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Theoretical investigation on photochromic diarylethene: A short review

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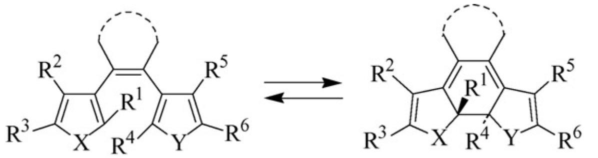
ABSTRACT

This paper presents a review of our reported theoretical studies that we performed to identify experimental spectroscopic data (NMR, Raman, IR, and ESR), find applications that utilize transport property (hole and electron), design the environmental field effect around a molecule (polymer and crystal), and to elucidate nonlinear response properties. Moreover, new results on thermal stability and reaction in crystalline state are also included. We put emphasis on how theoretical studies on photochromic systems contributed to an understanding of the experimental data on a molecular level.

1. Introduction

Organic photochromic molecules have raised considerable interest owing to their potential applications to optical memory and molecular switches [1]. Among the various photochromic molecular systems, diarylethene (DAE), whose general form is shown below, is one of the most promising organic photochromic molecules because of its high fatigue resistance. Recently, the number of experimental studies on various kinds of DAE molecules has increased. These studies are attempting to realize various potential applications [2]. In contrast, although it is necessary to understand the detailed mechanism of reactions and to establish guiding principles for designing required properties in future industrial applications, theoretical research is rather limited. Accordingly, we have performed theoretical molecular orbital and first-principles studies on organic photochromic molecules.

This paper presents a review of our reported theoretical studies with the addition of some recent results. Theoretical studies have been presented to (i) explain the origin of thermal stability [3]; (ii) design absorption wavelength [4]; (iii) discover the determining factor of quantum yield [5]; (iv) identify experimental spectroscopic data (NMR [6], Raman [7], IR [8], and ESR [4b,9]); (v) find applications that utilize the transport property (hole and electron) [10]; (vi) design the environmental field effect around the molecule (solvent [6a]; polymer [11] and crystal [12]), and (vii) elucidate nonlinear response properties [13]. We have already reviewed research pertaining to (i), (ii) [1b], and (iii) [5a]. In this report, we first show some new results on thermal stability, followed by a presentation of the remaining items from (iv) to (vi), placing emphasis on how theoretical studies contributed to an understanding of experimental data.



2. Thermal stability

We explained the remarkable thermal stability of DAE derivatives in terms of the Woodward–Hoffmann rules [14]. Fig. 1 shows the state correlation diagram (obtained by semi-empirical MNDO calculation [3a]) for thermally stable closed-ring isomers. It clarifies the thermal stability of DAE containing five-membered ring (on the left of Fig. 1), while DAE containing six-membered ring (on

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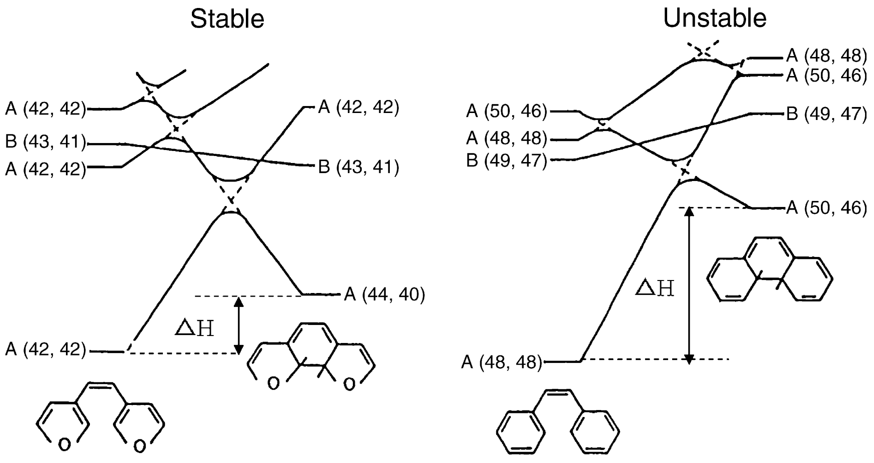

Fig. 1. State-correlation diagram of thermally stable (with five-membered ring) and unstable (with six-membered ring) closed-ring isomers. [3a].

the right of Fig. 1) is found to be less stable. The reason for this stability difference was interpreted by difference in the aromaticity of closed- and open-ring isomers [3]. This was demonstrated by theoretical computer-generated molecules (Fig. 2). These molecules are aromaticity-related components of open- and closed-ring isomers of the molecules shown in Fig. 1. Both of these molecules are consistent with the Woodward–Hoffmann rules, being in symmetry forbidden reactions. Their cyclization as well as their cycloreversion is triggered only by light, not by heat. However, the cycloreversion reaction of six-membered ring molecules by heat does occur, whereas the cycloreversion of five-membered ring molecules by heat does not. That is, the colored form of the closed-ring isomer with the six-membered ring is very unstable, owing to the considerable thermodynamic instability of the closed-ring isomer. This instability means that virtually the Woodward–Hoffmann rules are no longer valid. In fact, we showed that a simple difference in enthalpy (Δ*H* in Fig. 1) between ground state open- and closed-ring isomers is the criterion for determining the thermal stability of the colored forms [3].

Since we proposed this criterion to explain the thermal stability of DAE molecules, there have been no reported exceptions. To date, modifications have been made to synthesize various kinds of DAE derivatives using different substituents [2]. Indeed, they satisfy the criterion that we reported in 1988; namely, the smaller Δ*H*, the higher the stability. Fig. 3 shows typical examples of some recent calculations on the relative energy difference. We estimated the enthalpy difference for closed- and open-ring isomers for the various new DAE derivatives (in which there are remarkable differences in thermal stabilities) as a function of substituents. Experimental thermal stability [2] is closely correlated to the B3LYP/6-31G*-calculated Δ*H* for closed- and open-ring isomers in ground state. Note that the Δ*H* of the positively charged dication molecule (C in Fig. 3) is calculated with solvents by using the PCM method [15].

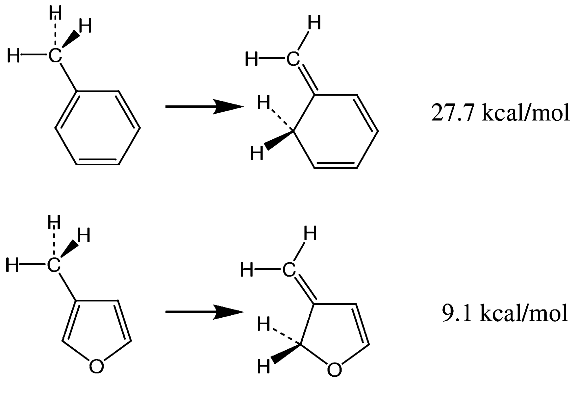

Fig. 2. Model molecules used for measuring difference in aromaticities of open- and closed-ring isomers.

3. Theoretical study to identify experimental spectroscopic data

3.1. NMR chemical shift

To determine the detailed structures of photochromic molecules, NMR chemical shift provides key information. First, we applied the ^1H NMR NOE technique to determine the colored form of photochromic spironaphtoxazine [16]. Then, we performed NMR chemical shift analysis on the DAE derivatives. For example, Uchida et al. determined the ratio of the anti-parallel conformer relative to the parallel conformer (see Fig. 4 for the conformers) in the equilibrium of open-ring isomers of 1,2-bis (2-methyl-3-benzothienyl)-perfluorocyclopentene [6b] and 1,2-bis (2-methyl-5-phenyl-3-thienyl)-perfluorocyclopentene [5d]. As shown in Fig. 4, a cyclization reaction is possible only via the anti-parallel conformer. Therefore, to find the factors that increase the population of anti-parallel conformer, it was necessary to monitor the equilibrium by using the chemical shift of proton NMR. Based on these NMR-shift data, a theoretical study provided a guiding principle for attaining large cyclization quantum yield which results from increased anti-parallel population both in ground state and excited state. Accordingly, molecules with large cyclization quantum yields were designed with the aid of theoretical calculations [5d].

Goldberg et al. reported NMR chemical shift calculations on 1,2-bis(3-methyl-2-thienyl)-perfluorocyclopentene (**1a** and **1b** in Fig. 4). Using the gauge including atomic orbital (GIAO) method [17], they calculated the ^1H NMR chemical shift for different atomic groups at the B3LYP/6-31G level. They then compared the calculated ^1H NMR shifts with experimental values to provide an aid to determine the ratio of conformers [6a,18]. To find the determining factor of cyclization quantum yield, it was necessary to assign experimental chemical shift values, since they reflect the ratio of the conformers.

The chemical shift of the methyl-group proton provides peaks strongly affected by the relative position of the two thiophene rings. If the methyl group faces the thiophene ring (as in the case of the anti-parallel conformer), the ring current induces a high magnetic

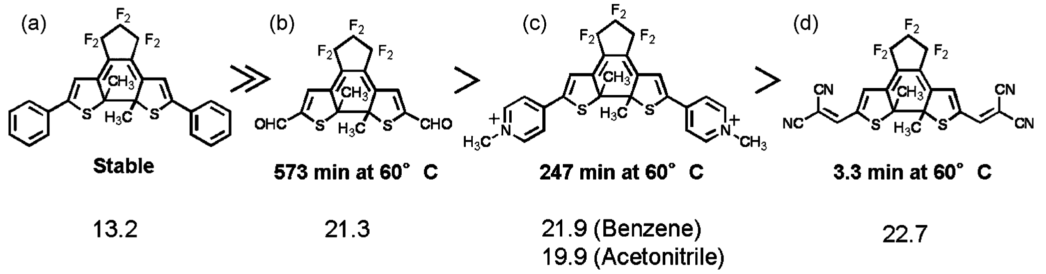

Fig. 3. Experimental thermal stability [2] and calculated relative energy difference ($\Delta H = E(\text{closed}) - E(\text{open})$) in kcal/mol by the B3LYP/6-31G* level. Solvents are considered for C, since it is a positively charged dication molecule.

field on the methyl protons (1.7 ppm by calculation). Conversely, when there is no such field on the methyl (as in the case of the parallel conformer), the chemical shift results in about 2.46 ppm. The calculations broadly reproduced these values. To confirm the ratio of the conformers, the temperature dependence of the chemical shift was also evaluated and compared with experimental data while the Boltzmann distributions of parallel and anti-parallel conformers were taken into account. The free energies were calculated as a function of temperature. As temperature increases, the chemical shift values shifted to higher magnetic field, they showed a similar trend both in calculation and experiments. The chemical shift of aromatic ^{1}H of thiophene rings exhibits weak temperature dependence, which is also consistent with experimental results [6a].

3.2. *Raman spectroscopy*

To clarify the ratio of conformers in 1,2-bis(3-methyl-2-thienyl)-perfluorocyclopentene (**1a**) (the same molecule as described above), Okabe et al. performed a steady-state FT-Raman spectroscopic study. B3LYP/6-31G** calculations were used to assign the observed bands [7a,b]. Although Majumdar et al. [19] previously calculated Raman intensities on DAE derivatives, a joint experimental/theoretical study was not done. Okabe et al. successfully separated the Raman shifts of prominent bands for the open- and closed-ring isomers in the 1300–1700 cm^{-1} spectral band. They are consistent with the results from the NMR temperature-dependent study mentioned above.

3.3. *IR spectroscopy*

Non-destructive readout capability is an indispensable condition for optical memory application. When recorded information is readout by light, which electronically excites photochromic compounds, the information is lost during the reading process. To avoid this information loss, several attempts have been made [20]. One important approach is to use readout light whose energy is too low to cause a photoreaction.

Zerbi and co-workers reported that one DAE derivative 1,2-bis[5′-(4″- methoxyphenyl)-2′-methylthien-3′-yl]-perfluorocyclopentene exhibits remarkable infrared (IR) spectral changes accompanying the photochromic reaction [21]. It has a strong IR absorption peak at 1495 cm^{-1} for the closed-ring isomer only (i.e., not for the open-ring isomer). This absorption changes can be used for non-destructive readout. Although the peak at 1495 cm^{-1} for the closed form is strong, the open-ring isomer also has absorptions in neighboring wavenumber regions. To achieve high signal/noise ratio, a clear separation of the bands between the open- and closed-ring isomers was desired.

Uchida et al. carried out theoretical frequency analysis calculations to obtain a molecule (from many possible DAE derivatives) having such separate IR spectra for both isomers. Theoretically they found that the DAE derivatives with benzothiophene rings have considerably separated IR spectra [8a]. Accordingly, they synthesized such a molecule, 1,2-bis(2-methyl-6-phenyl-1-benzothiophen-3-yl)-hexafluorocyclopentene (**2**). Its representative IR spectra, in which the spectra for the open- and closed-ring isomers are well separated, are shown in Fig. 5(a). The IR intensity of the closed-ring isomer **2c** is stronger than that of the open-ring isomer **2o** in the 1500–1700 cm^{-1} region (Fig. 5(a)). The spectra calculated by the Hartree-Fock method with the 6-31G basis is shown in Fig. 5(b).

To rationalize the reason the spectra are clearly separated, a theoretical study was in order. We assigned these vibrational modes of the closed-ring, 1543, 1591, and 1624 cm^{-1} peaks in the 1500–1700 cm^{-1} region. The observed 1543 cm^{-1} band is assigned to the two calculated vibrational modes, 1530 and 1533 cm^{-1} ((a) and (b) in Fig. 6). They are the in-plane skeleton vibration of the benzene ring in the benzothiophene of both the open- and closed-ring isomers. The strongest band intensity observed at 1591 cm^{-1} was assigned to the two calculated vibrational modes, 1582 and 1585 cm^{-1} ((c) and (d) in Fig. 6). The cyclization generated these two vibrations as a result of the interaction between the in-plane vibration of the benzene ring and the vibration of the central six-membered ring which contains two C=C bonds stretched by symmetric coupling. These vibrations appear in the closed-ring isomer, but not in the open-ring isomer. The calculated band at

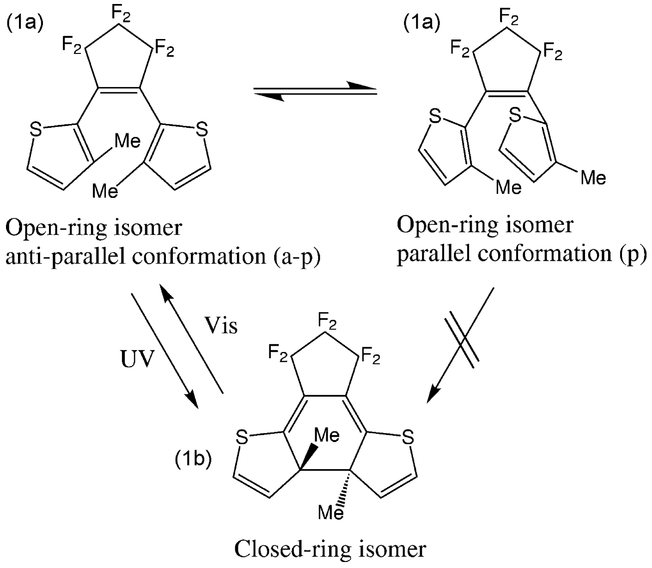

Fig. 4. Anti-parallel and parallel conformers in DAE open-ring isomers. Photochromic cyclization reaction (formation of **1b**) is only possible via anti-parallel conformer [2].

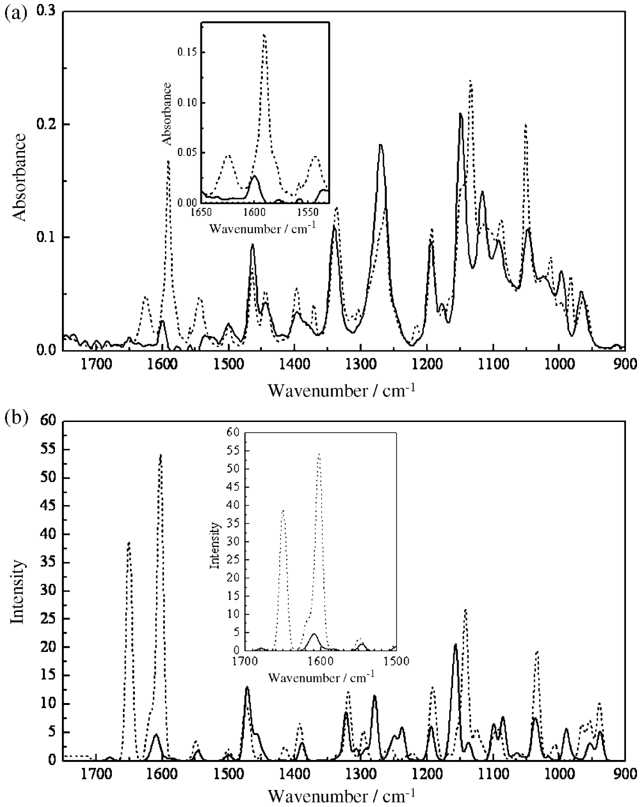

Fig. 5. Observed infrared spectra (a) of open-ring isomer **2o** (solid line) and closed-ring isomer **2c** (broken line) in CCl_4 solution (6.16×10^{-3} M), and calculated spectra (b) of **2o** (solid line) and closed-ring isomer **2c** (broken line).

1624 cm^{-1} was assigned to the experimental IR vibration mode at 1631 cm^{-1} ((e) in Fig. 6). It is an asymmetric coupling of stretching vibration of the two C=C bonds of the central six-membered ring. Moreover, it only occurs in the case of the closed-ring isomer. Taking advantage of these well-separated vibrations, Uchida et al. [8a] demonstrated a non-destructive readout experiment by using a polymerized derivative of molecule **2**.

As a natural extension of the joint experimental/theoretical study using IR spectroscopy, we performed two more studies. First, we applied a near-field technique [8c] to non-destructive readout using IR spectra of a DAE derivative. It was possible to achieve the resolution finer than the wavelength of the readout IR light. Therefore, by the near-field technique, a memory with high recording density could be produced. Second, in search for the spectral separation of the open- and closed-ring isomers, we analyzed the substituent effect on IR intensity (Fig. 7) [8b].

We determined the correlation between IR intensity and charge distribution. Charge distribution is one factor that determines IR intensity, i.e., a normal mode in which an atom that carries a large effective charge has a large vibrational amplitude and high IR intensity (as long as its symmetry allows the excitation). We analyzed the charge distribution by the generalized atomic polar tensors (GAPT) atomic charge [22]. For example, methoxy-group-substituted **3.3o** showed a noticeable peak around 1400 cm^{-1}. This peak is assigned to the calculated mode of 1376 cm^{-1}, as shown in the lower panel of Fig. 7. Note that it is not found for **3.1o**, **3.1c**, **3.2o**, **3.2c** or **3.3c**. The large IR intensity is due to the vibrations of the C=C double bond to which the methoxy group is attached. The methoxy group induces large atomic charges on these C atoms, resulting in the large IR intensity [8b].

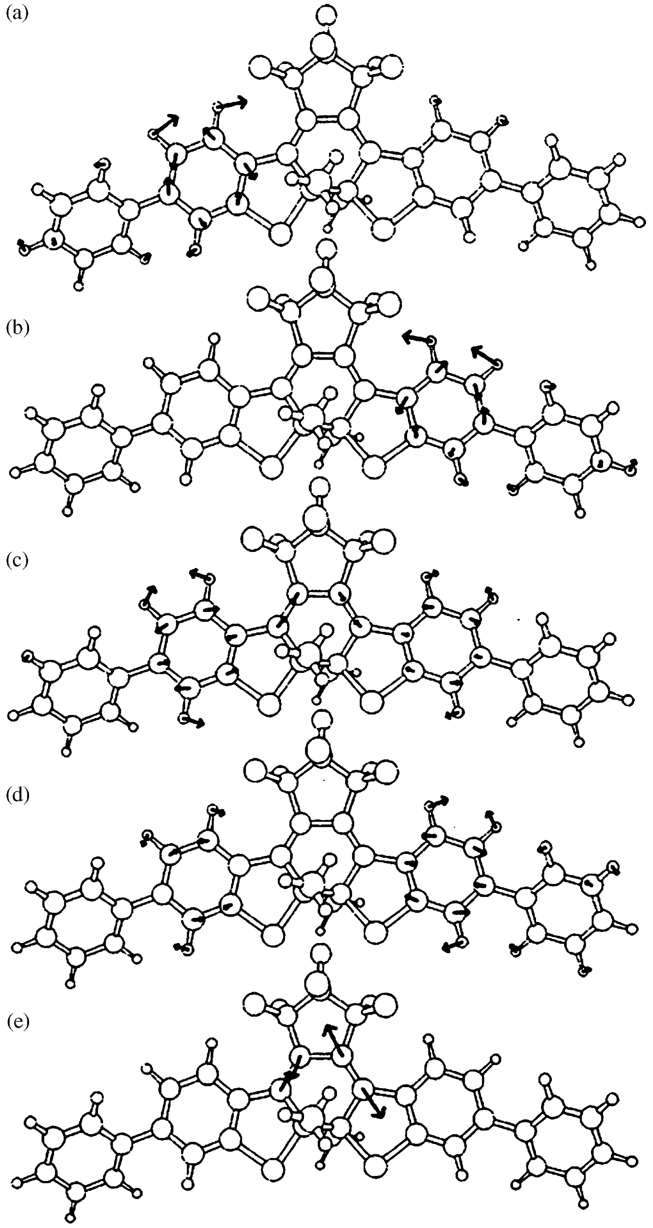

Fig. 6. IR vibration mode of **2c**. (a) 1530 cm^{-1}, (b) 1533 cm^{-1}, (c) 1582 cm^{-1}, (d) 1585 cm^{-1}, and (e) 1631 cm^{-1}.

3.4. ESR

Electron spin resonance (ESR) spectroscopy is an indispensable experimental technique for analyzing radical species. A reaction intermediate of the oxidative cycloreversion reaction of DAE, which is considered to be a cation radical, was investigated by ESR. Upon oxidation, bis(3-methyl-2-thienyl)-perfluorocyclopentene (**1b**) underwent a cycloreversion reaction. Although this kind of electrochemical cyclization/cycloreversion reaction of fulgides [23] and DAE [24–27] has been reported, and detailed studies of the oxidative electrocyclic reaction of DAEs were performed [28–31], the reaction mechanism has not yet been made clear. A direct analysis of the reaction intermediates by ESR spectroscopy was therefore performed by Matsuda et al. [9]. During the electrochemical oxidation, a nine-line ESR spectrum was measured. The cation–radical reaction intermediate is considered to give ESR signals. The spectrum of this cation radical DAE has

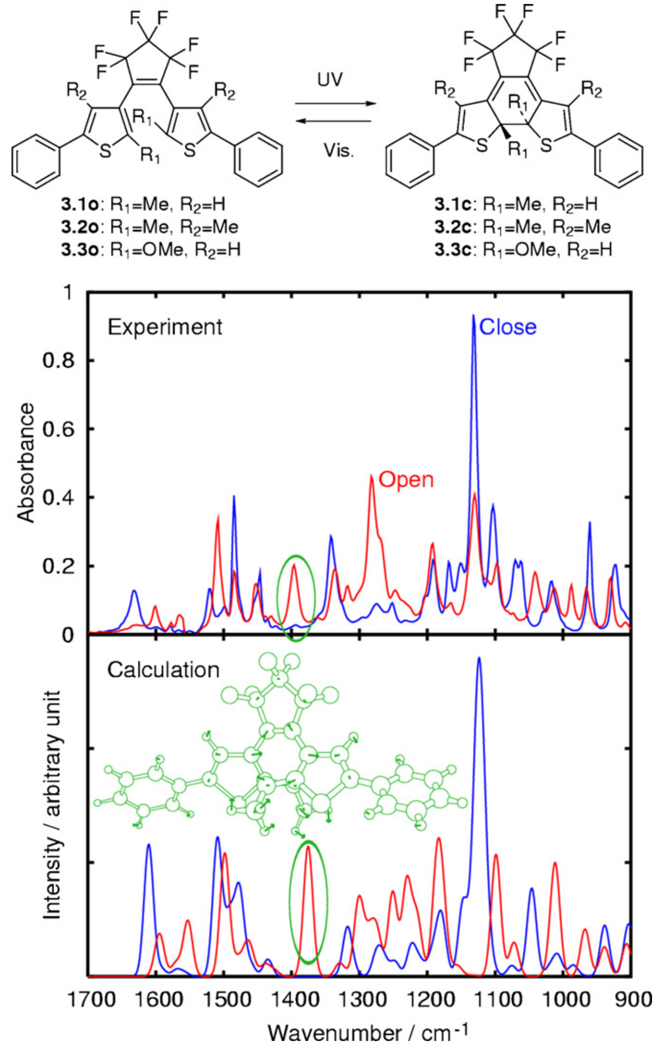

Fig. 7. Substituent effect on IR intensities. Upper panel: experimental IR spectra. Lower panel: computational IR spectra. Blue lines: IR spectra for closed-ring isomer. Red lines: IR spectra for open-ring isomer. Inset: computational vibrational mode of 3.3o of 1376 cm^{-1}.

been reproduced recently by a quantum chemical calculation [4b,9].

To reproduce the experimental ESR spectra, isotropic hyperfine coupling constants are calculated by quantum chemical calculations. The detail of the calculations is reported in [4b]. Neither the calculated ESR spectrum for open- (**1a**$^{+\bullet}$) nor closed-ring (**1b**$^{+\bullet}$) isomers could reproduce the measured ESR spectra (Fig. 8). They could only be reproduced by the superposition of the two spectra, **1a**$^{+\bullet}$ and **1b**$^{+\bullet}$. By comparing the calculated spectrum with the measured one, the **1a**$^{+\bullet}$:**1b**$^{+\bullet}$ ratio was determined to be 4:1 (Fig. 8). This ratio indicates that the conversion from the cation radical of the closed-ring isomer to the cation radical of the open-ring isomer is a fast reaction under the reported experimental condition [9].

By investigating the origin of the difference in the calculated ESR spectra of the open- and closed-ring isomers, we have a better understanding of the electronic structure of the cationic DAE. A large difference in the spectra of **1a**$^{+\bullet}$ and **1b**$^{+\bullet}$ is in the spectral width (Fig. 8(a)); i.e., the spectral width of **1a**$^{+\bullet}$ (open-ring isomer) is 32 G, whereas that of **1b**$^{+\bullet}$ (closed-ring isomer) is 17 G. The difference in the spectral width is due to the different spin-density distribution (Fig. 9).

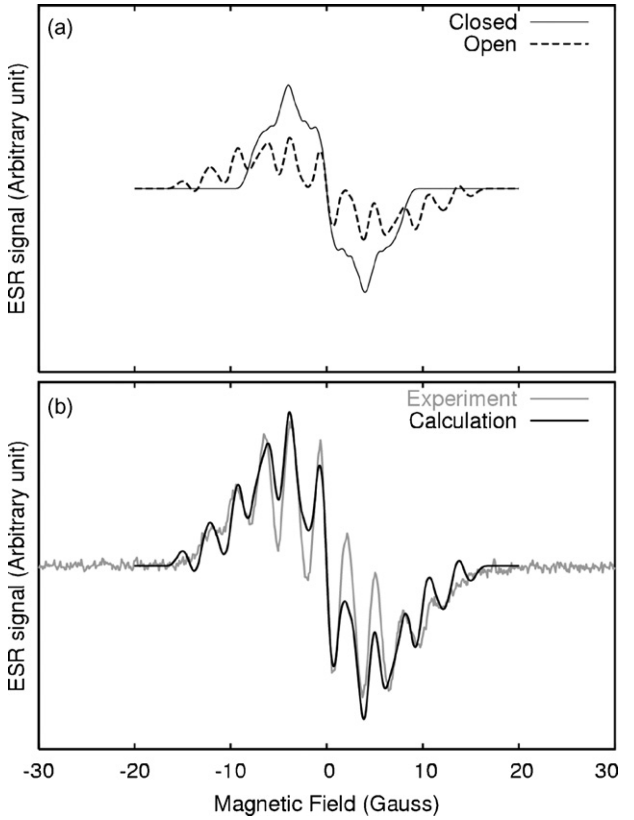

Fig. 8. Comparison between the experimental and quantum chemical computational ESR spectra. (a) Computational ESR spectra of **1a**$^{+\bullet}$ (dashed line) and **1b**$^{+\bullet}$ (solid line). (b) Experimental (gray line) and simulated (black line) ESR spectra of **1b** under electrolysis.

There are two main effects that contribute to the change of ESR spectral width.

(i) The spin density of the carbon atoms, identified by “1” in Fig. 9, is increased by the cycloreversion reaction. It results in the increase of the magnitude of hfcc’s (hyperfine coupling constants) of the H atoms of the neighboring methyl group.

(ii) The spin density of S atoms for the closed-ring isomer has a large value, whereas that of the open-ring isomer has a smaller value, note that the neighboring C atoms gain the spin density. (Those spin densities are identified by “2” in Fig. 9) The spin density on S atoms does not contribute to the hfcc’s magnitude, but the neighboring H atom does through the attached C atom.

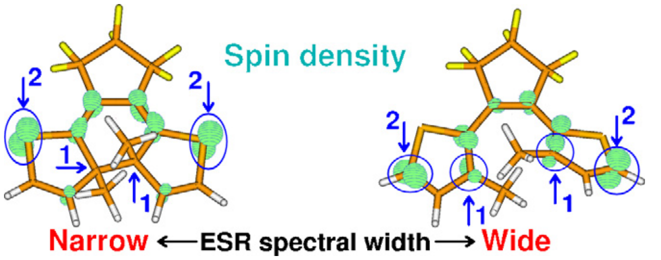

Fig. 9. Spin-density distribution of the closed-ring isomer (left) and the open-ring isomer (right) in the cationic state. The numbers with arrows indicate the position where large changes of spin density, which result in the large change in the isotropic hyperfine coupling constants, take place due to the cycloreversion reaction.

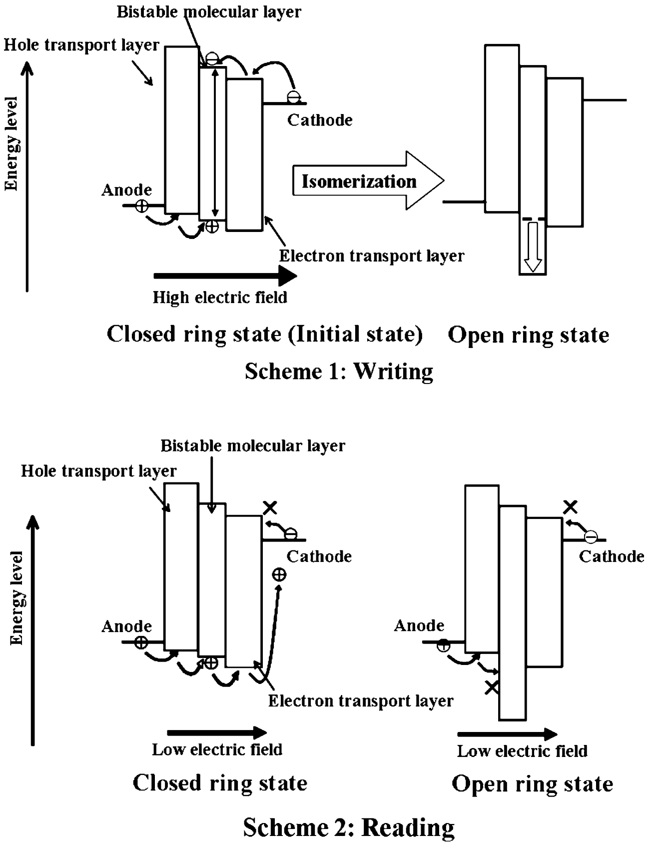

Fig. 10. Photochromism via the recombination of a hole and an electron—the principle of the new molecular memory device.

Effects (i) and (ii) both contribute more to the greater hfcc's magnitude of the open-ring isomer (higher value) than to that of the closed-ring isomer (lower value). Consequently, the ESR spectral width of the open-ring isomer is more than that of the closed-ring isomer [4b].

The change of the spin density in effect (i) is due to the change of the π-conjugation. However, that in effect (ii) is not trivial. This can be qualitatively explained by considering valence-bond resonance structures. As for the closed-ring isomer, the number of resonance structures for the radical on S is larger than that for the radical on other atoms. The radical on S of the closed-ring isomer is thus stabilized by the resonance. Unlike the closed-ring isomer **1b**, the open-ring isomer **1a** has an extended π-conjugation. Therefore, the number of resonance structures increases significantly for the open-ring isomer. The increase is larger for the radical on the π-orbital than on S. As a result, the radical on the π-orbital is more stabilized. The change of the spin density in (ii) above is thus attributed to the stabilization of the radical due to the resonance structures [4b].

The understanding on these effects can be used to analyze the ESR spectra of DAE; that is, we can extract information on the structures of intermediates and the reaction rates in the electrochemical cyclization/cycloreversion reactions.

4. Transport property of diarylethene

One of the most important applications of DAE is as a memory medium. Such a memory is based on an isomerization reaction of a bistable DAE molecule by electric-carrier injection. This was achieved by the recombination of a hole injected from the anode with an electron injected from the cathode on the DAE molecule, not by photoexcitation. Tsujioka et al. [10a,b] reported representative prototype studies of this application (Fig. 10).

The molecular orbital calculations supported this study by providing the electronic properties. The electron on the lowest unoccupied molecular orbital level and the hole on the highest occupied molecular orbital level of the molecule produce an excited state identical to that produced by photoexcitation; therefore, the molecule is transformed into another isomerization form. In the case of DAE, ionization potential IP of the molecule changes according to its isomerization form. The closed-ring isomer has IP of 5.7 eV, while the open-ring isomer has IP of more than 6.2 eV [10a,32]. Therefore, the readout of information is possible by detecting the electric current through the molecules; the current is affected by the difference in IP, reflecting the isomerization of the molecule.

An isomerization reaction via a cationic state for various DAEs has been investigated by electrochemical methods [4b,25,27,28]. This suggests the possibility of information recording by only hole injection into the DAE solid memory layer. The transporting hole in molecules does not disappear and so it can convert many closed-ring isomers into open-ring isomers, until it encounters an electron. This is a chain reaction. It contrasts with a simple encounter of a hole and an electron, which generates an excited state as a result of recombination; in other words, one recombination generates only one excited state. By taking advantage of this interesting chain reaction caused by a hole transport process, Tsujioka et al. [10b] demonstrated the generation of multiple open-ring isomers of DAE by one-hole injection via the cationic state in a solid-state memory layer.

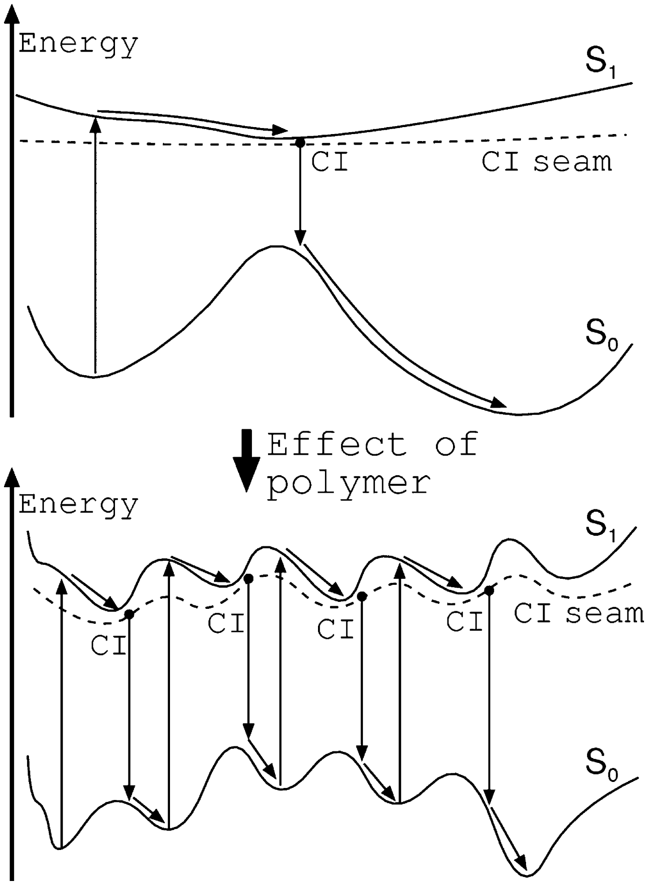

Fig. 11. Multiple local minima model.

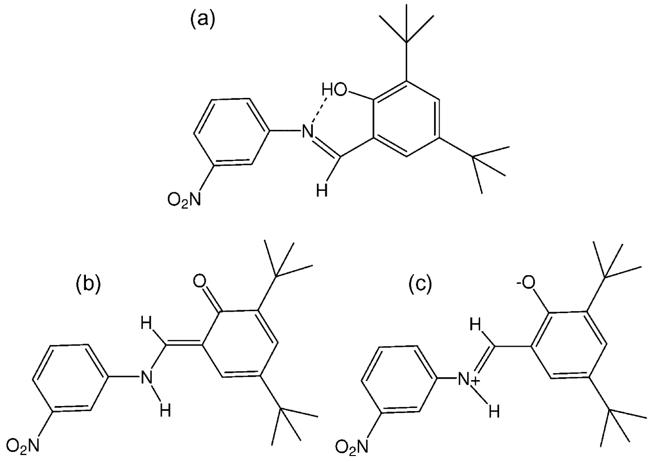

Fig. 12. Two isomers of salicylideneaniline: (a) OH (enol) form, (b) quinoidal form of NH (*trans*-keto) form, and (c) zwitterionic form of NH (*trans*-keto) form.

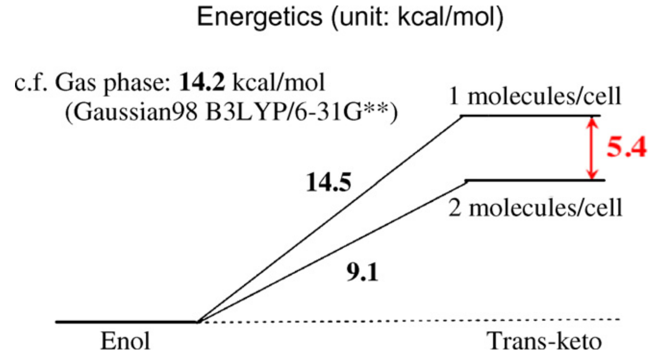

Fig. 14. Relative energy between OH (enol) form and NH (*trans*-keto) form (in kcal/mol). The calculation of "1 molecule/cell" is a model of gas phase, while that of "2 molecule/cell" corresponds to the crystalline state.

5. Environmental field effect in photochromism

Photochromism occurs in solutions, polymers, and crystals. The solvent effect in a solution is an experimentally well-known; especially, it is related to the polarity of the solvent [2,6a]. The challenge to theory is to provide an understanding of the environmental field effect in a polymer as well as in a crystal on a molecular level.

5.1. Photochromism in polymer

Novel experimental results of the environmental field effect in a polymer were reported by Fukaminato et al. [11] in their single-molecule photochromism studies. The central question is to understand why there is a fluctuation in quantum yield as a function of polymer properties. Among various properties of a polymer, glass-transition temperature (T_g) is shown to be an important one. That is, it is closely related to the fluctuation of the photochromic response in polymer [11]. To understand these experimental facts, utilizing numerical simulations, we devised a multiple local-minimum model that contrasts with a single minimum picture in solution. The schematic potential-energy surfaces of the multiple-local-minimum model are shown in Fig. 11. Further theoretical study on the details is in progress.

5.2. Photochromism in salicylideneaniline crystal

One interesting challenge to theory has appeared in regards to photochromism of salicylideneaniline. Salicylideneanilines belong to a class of the most popular compounds that exhibit photochromism as well as thermochromism in crystalline state. Harada et al. [33] investigated the reversible structural changes accompanying the photochromism of salicylideneanilines (*N*-3,5-di-*tert*butylsalicylidene-3-nitroaniline) in crystals by a combination of X-ray analysis and two-photon excitation (Fig. 12). Harada et al. claimed that the photo-driven tautomerization in the crystalline phase can easily occur through the motion of a pair of benzene rings, which is analogous to the pedal "crankshaft motion" of a bicycle.

This molecular crystal provides unique opportunities for theoretical studies [12]. One of the important questions is how to understand the extraordinary stabilization of the NH form in crystals, because most of the stable salicylideneaniline derivatives are OH form in solids as well as in solutions [34]. We thus performed first-principles band calculations [35] on the OH and NH forms of salicylideneaniline crystals. The calculation results are shown in Fig. 13. The energetics confirmed the stabilization of the NH form in the crystalline phase due to the intermolecular hydrogen bonds (Figs. 13 and 14). The effect of the molecular packing was also considered by comparing these two conformers with one molecule in gas phase (Fig. 14). For one molecule in a unit cell (as a model of gas phase) the difference between the OH and NH forms is 14.5 kcal/mol. This value by first-principles calculation is consistent with 14.2 kcal/mol by B3LYP/6-31G** calculation. The stabilization of the NH form due to the intermolecular hydrogen bond in the crystal is estimated to be 5.4 kcal/mol. From the analysis of the differential electron density, it appears that the intermolecular hydrogen–bond interaction is electrostatically reinforced by redistribution of the electron density. Note that the NH form in crystalline phase appears as a quinoidal form rather than a zwitterionic form by our calculation.

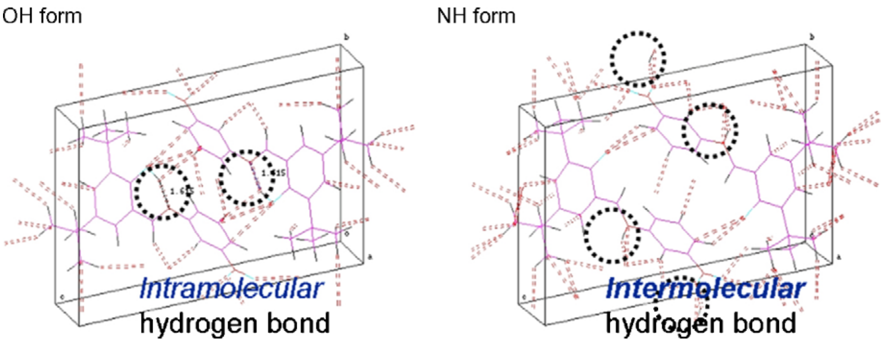

Fig. 13. Calculated structure of the salicylideneaniline crystal with two molecules in the unit cell: left OH form and right NH form.

5.3. *Photochromism of diarylethene crystal*

An extensive experimental study on the photochromism in crystal was carried out by Kobatake and Irie [36] for various DAE derivatives. We have carried out first-principles calculation on the photochromism of DAE ((1,2-bis(2,5-dimethyl-3-thienyl)-perfluorocyclopentene) crystalline state [37]. The question was to determine how photochromism can take place in the rigid field of a crystal and to explain the absorption spectra of closed-form crystal (absorption wavelength: 535 nm, which is different from that of closed-form solution, 505 nm). The same method of the first-principles calculations as the previous one [35] was used. By using the calculated structure of the closed form, a TD-DFT calculation gave an absorption wavelength of 545 nm. This value is consistent with the experimental value of 535 nm, which was measured to closed-ring isomer in the crystal of open-ring isomer [38]. Although the optimized structure by first-principles calculation for the open-ring isomer reproduced the X-ray data well, for the closed-ring isomer, it showed a slight difference between X-ray data and calculated data. Given the occupation factor 0.094 of the photogenerated closed form, the discrepancy in the data is still to be investigated in future. The detailed analysis is ongoing.

6. Nonlinear-response property or multi-photon reaction

Nonlinear-response properties of DAE derivatives have not been well investigated; only a few reports have appeared [13b–e]. It will therefore be an interesting future research field. One exception is a study reported by Miyasaka et al. [13a], who found that the quantum yield of cycloreversion of diphenyldiarylethene **3.1C** at the stepwise multi-photon excitation increased more than 50 times relative to the normal one-photon excitation. Although the detailed mechanism of this interesting result remains unknown, a possible explanation was suggested by Guillaumont et al. [5b] on the basis of the excited-state potential surfaces obtained at the CASSCF level. The position of the transition state shifted to a closed-ring isomer as the energy of the potential surface increased; that is to say, the TS (transition state) of S_0 was located almost in the middle of closed- and open-ring isomers, while that of S_1 shifted considerably towards the closed-ring isomer, and that of S_2 shifted even more to the closed-ring isomer. The barrier at the TSs from the closed-ring isomer to the open-ring isomer also changes proportionally; that is, as the energy of the state becomes higher, the barrier to the TS decreases. These features indicate that the cycloreversion can happen more easily in the higher state than in S_1. However, the accuracy of the current calculations is still insufficient to correctly describe the details of the electronic structures. This is one of the most challenging future subjects to theoretical study.

7. Concluding remarks

Organic photochromic molecules hold a unique position in which the molecular properties directly reflect the function of devices, contrasting with most of currently realized industrial materials whose functions are determined in terms of aggregations or composites. In an attempt to clarify the detailed mechanism of photochromism of DAEs, we presented a review of our theoretical studies with recent new results. We put emphasis on how theoretical studies contributed to an understanding on a molecular level of the experimental results [39].

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