

Review Commentary

Quantum yields and potential energy surfaces: a theoretical study

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ABSTRACT: A theoretical study on quantum yields (QYs) of the photochromic cyclization and cycloreversion reactions is presented. It is shown that the thermodynamic relative stability of various energy minima on the ground state is primarily important for the cyclization reactions. On the other hand, the profile of the excited state potential energy surfaces (PESs) and the locations of conical intersections (CI) are important for the cycloreversion reactions. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; quantum yield; theoretical study; potential energy surface

INTRODUCTION

Photochromism is an interesting research subject, since its potential application to the molecular switches and molecular memories is expected in the near future.¹ In order to be an industrially feasible material, several physical properties such as the thermal stability, fatigue resistivity, magnitude and position of absorption bands and the optimum quantum yields (QYs) are required. Amongst many photochromic molecules, diarylethene derivatives are one of the most promising photochromic families, because of their distinct photochromic performances as well as the extraordinary fatigue resistivity.^{1,2}

We have previously reported a series of theoretical studies on the photochromic properties of diarylethenes. The thermal stability has been elucidated with the state correlation diagram, and the discussions whether the possible photochemical and thermal reactions are symmetry allowed or forbidden have been done.^{3a}

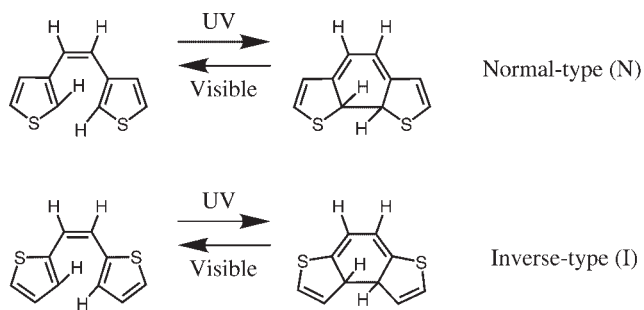
Although fatigue resistivity is the most critical request for the industrialization of all organic materials, theoretical approaches to it are powerless unless the mechanism of degradation processes or side reactions are clarified. Therefore this problem has been solved only by experimental approaches. On the other hand, the problem how to design the properties of absorption bands^{3b} has been investigated theoretically for several industrially important dyes.^{3c} Although the guiding principles for thermal stability as well as the designing properties of absorption bands were proposed and their validity ascertained,^{3a,b} the last property, that is, how to control the QYs of the photochemical reactions, is the most difficult subject, since the mechanism which determines the value of the QYs remains counter-intuitive, due to a paucity of detailed experimental information on the excited states.

The QY is an important property from the viewpoint of applications. For example, in the molecular memory – oriented application, for the sake of a device's efficiency, a large QY is expected in cyclization as well as in cycloreversion. In some applications, such as write-once media, the QY of either of the back-and-forth reactions should be zero.

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Non-destructive read out of the memory is an indispensable condition for the rewritable optical memory media using photochromic compounds. Because the irradiation of light which is absorbed by the compound should induce photoreaction, some idea to prevent the destruction of the memory is necessary. As a trial approach, we have studied the use of regular IR light^{4a} and the IR light in the near field.^{4b} Alternatively, if QY is wavelength-dependent and there is a wavelength which still has the absorption but the QY is zero, the problem is solved: We can read the data by checking the absorption without inducing the photoreaction, and we can erase the data by the light where the QY is non-zero. Although there are many experimental studies on QY of various diarylethene derivatives¹, the principle which determines QY is so unclear that the examination of the structure – QY relationship of the reported compounds did not give the answer. For example, a molecule showing QY = 1.0 in crystal and 0.59 in hexane,^{5a} whereas another molecule showing QY = 0.0 in crystal and 0.35 in hexane^{5b} (*vide infra*). In this case, we believe that the theoretical study to clarify the relationship between the structure and QY will be effective.

In this paper, we will first review our previous theoretical studies on QY, and will then report a new feature that determines QY as a reflection of the energy profile of the excited state potential energy surfaces (PESs). The potential energy profiles of two model reactions are compared, taking into account in particular its relation to the cycloreversion QY. These two model molecules are the elemental frame of various derivatives. We call these two photochromic diarylethene models as ‘Normal type (N)’ and ‘Inverse type (I)’, respectively.



METHOD

Ab initio molecular orbital method was used for all the calculations. For the most part we used the 6-31G basis sets and the complete active space self-consistent-field (CASSCF) method. The active space of CASSCF (10,10) was employed, where the numbers of π -electrons and orbitals are represented in the parenthesis, respectively. That is to say, 10 electrons were placed in the 10π orbitals

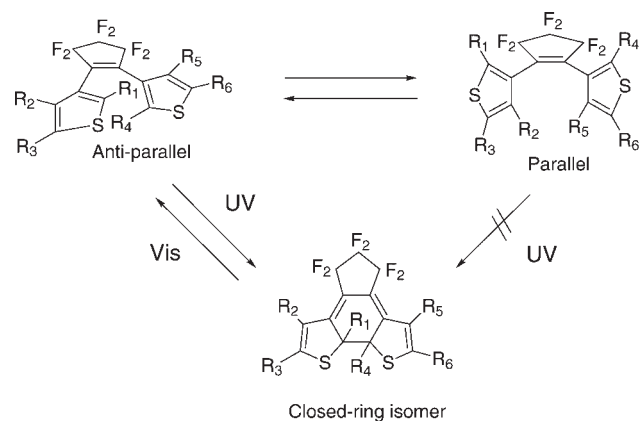
for the open-ring isomers. For the closed-ring isomers, the 10π orbitals correspond to the 2σ and 8π orbitals. It is known that for the check of the dynamic correlation effect and the basis set dependency, the additional calculations of CASSCF (14,14) with the active space including four more σ electrons and σ orbitals of the C—S bonds, as well as CASSCF (10,10) with the 6-31G* basis sets and CASPT2 (10,10) were necessary.^{2d,e} These additional studies were intensively performed on the frame model molecule of the (N)-type and reported in the cited reference. This will be mentioned later. We used the GAMESS,⁶ MOLCAS⁷ and MOLPRO⁸ program packages.

RESULTS AND DISCUSSION

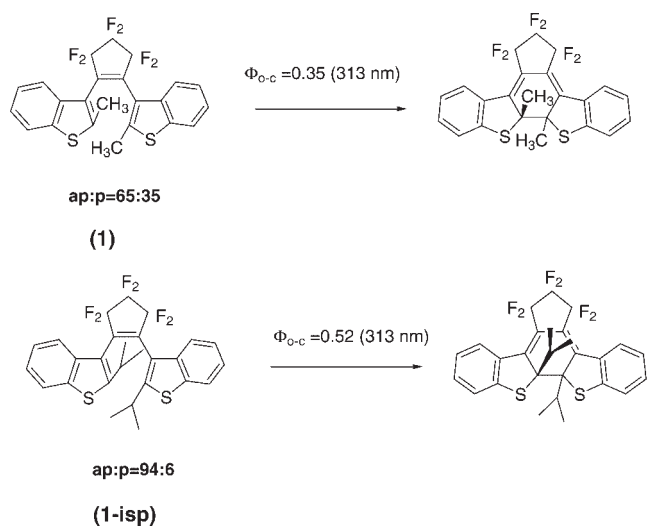
Cyclization quantum yield dependence on ground-state population of conformers

A theoretical study which attempted to shed light on the determining factor of the cyclization QY has been reported.⁹ The motivation of the study was to understand the interesting experimental result that whereas the replacement of methyl groups at C-2 of both benzothienophene rings of 1,2-bis(2-methyl-3-benzothieryl)perfluorocyclopentene **1** with isopropyl groups was effective to increase the cyclization QY,¹⁰ it was not effective for 1,2-bis(2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene **2**. As shown in Scheme 1, there are anti-parallel and parallel conformations for the open form of both **1** and **2**.¹⁰ Upon irradiation of UV light, the anti-parallel conformer can cyclize to be a closed form, while the parallel conformer cannot cyclize, and therefore the population of the two conformers is directly related to the cyclization QY.

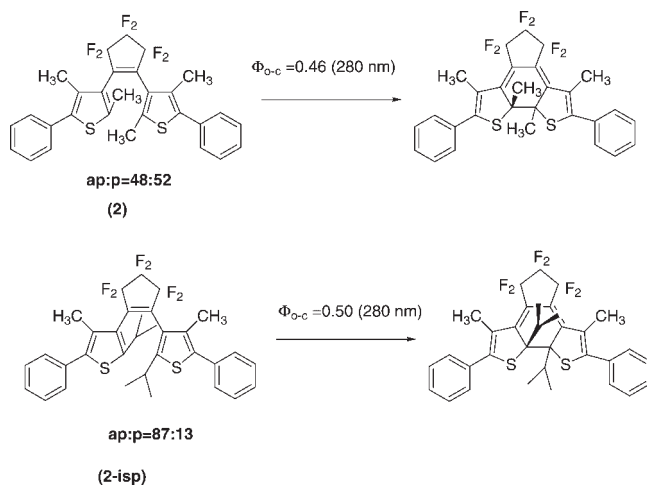
Indeed, the introduction of isopropyl groups increased the QY from 0.35 of **1** to 0.52 of **1-isp** as a result of the increase in population of anti-parallel conformer of **1-isp** (94:6) compared to that of **1** (65:35), determined by ¹H NMR.¹⁰



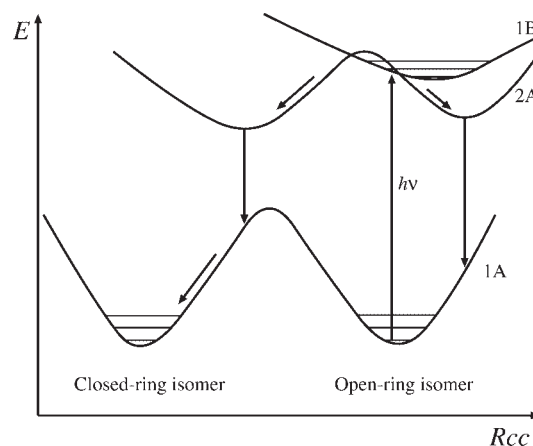
Scheme 1. Parallel and Anti-parallel conformers



Although the population of the anti-parallel conformer increases in the case of the **2-isp**, the QY does not increase correspondingly.⁹



The CASSCF-obtained excited state PES⁹ explains the reason why the population increase of anti-parallel conformer does not contribute to the increase in the cyclization QY. For **2** and **2-isp** molecules, the PES of cyclization is schematically shown in Scheme 2. On UV irradiation the open-ring conformer of the ground state will be excited to the allowed 1B Franck-Condon (FC) state, (direct excitation to 2A from 1A is symmetry forbidden), then the excited state must shift onto 2A state, since the ground state is A state. In fact the CASSCF results show that there is 2A state near the 1B state.^{9b} If the relaxation from the 1B FC state proceeds towards the non-reactive side (to the right direction in Scheme 2) via 2A to 1A state, it turns out to be no reaction and a simple return back to the initial open ring ground state of 1A. If the minimum of 1B is located sufficiently left compared to the position depicted in Scheme 2, then the shift will be in favour of the cyclization. It is the case of **1** and **1-isp**,



Scheme 2. Potential Energy Surfaces of Cyclization Reaction

where the anti-parallel population of the ground state is directly related to the cyclization QY, while in case of **2** and **2-isp** the situation is just as shown in Scheme 2. Therefore the increase in the anti-parallel population at the ground state is not sufficient to determine QY. In general, it is also necessary to consider the profile of the excited state PES. Its importance will be discussed later.

Comparison of cyclization quantum yields in crystals and in solution

Experimental measurements of cyclization QYs were also carried out in crystals for **1** and **2**. Surprisingly, **2** showed the QY 1.0 in crystals and 0.59 in hexane solution.^{5a} By contrast, the QYs of **1** are 0 in crystals and 0.35 in hexane.^{5b} To explain these results, both the structural and theoretical studies were required. Kobatake *et al.*^{5b,11} carried out X-ray crystallographic analysis of a number of diarylethenes, and concluded that when the distance between two bond-forming carbon atoms (hereafter denoted as R(C—C)) in open forms is longer than 4 Å no cyclization is possible in crystals. As the R(C—C) of **1** was 4.353 Å by X-ray and 4.477 Å by calculation at the HF level, the cyclization QY in crystals was 0. On the other hand, as the R(C—C) was 3.507 Å and 3.797 Å by X-ray and HF level calculation, respectively, the QY of **2** was 1. These results were reproduced on the theoretical PES of the excited states of **1** and **2**, as shown in Fig. 1.¹² Geometrical relaxation started from the FC state when generated from the stable anti-parallel structure led smoothly to the geometry of the closed form for **2**, but did not for **1**. It is notable that there is no energy barrier in cyclization path on the excited state PES, which is different from the ring-opening cyclor-eversion reactions. This will be mentioned later.

The cyclization QYs in hexane solution were explained by the argument of the population of anti-parallel and parallel conformers, together with an additional analysis of ground-state vibrations.¹² As for **2**, it is natural to

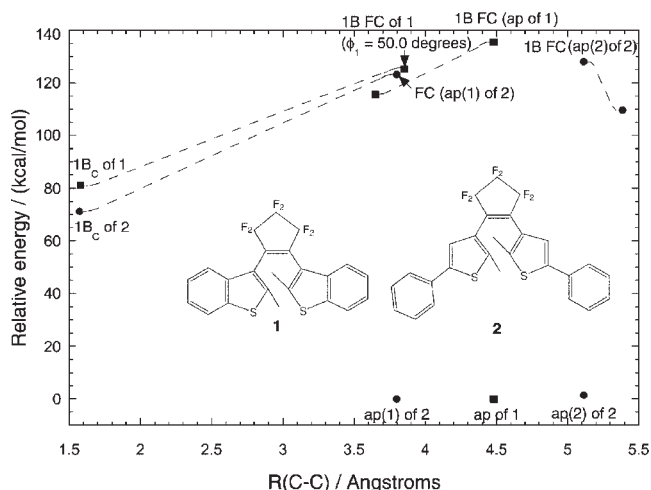


Figure 1. Cyclization PES for the molecule (1) with squares, and (2) with circles (Reference)¹². When the geometry relaxation from the 1B FC state of (1) with $R(C-C) = 4.477 \text{ \AA}$, no cyclization is observed (corresponding to the reaction in solid). With an aid of low energy vibrational mode having a twist angle of 50° , the cyclization does occur (corresponding to the reaction in solution). As $R(C-C)$ distance of 1B FC state of (2) is less than 4 \AA , which is the critical distance (Reference 11), this state relaxes smoothly towards the cyclization, shown with circles. Energies are obtained by optimizing other geometries by fixing $R(C-C)$ at different distances by CIS method with 6-31G basis set

assume that **2** can take the anti-parallel conformation with less than 4 \AA $R(C-C)$ in solution. On the other hand, as the most stable anti-parallel conformation of **1** has longer $R(C-C)$ than 4 \AA in solution, it may not take the conformation that is ready to cyclization. However, the cyclization of **1** does occur in solution. To explain this result, the theoretical vibrational frequency analysis can be employed.¹² The ground-state PES of anti-parallel conformer of **1** is so shallow that the conformation with the $R(C-C)$ shorter than 4 \AA can have population in a soft environment such as hexane solution by the aid of vibrations with very low frequencies, which is impossible in rigid environment such as in crystal.

Quantum yield of cycloreversion: the potential energy surface (PES) of (N)-type

The study of the QY in cycloreversion was necessary to elucidate a substituent effect at the C-5 positions of the thiophene rings. When the conjugation of the substituents at C-5 was longer, the cycloreversion QY was smaller. It was interpreted by evaluating the energy gradient, which is the intra-molecular force at the FC state of the closed form. The energy gradient of the FC state which determines the driving force of the cycloreversion reaction becomes small when the conjugation of the substituent increases. Thus, only information about the electronic properties in the FC state could provide a

satisfactory explanation¹³ without obtaining the precise PES of the excited state. We were able to do this, because we were dealing with a series of the same sort of substituents which differed only in the size of the conjugation.

In more general cases, the positions and the type of substituents are significantly different. We therefore clarified the PES profile to explain the experimental results shown in Fig. 2.¹ Thus the cross section of the PES was calculated for the model frame molecule of the (N)-type by fixing only $R(C-C)$ at different distances among the molecular geometrical variables, expecting that the critical energy profile and specific features on the PES such as energy minima, saddle points, and position of Conical Intersections (CI) would be obtained. Then the substituent effect was taken into account by calculating molecules with substituents at the designated positions.

The PESs and CI positions of (N)-type molecule were obtained¹⁴ and depicted in Fig. 3. For the ground state and two lower excited states (2A and 1B), we calculated the cross section of PESs by fixing only $R(C-C)$ at different distances among the molecular geometrical variables within C_2 symmetry. The $R(C-C)$ is defined as the distance between the two reactive carbon atoms as before. The optimized saddle points and stationary points with C_2 symmetry were verified to be local minima by the frequency analysis. Although the calculations of CI were carried out without symmetry, the symbols of C_2 symmetry were used for the better understanding. Detailed check of the basis set and dynamic correlation were performed and reported in the references.^{14a,b}

Irradiation of visible light to the closed form generates the excited 1B state via an allowed transition, and then moves to the 2A dark state¹⁵ via the CI point of 1B/2A CI (C) (C means closed form side). The excited state will have lifetime on the 2A state. During the thermal fluctuation around 2Ac (local minimum on 2A PES) the system will have enough time to traverse over the transition state between 2Ac and 2Ao. It stays near the local minimum around 2Ao, then the cycloreversion reaction occurs by passing through the CI point of 2A/1A CI (O) (O means open form side). Since the obtained PES and the location of CIs are for the frame molecule, and do not involve all the flexibility of real molecules (e.g. the perfluorocyclopentene part is truncated from all molecules; shown in Figs 2 and 4), it is difficult to consider other non-radiative relaxation or emission which can compete with the cycloreversion reaction. Although it is beyond the scope of the available knowledge of today to evaluate these probabilities, we would assume that the most fundamental factor that determines QY is the probability that the system undergoes from 2Ac to 2Ao. If this hypothesis is correct, the energy difference (ΔE) between 2Ac and 2Ao predicted by theoretical calculation may be an index of the cycloreversion QY. In fact, for the various derivatives of diarylethenes shown in Fig. 2, an interesting correlation between the experimental QY and

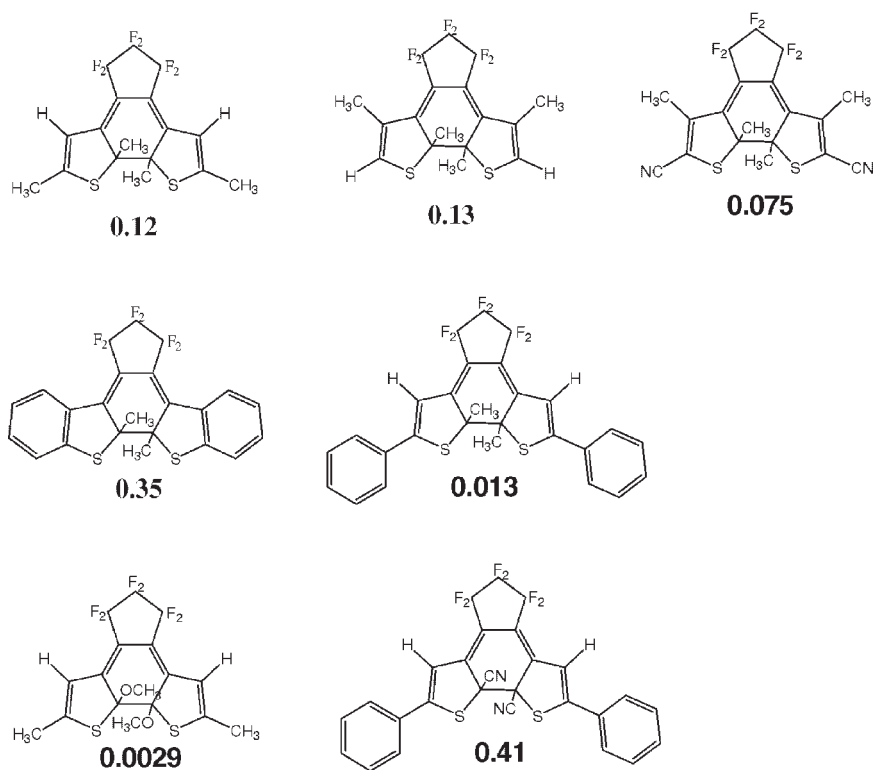


Figure 2. Experimental QY in cycloreversion (Reference 1)

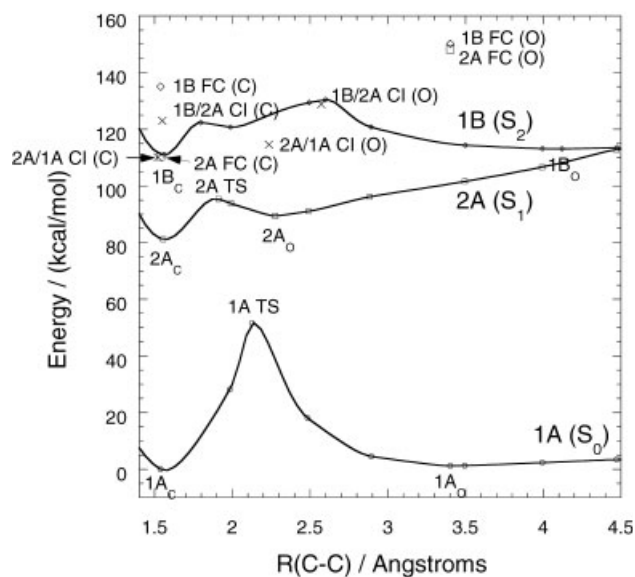


Figure 3. PES of the (N)-type frame molecule. Each point is obtained by the state specific CASSCF(10,10) method with 6-31G basis set, by fixing R(C-C) at different distances and optimizing other geometrical freedoms. Stationary points (1A_o, 1A_c, 2A_c, 2A_o, 1B_c and 1B_o) and saddle points (1A_{TS}, 2A_{TS} and 1B_{TS}) are obtained without geometry constraints at the C₂ symmetry, and verified by frequency analysis. Conical Intersections (2A/1A CI(C), 2A/1A CI(O), 1B/2A(C), 1B/2A(C') and 1B/2A(O)) are obtained by the state-averaged CASSCF(10,10) method. FC denotes Franck-Condon state. Refer to text and References 14b and 15b for details

ΔE has been obtained, as shown in Fig. 4. If this is not a coincidence, the correlation can guide us to the method of molecular design having appropriate QY through the calculation of ΔE . Indeed, two newly synthesized molecules¹⁶ in which the methyl groups at the C-2 positions on the thiophene rings were replaced by cyano groups (CN) and by methoxy groups (CH₃O) showed fairly good correlation ($\Delta E = -0.8$ kcal/mol and $\Delta E =$

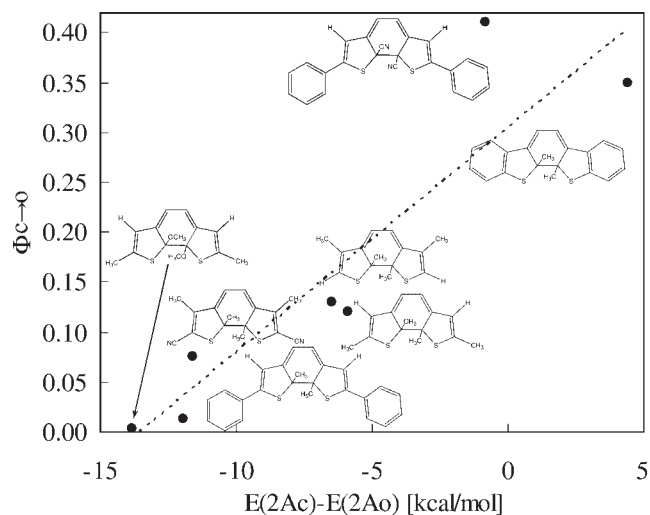


Figure 4. Correlation of experimental QY with calculated $E(2Ac) - E(2Ao) (= \Delta E)$. Two points are added in the previously reported data (Reference 14a); 2, 2'CN- ($\Delta E = -0.8$ kcal/mol) and 2, 2' CH₃O- ($\Delta E = -13.8$ kcal/mol), for which the same level of calculation of CASSCF(10,10)/6-31G were used

–13.8 kcal/mol, respectively). They are shown in Fig. 4, in which other points are the same as the previously reported values.^{14a} It suggests that the forwarding probability¹⁷ from 2Ac to 2Ao, which is strongly correlated to the energy difference (ΔE) between 2Ac and 2Ao, turns out to be the dominant QY determining factor.

Quantum yield of cycloreversion: the potential energy surface (PES) of (I)-type

Although the QYs of photocyclization reactions are not so small in general and often reach 1.0 in crystals as mentioned in Section “Comparison of Cyclization Quantum Yields in Crystals and in Solution”, the QYs of cycloreversion reactions are various and do not usually exceed 0.5 (Fig. 2). One of the exceptions was reported by Uchida *et al.* for the (I)-type compound. The experimental QY of 0.58 was recorded for 1,2-bis(3,5-dimethyl-2-thienyl) perfluorocyclopentene,¹⁸ which provides an opportunity to carry out the theoretical analysis to compare the properties of PESs of (N)- and (I)-type diarylethenes.¹⁹

The PES of the cycloreversion reaction for the (I)-type frame molecule was obtained by the calculations with the same method as previously adopted.^{14a,b} The results are summarized in Fig. 5 and in Table 1. It should be noted that there is no barrier, or only a very small one if anything, on the 2A surface from the closed form to the open form. On irradiation by visible light, the photochemically allowed FC state on 1B is generated. Although the location of CIs was not obtained, the excited state in the 1B state may shift onto the 2A state in a similar way to

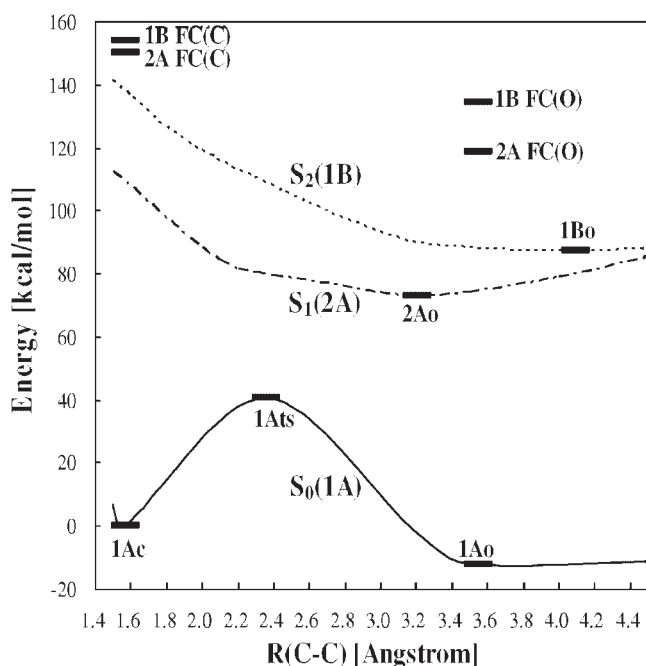


Figure 5. PES of the (I)-type frame molecule calculated by the CASSCF(10,10)/6-31G method

Table 1. R(C–C) and energies of (I)-type frame molecule of the representative points, obtained at the CASSCF(10,10)/6-31G level

State structure	R(C–C) [Å]	Energy [kcal/mol]
1Ac	1.568	0.0 ^a
1Ats	2.354	40.9
1Ao	3.546	–12.4
2A FC(C)	1.568	150.3
2Ao	3.203	73.3
2A FC(O)	3.546	125.8
1B FC(C)	1.568	153.9
1B FC(O)	3.546	134.7
1Bo	4.089	87.5

^a $E_{\text{CAS}}(1\text{Ac}) = -1178.2040065687$ au.

the (N)-type molecule if there is an effective CI, as it is assumed from the shape of the PES. If an effective CI does not exist, the excited state on 1B state arrives at the open form region, where the cycloreversion reaction would occur to give the ground state open form. The shape of PES suggests that as the cycloreversion reaction would not suffer retardation from the barriers, it is so smooth that the QY of the (I)-type would have a large value. In fact, the recorded QY of 0.58 for 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene is a remarkably large value as the cycloreversion QY.

Quantum yield of cycloreversion: the comparison of (N)- and (I)-type molecules

Given that the difference of the 2A state energy profile between the (N)- and (I)-type molecules provides an explanation for why cycloreversion QYs in the (I)-type

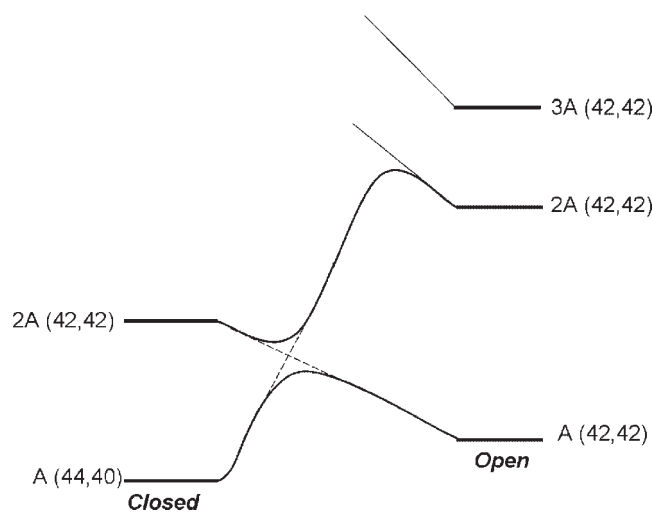


Figure 6. State correlation diagram of the (N)-type molecules. In parentheses are the number of electrons belonging to a and b orbital symmetry with C_2 symmetry. For example, A(44,40) means the ground state of the closed form having the state symmetry of A, composed of 44 electrons with a symmetry orbitals and of 40 electrons with b symmetry orbitals. Refer to Reference 3a for details

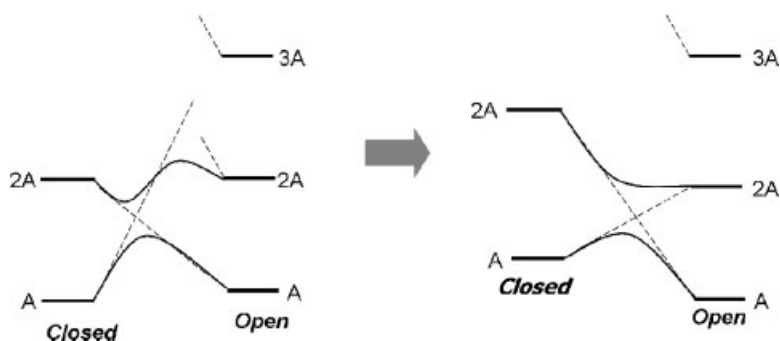


Figure 7. Proposed diagram design from diabaticization

are large, the next step is to elucidate the origin of the barrier. This barrier is evident from 2Ac to 2Ao in the 2A surface of the (N)-type, whereas it is absent (or negligible) in the 2A surface of the (I)-type. Since it is difficult to find experimental information²⁰ on this question, we have interpreted it with the aid of diabaticization, which mathematically corresponds to the inverse operation of diagonalization. It provides information on the state correlation. In this regard, a previously reported state correlation diagram^{3a} for the (N)-type was adopted as the base of the qualitative diabaticization (Fig. 6). We have shown that the ground state electronic structure of the closed form correlates not with the lowest excited state but with the higher excited state of the open form, and so the origin of the barrier seems to be ascribable to this correlation.

In order to increase the QY, the barrier on the 2A surface needs to be very low, or ideally zero. Attempting to decrease the barrier is not likely to change the correlation of the electronic states, because the central frame of the reaction from 1,3-cyclohexadiene to 1,3,5-hexatriene remains unchanged in all the cyclorversion reactions, whether they are (N)- or (I)-types. Instead, if we could change the relative thermodynamic stability of the ground state between closed and open forms, we would be able to change the excited state levels of both sides proportionally. Thus, it might be the answer to remove the barrier on 2A surface entirely. This hypothesis is schematized in Fig. 7. As shown at the right half of Fig. 7, the energy-level increase in 2A state at the closed form will remove the barrier on the 2A surface. We consider it as an explanation for the energy profile of the

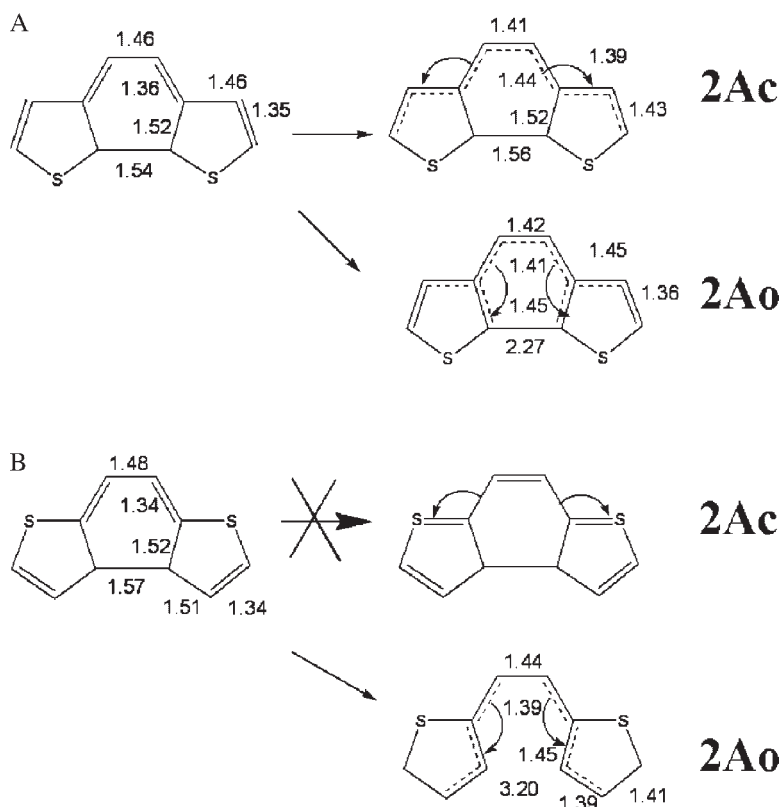


Figure 8. Intermediates on the 2A excited state obtained by calculation

(I)-type reaction having no barrier on 2A (shown in the 2A surface in Fig. 5).

The presence of the barrier on 2A state in the (N)-type and the absence of it in the (I)-type are closely related to the possible intermediate on the excited state. Theoretically obtained geometries^{14b} for 2Ac and 2Ao of (N)-type are shown in Fig. 8a. The reactive carbon distances R(C—C) of 2Ac and 2Ao are 1.56 Å and 2.27 Å, respectively, indicating that 2Ac can be a stable intermediate on the excited state whose R(C—C) is close to the bond length of the normal single bond at the ground state. On the other hand, the geometries for the (I)-type are shown in Fig. 8b (refer also to Table 1). Although the optimized structure corresponding to 2Ac was not obtained, the structure of 2Ao having 3.20 Å of R(C—C) was obtained by the calculations using the same method. Because there is no stable intermediate corresponding to 2Ac, the intermediate 2Ao is generated directly from FC(C) on 2A surface. The reason for the existence and non-existence of the intermediate in the excited states, depending on whether it is (N)-type or (I)-type, will be a future subject for quantum chemistry.

CONCLUSION

Due to a paucity of detailed experimental information on the excited states, the explanation of magnitude of QY of photochemical reactions remains counter-intuitive. Therefore, a theoretical study on QY of the photochromic cyclization and cycloreversion reactions of diarylethenes with two distinct structural features, (N)-type and (I)-type, has been presented. The population of the conformation as well as the shape of PESs of the excited states are important. It was shown that the energy profile of the excited states PESs was critical, in particular the energy barrier on the dark 2A state turned out to be the determining factor of the QY. The shape of PES in the (N)-type and the (I)-type reflected the limited and large QYs of the cycloreversion reaction, respectively.

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REFERENCES

- Irie M. *Chem. Rev.* 2000; **100**: 1685–1716.
- (a) Crano JC, Guglielmetti RJ (eds). *Organic Photochromic and Thermochromic Compounds*, Vol. 1, *Main Photochromic Families*. Plenum: New York, 1999; (b) Crano JC, Guglielmetti RJ (eds). *Organic Photochromic and Thermochromic Compounds*, Vol. 2. *Physicochemical Studies, Biological Applications, and Thermochromism*. Plenum: New York, 1999; See Chapter 5 for Molecular Modeling Calculations, pp. 241–260; (c) Olivucci M (ed.). *Computational Photochemistry*. Elsevier: Amsterdam, 2005; See Chapter V for Photochromic Molecules by Worth GA, Bearpark MJ, Robb MA; (d) See Chapter II of the Reference 2c for the discussion of the ab-initio method for excited states. The detailed information on the quality of the wave functions (CASSCF, CASPT2), dynamic correlation and basis sets are presented by Merchan, M and Serrano-Andres, L; (e) Domcke W, Yarkony DR, Koppel H (eds). *Conical Intersections: Electronic Structure, Dynamics & Spectroscopy*. World Scientific: New Jersey, 2004.
- (a) Nakamura S, Irie M. *J. Org. Chem.* 1988; **53**: 6136–6138; (b) Uchida K, Nakamura S, Irie M. *Bull. Chem. Soc. Jpn.* 1992; **65**: 430–435; (c) Adachi M, Murata Y, Nakamura S. *J. Am. Chem. Soc.* 1993; **115**: 4331–4338.
- (a) Uchida K, Saito M, Murakami A, Kobayashi T, Nakamura S, Irie M. *Chem. Eur. J.* 2005; **11**: 534–542.; (b) Takata A, Saito M, Yokojima S, Murakami A, Nakamura S, Irie M, Uchida K. *Jpn. J. Appl. Phys.* 2006; **45**: 7114–7120.
- (a) Yamada T, Muto S, Kobatake S, Irie M. *J. Org. Chem.* 2001; **66**: 6164–6168; (b) Kobatake S, Yamada T, Yamada M, Irie M. *J. Am. Chem. Soc.* 1999; **121**: 8450–8456.
- Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA. *J. Comput. Chem.* 1993; **14**: 1347–1363.
- MOLCAS 5.1, Andersson K, Barysz M, Bernhardsson A, Blomberg MRA, Carissan Y, Cooper DL, Cossi M, Fleig T, Fülischer MP, Gagliardi L, de Graaf C, Hess BA, Karlström G, Lindh R, Malmqvist P-Å, Neogrady P, Olsen J, Roos BO, Schimmelpennig B, Schütz M, Seijo L, Serrano-Andrés L, Siegbahn PEM, Ståhring J, Thorsteinsson T, Veryazov V, Wierzbowska M, Widmark P-O, Lund University: Sweden, 2001.
- MOLPRO 2000.1, Werner H-J, Knowles PJ, University of Birmingham.
- (a) Uchida K, Guillaumont D, Tsuchida E, Mochizuki G, Irie M, Murakami A, Nakamura S. *J. Mol. Struct. (Theochem)* 2002; **579**: 115–120; (b) To predict the relative positions of the relatively ionic character 1B state and the neutral character 2A state in energy is difficult. The detailed discussions are reported for general polyene molecules, for example, Nakatsuji H, Kitao O, Komori M. In *Lecture Notes in Chemistry*, 50, Mukherjee D (ed.), pp. 101–122, Springer-Verlag: Berlin Heidelberg 1989, and references cited therein.
- Uchida K, Tsuchida E, Aoi Y, Nakamura S, Irie M. *Chem. Lett.* 1999; **28**: 63–64.
- Kobatake S, Irie M. *Bull. Chem. Soc. Jpn.* 2004; **77**: 195–210.
- Asano Y, Murakami A, Kobayashi T, Kobatake S, Irie M, Yabushita S, Nakamura S. *J. Mol. Struct. (Theochem)* 2003; **625**: 227–234.
- Nakamura S, Kanda K, Guillaumont D, Uchida K, Irie M. *Non-linear Opt.* 2000; **26**: 201–205.
- (a) Guillaumont D, Kobayashi T, Kanda K, Miyasaka H, Uchida K, Kobatake S, Shibata K, Nakamura S, Irie M. *J. Phys. Chem. A.* 2002; **106**: 7222–7227; (b) Asano Y, Murakami A, Kobayashi T, Goldberg A, Guillaumont D, Yabushita S, Irie M, Nakamura S. *J. Am. Chem. Soc.* 2004; **126**: 12112–12120.
- (a) The results obtained by the CASSCF level of the calculations are shown in Figure 3. However, for the accurate relative position of 1B and 2A, dynamic correlations are to be considered as was discussed in reference 14b. Nonetheless, it is likely that the shift from the photochemically allowed 1B state to the dark 2A state will occur in the cycloreversion reaction, and the QY factor will be determined by the energy profile of the 2A PES on the basis of the fact that the experimental QY reflects the value ΔE as discussed in 3.3; (b) The relative position of CI such as the energy level of 2A/1A CI(O) from 2Ao will be sensitive to the substituents that are truncated in the frame molecule shown in Figure 3. See the Reference 14b for the detailed discussion.
- Morimitsu K, Kobatake S, Nakamura S, Irie M. *Chem. Lett.* 2003; **32**: 858–859.
- In the correlation shown in Figure 4, there are at least two approximations. The first one is that the value ΔE is used instead of the transition state energy. The second one is that the locations of CI for each molecule are not determined; the CIs have been obtained only for the frame model molecule (N), in which the energy gap of 2A/1A CI (O) from the 2Ao minimum is large. As

- was discussed in reference 14b, the position of the CI can also be the critical factor. These are important subjects of the future study as well as the dynamics of the trajectories.
18. Uchida K, Irie M. *Chem. Lett.* 1995; **24**: 969–970.
 19. A theoretical study on (I)-type cyclization focusing on the rotational isomerization and QY in various molecules is reported. Experimental NMR chemical shifts as a function of temperature are used to monitor the isomerization; Goldberg A, Murakami A, Kanda K, Kobayashi T, Nakamura S, Uchida K, Sekiya H, Fukaminato T, Kawai T, Kobatake S, Irie M. *J. Phys. Chem. A.* 2003; **107**: 4982–4988.
 20. Electrochemical approaches can be an aid for additional experimental information. The theoretical and experimental joint studies on cycloreversion reactions by electrochemical methods are reported: (a) Matsuda K, Yokojima S, Moriyama Y, Nakamura S, Irie M. *Chem. Lett.* 2006; **35**: 900–901; (b) Yokojima S, Matsuda K, Irie M, Murakami A, Kobayashi T, Nakamura S. *J. Phys. Chem. A.* 2006; **110**: 8137–8143.