2** do not show a measurable temperature dependence in the chemical shift due to the energy difference of more than 1 kcal/mol. The higher energy conformer with the C_s symmetry is practically invisible. The aromatic ^{1}H NMR chemical shifts of thiophene rings exhibit a weak temperature dependence (Figure 6b). The ring-current effect is small, and different conformers peaked at almost the same

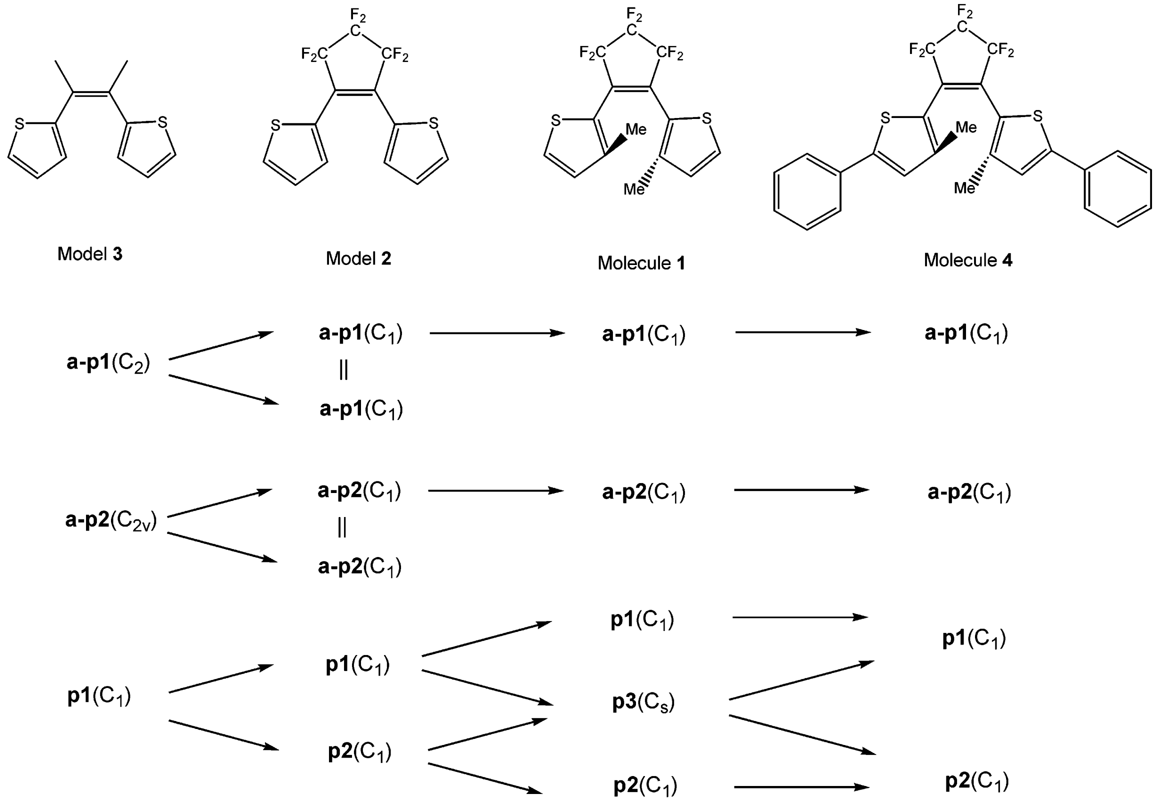


Figure 8. Evolution of the molecular hierarchy as the addition of the substituents.

TABLE 7: Ground-State Minima of Model 3

properties	**p1** (C_1)	**a-p1** (C_2)	**a-p2** (C_{2v})
ΔE (kcal/mol)	0	0.082	1.04
ratio	49	43	8
(ξ_1,ξ_2)	(180,−37)	(24,24)	(180,180)
R_{SS} (Å)	5.05	6.77	3.22
R_{CC} (Å)	4.99	3.32	6.18

TABLE 8: Ground-State Minima of Model 2

properties	**a-p1** (C_1)	**a-p2** (C_1)	**p1** (C_1)	**p2** (C_1)
ΔE (kcal/mol)	0.92	0.33	0.16	0
(ξ_1,ξ_2)	(30,36)	(−137,140)	(−40,151)	(−44,159)
(φ_1,φ_2)	(−175,164)	(−176,164)	(176,−164)	(−164,175)
R_{CC} (Å)	3.33	5.85	4.62	4.85

positions. The agreement between the experimental and calculated results supports our analysis of the different conformers on the ground-state PES.

Excitation Energies. The excitation energies of **a-p1** and **p1** conformers were calculated using time-dependent DFT (TDDFT) method[19] and compared with the experimental temperature-dependent absorption spectrum. The experimentally obtained absorption spectrum in 2-methyltetrahydrofuran (2-methyl-THF, $\epsilon = 7.58$) solution had a broad feature, which separated into two overlapping peaks with maxima at 337 and 355 nm as temperature decreased (Figure 7). The TDDFT calculations gave a peak at 355 nm for the **a-p1** conformer and another peak at 377 nm for the **p1** conformer with almost equal oscillator strengths (Table 6). The thermal interconversion between the two conformers is less probable at low temperature due to a potential barrier that resulted in two shoulders in experiment. Thus, the calculated two absorption peaks at 355 and 377 nm may correspond to the observed two shoulders at 337 and 355 nm. Still, we have to make a precaution that there is a possibility that an unidentified species such as aggregated molecules are responsible for the shoulder in the experimental spectrum (Figure 7). To resolve this point, further experimental investigation is needed. The origin of a slight red shift observed in the absorption peak in Figure 7 at low temperature is not clear at this stage, although the freezing of the solvent may be a possible explanation.

Conformer Population Changes, as Substituents Increase

We have thus far shown that the ground-state conformation change is an important determining factor for QY. A desired high QY is dependent on the population of favored (for cyclization reaction to occur) conformation. Therefore, it is important to understand how the population is determined as a function of substituents. To understand the origin of population changes in various conformers, we have studied additional two model systems: one in which C_5F_6 part was replaced by two hydrogen atoms and the other in which two CH_3 substituents also were replaced by two hydrogen atoms. Comparing these models with the real molecules, the distribution of the favored population associated with the skeleton (reaction center of the molecule) and/or that associated with substituents are clarified. A schematic picture is shown in Figure 8, displaying how the population of each conformer diversifies as substituents increase.

The first model molecule without cyclopentene ring or CH_3 (see model **3** in Scheme 2 and Figure 8) has three conformers on the ground-state PES with two symmetrical and one asymmetrical structures[20] (Table 7). The energy ordering of the conformers is

$$E(\mathbf{p1}) < E(\mathbf{a\text{-}p1}) < E(\mathbf{a\text{-}p2}).$$

Four stable minima of the molecule without the methyl group (Model **2**, Scheme 1 and Figure 8) were obtained (Table 8). The highest energy C_s conformer of the real Molecule **1** (see

TABLE 9: Ground-State Minima of Molecule 4

properties	**a-p1** (C_1)	**a-p2** (C_1)	**p1** (C_1)	**p2** (C_1)
ΔE (kcal/mol)	0	1.47	−0.019	1.74
ratio	46	4	48	2
(ξ_1,ξ_2)	(40,44)	(149,109)	(−46,142)	(−40,120)
(φ_1,φ_2)	(161,−178)	(159,−170)	(175,−154)	(−165,178)
R_{CC} (Å)	3.65	5.57	4.5	4.38

p3 (C_s) in Figure 8) turned out to be similar in geometry to the transition state in the Model **2** molecule. The energy gap between the conformers becomes lower, and the energy ordering is opposite to that of the Molecule **1**.

$$E(\mathbf{p2}) < E(\mathbf{p1}) < E(\mathbf{a\text{-}p2}) < E(\mathbf{a\text{-}p1}).$$

Comparing the Models **2** and **3** shows that the attachment of the cyclopentene ring removes the symmetry, thereby changing the energy order of the conformers (Figure 8 and Tables 7 and 8). The reason for the symmetry reduction is the distortion of the cyclopentene ring, which gives rise to additional conformers of the C_1 symmetry. Two C_1 conformers of Model **2** are derived from **a-p1** (C_2) as well as from the **a-p2** (C_{2v}) conformer of Model **3**. The **p1** (C_1) conformer of Model **3** induces two nondegenerate conformers. Thus, cyclopentene ring is the origin of various conformers (Tables 7 and 8 and Figure 8).

In Molecule **4** with a phenyl ring (Table 9 and Figure 8), four stable minima were obtained. It turned out that **p1** conformer becomes the most stable one:

$$E(\mathbf{p1}) < \mathrm{E}(\mathbf{a\text{-}p1}) < E(\mathbf{a\text{-}p2}) < E(\mathbf{p2})$$

The addition of the phenyl ring to the Molecule **1** not only changes the energy order but also decreases the energy difference between conformers. The difference about 1.5 kcal/mol is large enough to rule out **a-p2** and, consequently, **p2** conformers from the consideration. In fact, the phenyl group in Molecule **4** makes the **p1** conformer most stable (Table 9), which is not a reactive conformer. It is consistent with experimental results that the cyclization QY of Molecule **4** decreased to 0.17[21] from 0.54[22] of molecule **1**.

Conclusions

An analysis of the parameters that influence the quantum yield is presented. We have addressed the importance of conformer distribution in the ground-state potential energy surface as a determining factor of QYs. The calculated results were compared to X-ray, proton NMR, and absorption spectra. By using the calculated model molecules, the population changes among the conformers are analyzed as substituents increase, providing an insight for stabilizing the favored conformation for the cyclization reaction.

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