An ab Initio MO Study of the Photochromic Reaction of Dithienylethenes

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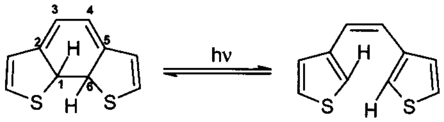
An ab initio MO study on a model system for photochromic compounds containing a dithienylethene unit is presented. On the basis of the obtained potential energy profile, a rationalization is provided for the proposed mechanism of the experimentally observed stepwise multiphoton process in the ring-opening cycloreversion reaction. An explanation, which correlates the experimental quantum yields with the calculated properties as a function of substituent effects, is provided. A method has been developed which can be utilized as a guiding principle for future molecular design.

I. Introduction

Photochromism is the reversible transformation of a chemical species between two forms with different structures by photoirradiation.[1] Photochromic materials have attracted much attention because of their potential applications in optelectronic devices.[2,3] The properties required for optelectronic applications and especially for optical memory media are thermal irreversibility, fatigue resistance, rapid response, high sensitivity, and nondestructive readout capability. Among photochromic systems, dithienylethene derivatives are one of the most promising systems for these applications. Various types of thermally stable[1,2,4] and fatigue-resistant[2] dithienylethene derivatives have been developed. They undergo a cyclization/cycloreversion electrocyclic reaction upon UV and visible irradiation.[1,2] The quantum yields of the photochromic reactions as well as the absorption maximum can be controlled by the substituents introduced into the aryl groups.[5−9] Despite the intense investigation of this family of compounds, the coloration/decoloration mechanism is not precisely known and a full understanding of the photochemical reaction is necessary to be able to design dithienylethene derivatives with improved characteristics.

Time-resolved experimental studies[10−15] have shown that both cyclization and cycloreversion reactions take place in the picosecond time domain and that these transformations do not involve the triplet states. The rate constant for the cyclization reaction has been measured for several dithienylethene derivatives and determined to be less than a few picoseconds. The cycloreversion reaction has been measured to take place with a rate constant of 2−3 ps for 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride and 325 ps for 1,2-bis(5-formyl-2-methyl-3-thienyl)perfluorocyclopentene.[13,14] For the latter system, a detailed analysis of the transient absorption spectrum by collective electronic oscillator (CEO) on the basis of the INDO/S Hamiltonian has indicated the presence of a precursor in the cycloreversion reaction from which the ring-opening and radiationless deactivation competitive processes take place.[14]

SCHEME 1



Recently, the enhancement of the quantum efficiency of the cycloreversion reaction has been obtained by irradiation with a picosecond laser.[16] It has been concluded that the stepwise multiphoton process is the origin of the increase of the quantum efficiency. To rationalize the observation and to achieve a better understanding of the reaction mechanism, detailed knowledge of the potential energy surfaces in the lowest excited states is essential. Owing to the size of the systems, until now, semiempirical studies of the potential energy surfaces of some dithienylethene derivatives have been reported.[17]

We present here the results of an ab initio MO study for a model system of dithienylethene derivatives (shown in Scheme 1), which provides an understanding of the mechanism of the stepwise multiphoton process in the cycloreversion reaction. This study is a natural extension of our previous molecular design oriented theoretical studies[4] on dithienylethene derivatives, and is a first step toward a full understanding of the reaction mechanism. What is particularly important, the substituent effect in that the cycloreversion quantum yield changes as a function of substituents shown in Chart 1, has been studied. We present the first example of the correlation between experimental quantum efficiency and calculated properties in this family of compounds.

II. Computational Methods

Stationary points on the potential hypersurfaces of the ground and low-lying singlet excited states were located from ab initio complete active space self-consistent-field (CASSCF) calculations under the C_2 symmetry constraint. Harmonic frequencies were calculated at the optimized structure at the same level of

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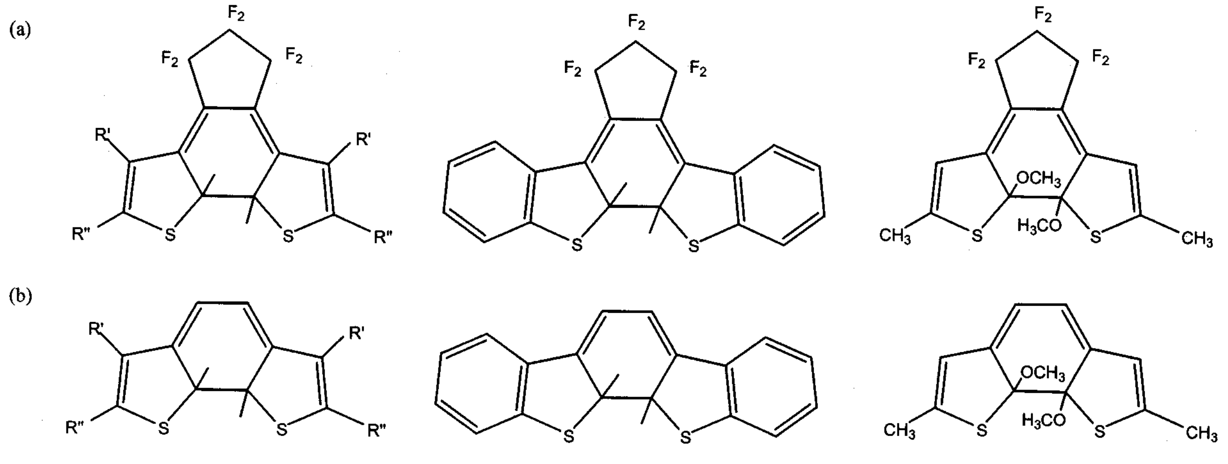
CHART 1



0 :R'=R"=H
1 :R'=CH3, R"=CN
2 :R'=CH3, R"=H
3 :R'=H, R"=CH3

4

5

accuracy to confirm the resulting structure to be a minimum or a saddle point. Due to the large size of the system and as our interest lies on the exploration of the potential energy surface, some limitations concerning the size of the basis set and of the active space of the CASSCF were unavoidable. The results reported here were obtained using a 6-31G basis set. The active space of the CASSCF(10,10) includes 10 orbitals occupied by 10 electrons. It comprises 10(π,π*) orbitals for the open-ring isomer and 8(π,π*) plus the 2(σ,σ*) orbitals of the C−C reactive bond which is broken during the course of the photoreaction for the closed-ring isomer. Some preliminary calculations were done with a larger active space to select the proper orbitals to describe the ground and excited states. Some additional test calculations with the 6-31G* basis set including polarization functions were done. The increase of the size of the active space as well as the basis set did not lead to significant structural differences on the lowest energy structures. For the important stationary points (Ac and Ao, to be described later) of the model system, and five substituted systems, CASSCF(12,14) calculations with 12 orbitals and 14 electrons have also been carried out, where the lone pairs of sulfur atoms are included in the active space. The oscillator strengths were computed at the TD-DFT level with the B3LYP functional and the 6-31G basis set. The calculations were performed with the Gaussian 98[18] and GAMESS[19] program packages.

III. Results and Discussion

The geometries of the open-ring and closed-ring isomers were optimized in the ground and excited states. The resulting optimized structures with many unique features are shown in Figures 1 and 2. The corresponding energies are given in Table 1. Figure 3 shows the energy profile for the reaction. The discussion is divided into (i) a brief discussion of the cyclization reaction, (ii) a discussion of the cycloreversion reaction, (iii) a discussion of the multiphoton gated process, and (iv) a discussion of the substituent effects on the quantum yield.

Cyclization Reaction. The energy profile of the potential surface is schematically shown in Figure 3 as a function of the internuclear distance (q) between two reactive carbon atoms (C1 and C6 in Scheme 1). The geometry optimizations on the excited potential surface show that the open-ring isomer relaxes in the direction of the cyclization reaction, simultaneously undergoing important structural deformations.[20] As shown in Figure 1, the distance q decreases from 3.402 Å in the ground state to reach 2.274 Å in the 2A state (2Ao point), 1.799 Å in the 1B state, and 2.030 Å in the 3A state (3Ao point). The dihedral angle formed by the C1, C2, C3, and C4 carbon atoms (see Scheme 1) decreases from 42.8° in the ground state to reach 12.4° in the 2A state, 22.1° in the 3A state, and 13.8° in the 1B state.

Upon excitation to the 1B state, the state will relax to the minimum having a C−C bond distance of $q = 1.779$ Å, or crossover into the 2A state, and then relax to the 2Ac ($q =$

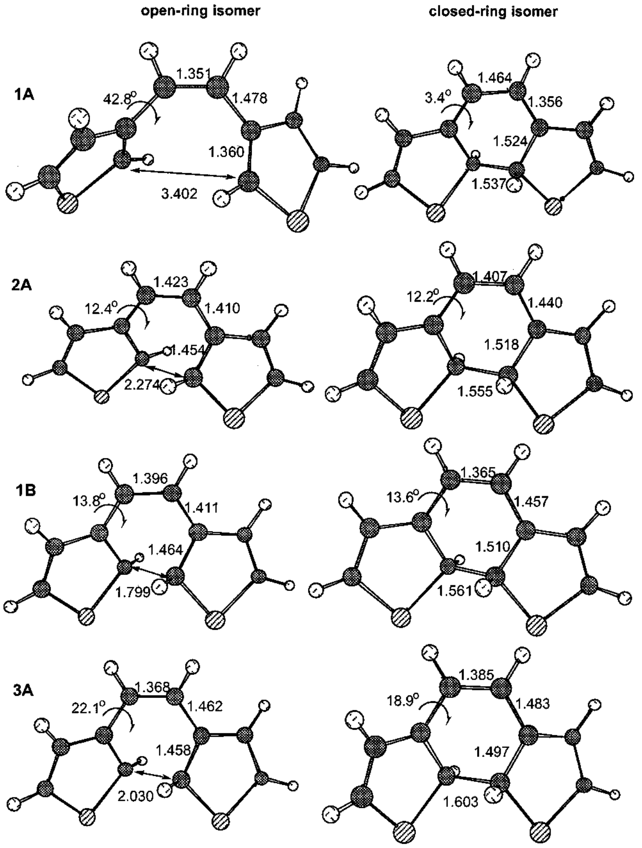


Figure 1. Optimized structures of open-ring and closed-ring isomers in the ground and excited states obtained at the CASSCF(10,10) 6-31G level.

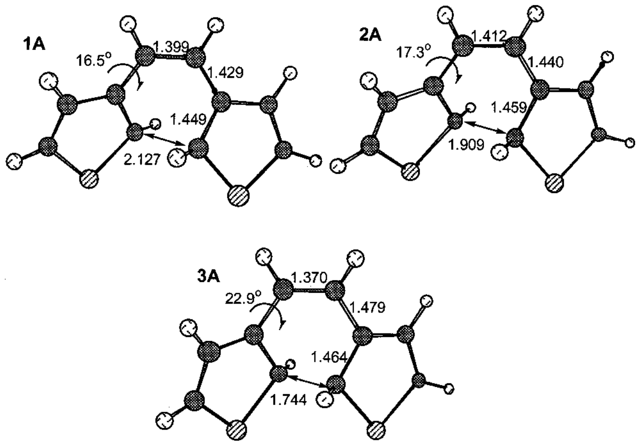


Figure 2. Transition-state structures located on the 1A, 2A, and 3A potential energy surfaces at the CASSCF(10,10) 6-31G level.

1.555 Å) or 2Ao ($q = 2.274$ Å) minimum. The 2Ao minimum is located between the closed-ring and open-ring isomers. From this 2Ao point, the system may decay to the ground-state closed-ring or open-ring isomer (see Figure 3). The presence of a common intermediate in the electrocyclic reaction has already been proposed by Celani et al.[21,22] as a result of a theoretical investigation of the electrocyclic reaction of cyclohexadiene/hexatriene. In these studies, the authors report a detailed characterization of the 2A potential surface and have shown that the decay to the ground state occurs through a conical intersection located about 1 kcal/mol above the common intermediate whose structure closely resembles that of the 2Ao intermediate.[21,22]

To discuss the detailed dynamics of the current molecule on the excited-state potential surfaces, it would be necessary to locate all the important conical intersections.[21b] On account of the size of the molecule, we have limited our study to determination of the important stationary points, which have led to the correlation between experimental data and calculated properties. The interpretation of experimentally observed fluorescence[2] from the exited state of the open-ring isomer will be reported elsewhere.

Cycloreversion Reaction. Though there is a drastic geometrical change, of distance q from 3.402 to 2.274 Å (2Ao), in the cyclization reaction (Figure 3), the geometrical parameters of the excited state of the closed-ring isomer remain very close to those of the initial ground-state structure. Consequently, the high concentration of states with similar energies suggests the complex nature of the cycloreversion reaction mechanism. The largest geometrical deviations from the ground-state structure are observed for the 3A state (3Ac point). The elongation of the bond length q is 0.07 Å for the 3A state (3Ac point), and less than 0.03 Å for the 1B and 2A states (2Ac point) (see Figures 1 and 3). Several attempts to optimize the 2B state failed because of convergence problems during the course of the optimization cycles.

Transition states (TSs) with one negative frequency were found between the two minima of each of three A potential energy surfaces. The energy of the TS of the 1A ground state, 46 kcal/mol higher than that of the closed-ring isomer, indicates that the thermal cycloreversion reaction is difficult and reflects that it is symmetry forbidden[4] according to the Woodward−Hoffmann rules.[2] The TSs on the 2A and 3A surfaces are located at the closed-ring side (left side in Figure 3). The structures are shown in Figure 2. The two minima and the transition state of each surface are connected through the rotation of the two thiophene units. The energy barrier along with the q from the minimum of the closed-ring side toward the minimum of the open-ring side decreases on going from the 1A surface (46 kcal/mol) to the 2A (6 kcal/mol) and 3A (1 kcal/mol) surfaces. It suggests that the cycloreversion reaction will be favored if it occurs on the higher A surface, as shown in Table 2, to be discussed later.

The fate of the excited closed-ring isomer is difficult to predict. According to the obtained scheme shown in Figure 3, upon excitation to its 1B state, the system may reach the 2A state or decay to the ground-state closed-ring isomer. Depending on the position of the 1B/2A crossing point on the potential energy hypersurfaces, the 2Ao or 2Ac point will be populated.

As the energy profile (Figure 3) shows, there are minima of 2A and 3A whose C−C bond distances are very similar to that of the 1A closed form. In fact the existence of the minima characterizes the main feature of cycloreversion. Going from this 2Ac closed-ring excited state to 2Ao, there is a barrier caused by C−C bond fission, whereas coming from the open-ring excited state, there is no barrier toward 2Ao on the 2A (or 1B) surface, irrespective of the fact that three double bonds are changing to two double bonds and one σ bond. When the system arrives at the 2Ao point, both cyclization and cycloreversion are anticipated, since 2Ao is located in an intermediate position. The rate of population on 2Ao by the cycloreversion process will be less than the rate of population from the cyclization process, because of the presence of an energy barrier. This is consistent with the experimental observations indicating a larger quantum yield in the cyclization than in the cycloreversion reaction of dithienylethene derivatives.[14]

Multiphoton Gated Photochromic Reaction. We have recently reported[16] a significant increase in the quantum yield (more than 50 times) for the cycloreversion reaction by using a high-intensity picosecond laser pulse irradiation. The laser-

TABLE 1: CASSCF(10,10) Energies (au) of the Lowest Singlet Excited States of the Open-Ring and Closed-Ring Isomers Corresponding to the Ground-State and Excited-State Optimized Structures[a] TD-DFT Oscillator Strengths f

	open-ring isomer		closed-ring isomer		
electronic state	vertical energy[b]	optimized structure	vertical energy[b]	optimized structure	transition state
1A	**−1178.21359**	**−1178.21359**	**−1178.21595**	**−1178.21595**	**−1178.13978**
2A	**−1177.98418**	**−1178.07945**	**−1178.04377**	**−1178.09264**	**−1178.06996**
	($f = 0.00$)	**−1178.08613**[c]	($f = 0.03$)	**−1178.09552**[c]	
1B	**−1177.97920**	**−1178.02690**	**−1178.00172**	**−1178.04511**	
	($f = 0.15$)		($f = 0.14$)		
2B	**−1177.95468**		**−1177.98663**		
	($f = 0.07$)		($f = 0.01$)		
3A	**−1177.96925**	**−1178.02293**	**−1177.97426**	**−1178.01800**	**−1178.01633**
	($f = 0.00$)		($f = 0.01$)		

[a] f = TD-DFT oscillator strength. [b] Vertical energies were obtained by state-averaged CASSCF calculations, in which the 1A, 2A, and 3A states (or 1B and 2B states) were included with equal weight. [c] CASSCF(12,14) calculation.

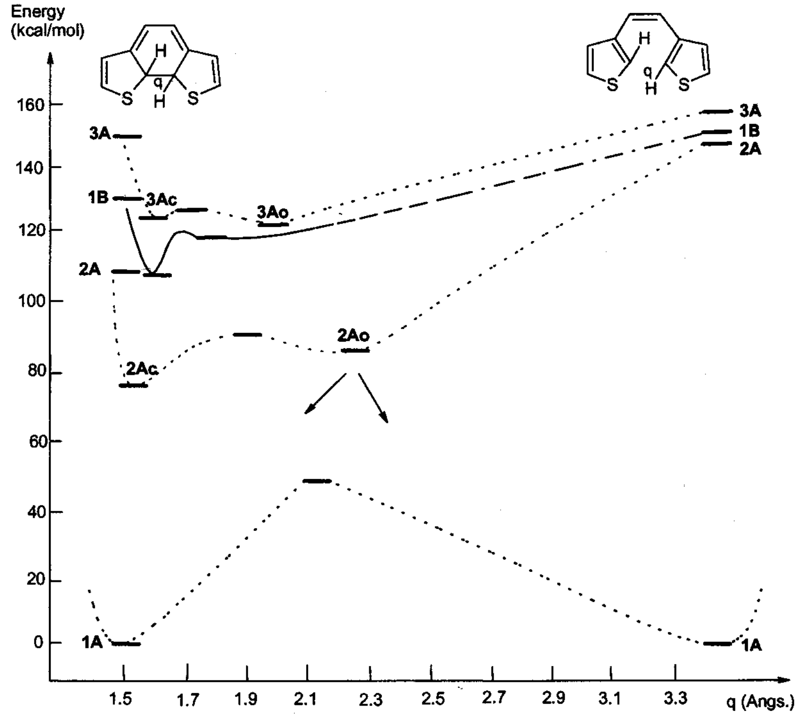


Figure 3. Potential energy profile of the model system.

TABLE 2: Comparison of the Calculated Properties of Model System 0 on the 1A, 2A, and 3A Potential Energy Surfaces

	1A	2A	3A
energy barrier from closed- to open-ring isomers (kcal/mol)	46	6	1
NO occupation number of σ^* at Ac	0.0189	0.0197	0.0237
C$-$C bond length at Ac (Å)	1.537	1.555	1.603
dihedral angle at Ac (deg)	3.4	12.2	18.9

induced enhancement of the quantum efficiency has been attributed to a stepwise multiphoton process such as So + $h\nu$ → S1 and S1 + $h\nu$ → Sn, which leads to the population of higher-energy excited states.

Although the detailed discussion of the dynamics should be based on the data of conical intersections and accurate calculations of higher excited states, which will be a subject of future study, this experimental result can be consistent with the shape of the potential energy curves shown in Figure 3. The energy barrier from the closed-ring isomer to the open-ring isomer decreases from the 1A surface to the 2A and 3A surfaces. Two excited-state minima were separated by a small energy barrier (1 kcal/mol) on the 3A surface. The excitation of the closed-form isomer in its 3A state will lead via an almost barrierless process to the population of the 3Ao intermediate, which is the lowest energy point on the 3A surface. This surface is connected to the 3Ac point by a small energy barrier. The 3Ao intermediate is displaced along the cycloreversion reaction, and an increase of the quantum yield of the reaction can be expected upon its population. Furthermore, the calculated oscillator strengths corresponding to the excitations to the 2A and 3A states of the closed-ring isomers show considerably weaker values than for the 1B state (Table 1). This suggests that the direct pumping by a single photon to the higher A state is less favored than the process via a gate state with a larger oscillator strength. Thus, the gated stepwise multiphoton process is supported with the profile shown in Figure 3.

The results of the current calculation (Figure 3) can indicate that either the direct pumping through two-photon excitation from the 1A state to the 2A or 3A state or the stepwise process is possible. Although the current calculation is not sufficient to

TABLE 3: Optimized Distance q (Å) of the Unsubstituted (0) and Substituted (1−5) Model Systems in the 2A State, Energy Difference ΔE (kcal/mol) between 2Ac and 2Ao, Natural Orbital Occupation Number of σ^* in 2Ac, and Experimental Quantum Yield ϕ_{c-o} for the Cycloreversion Reaction of the Corresponding 1,2-Dithienylperfluorocyclopentenes

system	method	q(2Ac)	q(2Ao)	ΔE(2Ao − 2Ac)	NO occupation	ϕ_{c-o}	note
0	CAS(10,10)	1.555	2.274	8.3	0.01973		
	CAS(12,14)	1.558	2.245	5.9	0.01998		
1	CAS(10,10)	1.585	2.385	11.6	0.02140	0.075	a
	CAS(12,14)	1.586	2.346	9.5	0.02154		
2	CAS(10,10)	1.587	2.400	6.4	0.02155	0.13	b
	CAS(12,14)	1.589	2.367	4.5	0.02174		
3	CAS(10,10)	1.588	2.424	5.9	0.02162	0.12	c
	CAS(12,14)	1.590	2.390	4.0	0.02178		
4	CAS(10,10)	1.603	2.385	−4.4	0.02254	0.35	d
	CAS(12,14)						
5	CAS(10,10)	1.570	2.308	13.9	0.02129	0.003	e
	CAS(12,14)	1.572	2.265	11.4	0.02152		

[a] Measured by 588 nm in decalin (ref 25). [b] Measured by 492 nm in hexane (ref 26). [c] Measured by 533 nm in hexane (ref 32). [d] Measured by 517 nm in hexane (ref 27). [e] Measured by 547 nm in hexane.

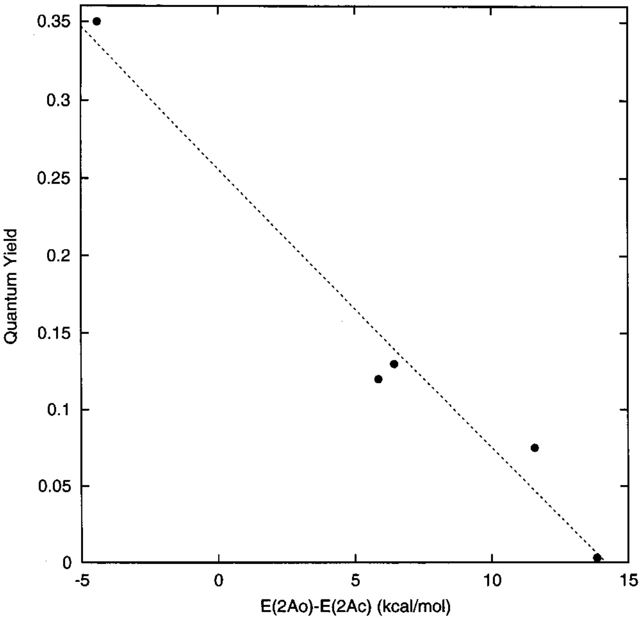


Figure 4. Correlation of the experimental quantum yield with the calculated energy difference.

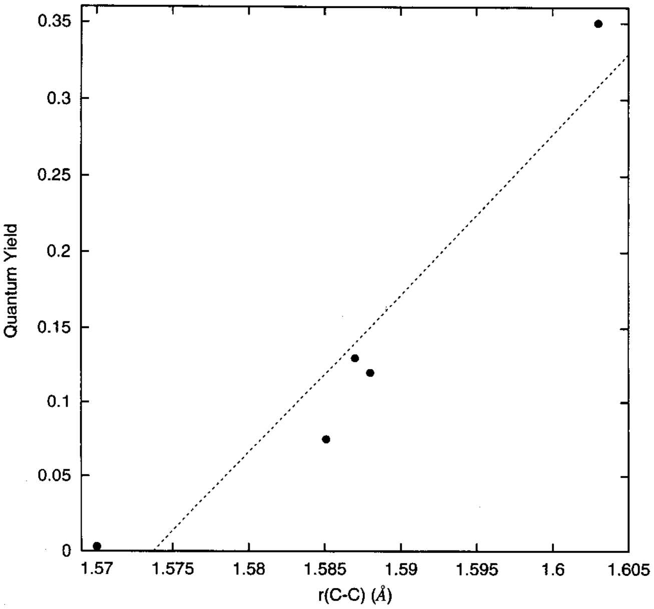


Figure 5. Correlation of the experimental quantum yield with the optimized C−C bond length *r*(C−C) in the 2Ac state.

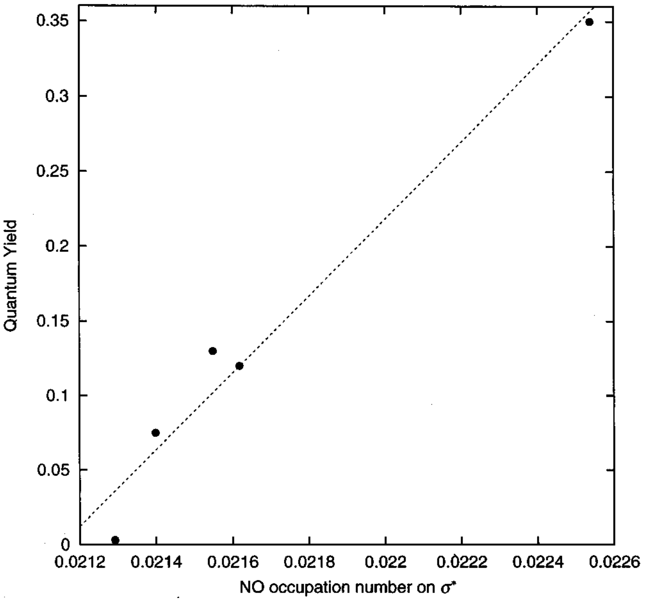


Figure 6. Correlation of the experimental quantum yield with the natural orbital occupation number of the σ* orbital in the 2Ac state.

distinguish these two, the calculated properties indicate how the cycloreversion reaction is favored in each A state. The energy barrier from closed to open, natural orbital occupation number in the σ* orbital, C−C bond length (*q*), and dihedral angle of the closed form in each Ac state are shown in Table 2. These data suggest that the cycloreversion reaction will be favored if it occurs on the higher A surface.

Correlation between Experimental Quantum Yield and Calculated Properties. The analysis on the model system has provided an interpretation of the novel significant increase in the quantum yield[16] with high-intensity picosecond laser pulse irradiation. The important feature obtained by the calculation is the existence of a minimum on the 2A potential surface (Ac) in the cycloreversion reaction, which contrasts with the absence of a minimum in the reverse cyclization. To investigate the role of the minimum 2Ac in the cycloreversion reaction, we have studied the quantum yield of various dithienylethene derivatives in ordinary single-photon reactions. When the 2Ac point is populated, the quantum efficiency of the cycloreversion reaction will depend on the ability of the system to overcome the energy barrier between 2Ac and 2Ao.

The presence of substituents will affect the ability and may influence the quantum yield. To test the validity of this argument, we have carried out further calculations for various derivatives whose experimental quantum yields are measured. We have analyzed the energy difference between 2Ac and 2Ao (ΔE), internuclear distance (*q*) of the C−C bond in the optimized 2Ac state, and natural orbital occupation number of the σ* orbital in the 2Ac state.

Experimental quantum yields are reported for a series of derivatives having perfluorocyclopentenes in common as shown in Chart 1a. They are gathered in Table 3. The calculations have been carried out for the model systems shown in Chart 1b, where perfluorocyclopentene groups are replaced by two hydrogens.[28] The calculated energy difference ΔE (= E(2Ao) − E(2Ac)) is shown in Table 3, together with other properties. The CASSCF(10,10) calculations have been carried out; moreover, for most of the systems the CASSCF(12,14) calculations including the lone pairs of sulfur atoms have also been carried out (Table 3).

A higher quantum yield is associated with a lower ΔE of the model systems. The lowest ΔE is obtained with the benzothiophene group (system 4 in Table 3). With the methoxy substituent, on the contrary, the highest ΔE is obtained (system 5 in Table 3). The correlation between experimental quantum yields and the calculated ΔE is shown in Figure 4. The nature of the barrier may be projected in the strength of the C−C bond. In fact, the correlation has also been traced in the electronic and geometric properties of the 2Ac state. The experimental quantum yield and the optimized C−C bond distance *r*(C−C) (*q*(2Ac) values in Table 3) have shown a good correlation as shown in Figure 5. It is traced in the natural orbital occupation number of the σ* orbital in 2Ac, as shown in Figure 6.

This correlation is useful in practice; however, the following should be noted. Although it is desirable that the barrier between 2Ac and 2Ao is estimated, the type of reaction in question is the same type of C−C bond fission. Therefore, ΔE can be an index following the Hammond rule. As indirect evidence of the barrier, the temperature-dependent quantum yield has already been reported for system 1 of Chart 1a as well as for the same family of dithienylethene molecules.[25,29] As for the method, the current CASSCF method does not account for the dynamic correlation effects.[20,30] The limitation of C_2 symmetry should also be considered, since there are examples of the excited state having lower symmetry than the ground state.[31] The zero-point energy is not considered.

To our knowledge, this is the first time that a reasonable correlation between the experimental quantum yields for the photochemical cycloreversion reaction and the calculated values has been presented. It is possible to use this correlation as a guiding principle of the molecular design.

IV. Conclusion

An ab initio MO study on a model system of dithienylethene derivatives is presented. On the basis of the obtained potential energy profile, a rationalization is provided for the mechanism of the experimentally proposed stepwise multiphoton process in the cycloreversion reaction. The first example of a rational correlation between experimental quantum yields and calculated properties as a function of substituent effects in this type of system has been demonstrated. It is possible to use the correlation as a guiding principle of future molecular design.

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(20) The two lowest electronic excited states are the 1B and 2A states. The 1B state is dominated by the single excitation from the HOMO to the LUMO ($\pi \rightarrow \pi^*$) and presents a strong ionic character. The other low-lying excited state, 2A, is mainly covalent. The ground state 1A strongly interacts with the 2A and 3A excited states. CASSCF calculations suggest that the 2A state is the lower energy excited state. However, it has been previously shown for other aromatic molecules such as hexatriene (ref 23) or benzene (ref 24) that dynamic correlation effects can significantly decrease the energies of the ionic excited states, which may cause them to be incorrectly described at the CASSCF level.

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