

Theoretical Investigation of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride: A Thermally Irreversible Photochromic System

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A thermally irreversible photochromic system, 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (MTMA), has been studied by semi-empirical molecular orbital methods. There are one pair of stable conformations for the closed-ring form and three pairs for the open-ring form, each pair consisting of two mirror-image conformations. Interconversion between the parallel and anti-parallel conformations of the open-ring form is restricted due to high energy barriers. Only the anti-parallel conformation appears to be responsible for photochromic cyclization. Thermostability of the compound is attributed to an avoided crossing at high energy in the ground states of the isomers, whereas the photoreactivity can be explained by the mutually connected excited singlet (S_1) states of the isomers, forming a double well potential with a low energy barrier. The large solvent effects can be partly explained with the low dipole moment of the anti-parallel conformation of MTMA in the S_1 state. The large variation of quantum efficiency suggests that excess vibronic energy can be utilized to provide the activation energy for the photochromic reaction.

Introduction

Photochromism is a result of a reversible change in the molecular structure or in the distribution of molecular conformations during light irradiation.¹ On the basis of the nature of molecular change, it can be divided into various types including photo-induced *cis-trans* isomerization,² homolytic cleavage,³ hydrogen transfer,⁴ valence tautomerism,⁵ and cyclization of π -conjugated system.⁶ Intense attention has recently been focused on photochromic materials⁷⁻¹¹ because of potential application as media for information storage.¹² The primary requirements for the photochromic memory medium include thermal stability, fatigue resistance, high quantum yield, and accessibility by lasers. Unlike magneto-optic media,¹³ which is currently utilized for erasable optical memory devices based on the heat-mode optical recording method, photochromism can exploit the characteristic properties of light, such as frequency, phase, and polarization, leading to higher resolution and speed of writing and multiplex recording.¹⁴

Diarylethene derivatives that undergo cyclization/ring-opening upon irradiation were first introduced as photochromic compounds in late 1980's.¹⁴⁻¹⁷ The stilbene-like compounds with various aryl groups have been examined, and it has been reported that the diarylethene derivative with a low stabilization energy of the aromatic group tends to have a high energy barrier between the isomers, which results in high thermal stability of the closed-ring form.¹⁸⁻²¹ Among diarylethene derivatives, one of the most studied compounds is 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (MTMA),^{15,21,22} which is originally derived from another photochromic compound, *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene, by treating with KOH. The acid anhydride group effectively prohibits *cis-trans* transformation during photoreactions and generates slight bathochromic shifts of the electronic absorption bands. The com-

ound shows no thermochromic properties up to 300 °C, and the closed-ring form is stable more than three months at 80 °C.¹⁸ The compound is nearly fatigue-free in photochromic reactions. Reasonable photochromic performance has been demonstrated even after more than 10^4 cyclization/ring-opening trials.²¹ Studies also show its acceptable quantum efficiencies; the maximum efficiency is as high as 0.15.¹⁸ Due to the characteristic properties, MTMA is currently considered as an important model compound for rewritable optical memory media.

The open-ring form of MTMA undergoes cyclization by ultraviolet radiation (≈ 331 nm), whereas the closed-ring form undergoes ring-opening by visible light (≈ 552 nm) (Figure 1).¹⁸ The photochromic reactions have been performed in amorphous matrices as well as in solid or solution. With sufficient laser power, the photo-isomerization of diarylethene can be carried out within 100 ps,²¹ and effective methods that increase readout stability for written information have also been devised.^{14,20,21} It has been reported that the quantum yield varies by factor of four as a function of wavelength.¹⁸ Large Stock's shifts and multi-component exponential decays of the fluorescence have been observed in polar solvents.¹⁸ The reaction is generally explained by referring to the Woodward-Hoffman rule²³ based on π -orbital symmetries of hexatriene, the simplest frame work of the compounds. The cycloreversion reaction is allowed both photochemically in the conrotatory mode and thermally in the disrotatory mode. The reason for the exceptional thermal stability is traced to the fact that the disrotatory rotation

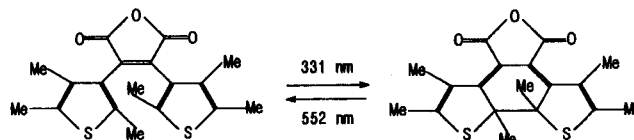


Figure 1. Photochromic isomerization between the open-ring and the closed-ring forms of MTMA.

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of the thienyl rings, although allowed by the symmetry of the compound for the thermal reaction, is essentially forbidden due to steric hinderance.²⁴ On the other hand, the photoisomerization reaction through conrotatory rotation of the thienyl rings readily takes place with high reversibility.

In this study, semi-empirical molecular orbital (MO) methods have been applied to MTMA. The geometries of conformations in the ground and the excited singlet (S_1) states have been examined, and the effects of conformations on reactivity have also been investigated. An explanation for the effects of solvent polarity to photochromic reactivity and Stock's shift of fluorescence of the compounds is also proposed.

Methodology

Calculations have been carried out using the Hartree-Fock Austin Model 1 (AM1)²⁵ included in MOPAC-6 package.²⁶ Hyperchem²⁷ was used to build the initial molecular structure, and to inspect the geometries of the isomers resulting from MO calculations. Full geometry optimizations without symmetry constraints were carried out to find the molecular structures of the isomers and their conformations. Figure 2 shows the numbering of carbon atoms for MTMA used in this study. For rotation of a thienyl ring, the torsional angle of the bond of carbons 3 and 6 to the plane of the ethylene group (carbons 1 and 2) is fixed at a given angle, and all other geometric parameters are optimized accordingly. In order to find stable conformations, the energy minima were searched while rotating a thienyl ring, and near each energy minimum a full geometry optimization was carried out. Similarly, to examine the reaction path of the cyclization, the interatomic distance between carbons 6 and 10 was gradually varied, and all other geometric parameters were adjusted at each given distance. For the S_1 state, the configuration interaction (CI) calculations were performed. The configurations were generated from the highest occupied and the lowest unoccupied orbitals of the ground electronic state utilizing MOPAC keyword "excited." Other than the CI part, the calculations for the excited state were carried out by basically the same procedure used for the ground state. Major calculations were performed on an IBM RS/6000, with supplementary calculations on a Pentium computer.

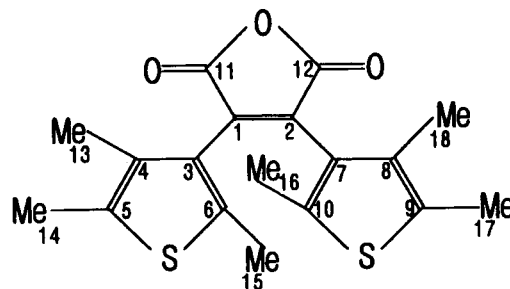


Figure 2. Numbering of carbon atoms of MTMA used in this study.

Results and Discussion

The calculated molecular characteristics of the conformations of MTMA in the ground and S_1 states are listed in Table 1. For the closed-ring form of MTMA, there are a pair of conformations, each being mirror image to the other, which are nearly planar with C_2 symmetry. One of the two adjacent methyl groups (carbons 15 and 16) of the two thienyl rings is placed above the molecular plane and the other below. The torsional angle of thienyl ring with respect to the plane of the ethylene group is 8.7° in the ground state. On the other hand, for the open-ring form of MTMA, calculated results indicate that there are three pairs of conformations, each pair consisting of the mirror images to one another. The three pairs of conformations of the open-ring form are illustrated in Figure 3. The conformations maintain twisted structures (the thienyl rings show about 60° rotation to the plane of the ethylene group), due to the steric hinderance between the methyl substituted thienyl rings. All conformations of the open-ring form have almost the same energies in the ground state; the energy difference is less than 1 kJ/mol (Table 1).

Shown in Figure 4 is the molecular energy as a function of rotational angle of a thienyl ring while other geometric parameters are fully relaxed. When the rotational angle of a thienyl ring is 0° or 180° , at which the ethylene group and the thienyl ring are located in the same plane, the molecule has the highest energy. Rotation of a thienyl ring does not lead to similar rotation of the second ring. During 360° rotation of a thienyl ring, the second ring swings back and

Table 1. Calculated Molecular Characteristics of MTMA

Electronic State	Isomeric Form	Conformation	ΔH_f^a	Angle ^b	$C_6-C_{10}^c$	Dipole Moment ^d
Ground (S_0)	Closed-ring		-180.0	8.72	152	6.05
		Parallel (a) ^e	-245.6	59.0 (-119)	435	6.33
	Open-ring	Anti-parallel (b)	-245.6	60.0	400	6.44
		Anti-parallel (c)	-245.6	119.0	556	6.21
Excited (S_1)	Closed-ring		72.5	18.7	157	7.35
		Parallel (a)	48.8	94.4 (-80.0)	428	12.6
	Open-ring	Anti-parallel (b)	52.5	37.2	214	7.96
		Anti-parallel (c)	44.0	89.5	482	12.5

^a Enthalpy of formation at 298 K in kJ/mol. ^b Rotational angle of thienyl ring in degree. The number in parenthesis is the rotational angle of the second ring when it differs from that of the first one. ^c Interatomic distance between carbons 6 and 10 in pm. ^d Molecular dipole moment in gas phase in Debye. ^e Molecular conformation illustrated in Fig. 3.

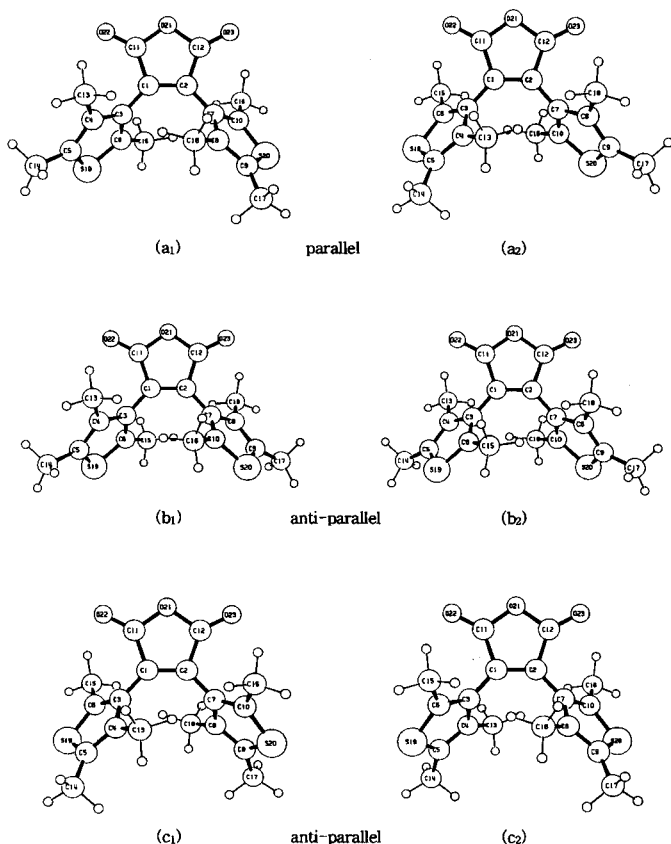


Figure 3. Stable conformations of the open-ring form of MTMA.

forth twice about 82° . Figure 4 also shows that there are four energy minima in 360° rotation of a thienyl ring. The two minima at -119° and -59.0° correspond to parallel conformations, a_1 and a_2 in Figure 3, respectively. They are believed to be easily interconvertible, due to the low energy barrier of 6.7 kJ/mol between the mirror images. At 60.0° and 119° , there are two more minima, which represent two anti-parallel conformations, b_1 and c_1 , respectively. These two conformations are also easily interconvertible over the low energy barrier of 6.0 kJ/mol (b_1 to c_1). Similarly, two

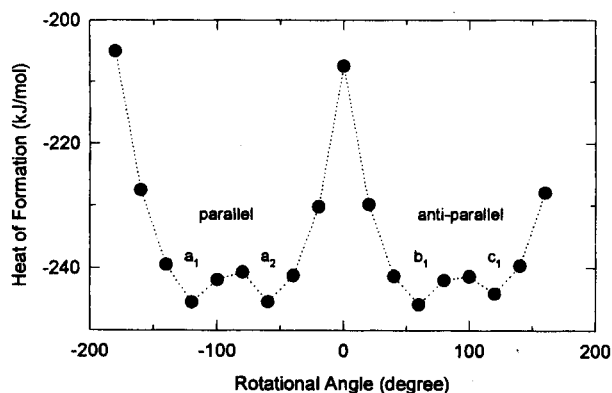


Figure 4. Molecular energy as a function of the rotational angle of thienyl ring in the ground state. The rotational angle is that of one of the two thienyl rings, which was fixed at a given value while full geometry optimization was proceeded.

more anti-parallel conformations, b_2 and c_2 , can be obtained when the second thienyl ring is rotated instead.

While fast interconversions are expected at room temperature between the parallel conformations as well as between the anti-parallel conformations, interconversion between the parallel and the anti-parallel conformations is hampered by high energy barriers, about 54 kJ/mol (Figure 4). Due to fast interconversion between conformations of the same type, they are no longer distinguishable each other in a slow time scale. Consequently, there appear to be only two conformations, parallel and anti-parallel ones, whose thienyl rings are perpendicular to the plane of the ethylene group. The fast interconversion between conformations of the open-ring form explains the observed NMR spectra of MTMA.^{15,19} Three methyl-proton peaks arise from the closed-ring form. On the other hand, six methyl-proton peaks are found in NMR spectrum of the open-ring form, indicating that there are two major conformations, and each peak is substantially broadened.¹⁷ The rate of interconversion, however, will decrease at low temperature, and methyl proton peaks from the different conformations of the open-ring form are expected to be splitted.

Because of aromaticity of the thienyl rings, the open-ring form is thermodynamically more stable than the closed-ring form. As a result, the closed-ring form is slowly converted to the open-ring form at high temperature. Thermostability of aryethene derivatives has been an important subject of studies ever since the compounds were introduced as photochromic materials.^{15,17,18} Two factors, the strain energy in the six-membered ring of the closed-ring form and the aromaticity of the aryl groups of the open-ring form, have been investigated by experimental as well as theoretical means. The strain energy in the molecular structure is turned out to be relatively less important, while the aromaticity of the aryl groups plays a major role.^{15,24} Destabilization due to destruction of the aromatic rings during the course of cyclization increases the energy of the ground state of the closed-ring form. The higher energy of the closed-ring form leads to the lower energy barrier for ring-opening.²⁴ The thermal stability of MTMA can be attributed to the relatively low aromaticity of thienyl ring in comparison with other aromatic rings. The energy difference between the open-ring and the closed-ring forms of MTMA in the ground state is estimated to be 66 kJ/mol in this study (Table 1).

Cyclization of MTMA is possible only in the conrotatory mode. Disrotatory rotation of the thienyl rings would cause extensive steric hinderance in the molecular structure, particularly due to the adjacent two methyl groups. It is also reasonable to assume that cyclization of MTMA originates only from the anti-parallel conformation. Slight conrotatory motion of the thienyl rings of anti-parallel conformation b (in Figure 3) leads to a molecular structure appropriate for cyclization. On the other hand, cyclization from the parallel conformation should include a conversion of the parallel conformation to the anti-parallel one by rotating a bulky thienyl ring 180° . This indicates that not all the open form of MTMA can be proceeded to cyclization, particularly in a short reaction time. It agrees with previously observed results. It has been demonstrated in a study on photoswitching effects of an aryethene that cyclization reaction of the

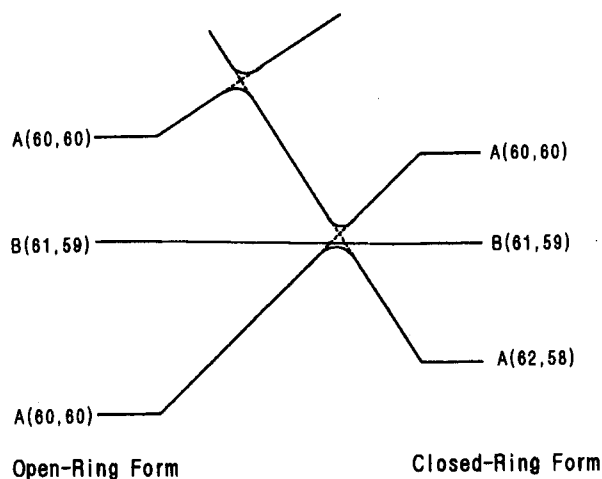


Figure 5. State correlation diagram of MTMA for cyclization in the conrotatory mode. The numbers in parenthesis are the numbers of electrons in molecular orbitals with symmetry representations A and B of the symmetry group C_2 .

diphenylethene derivative can be completed within 100 ps.²¹ Only a certain portion of diarylethene molecules (30-80%) actually undergoes the photoisomerization reaction.^{18,22} These results indicate that rotation of the bulky thienyl rings is in fact prohibited during the course of reaction, and the photochromic reaction occurs only from the anti-parallel conformation of the open form.

Shown in Figure 5 is the state correlation diagram of MTMA for cyclization/ring-opening reaction in the conrotatory mode, which proceeds under C_2 symmetry. The two thienyl rings are assumed to be in the anti-parallel orientation. Orbital symmetry forbids the conrotatory cyclization since the ground state of the open-ring form correlates with a highly excited state of the closed-ring form as shown by a dotted line in Figure 5. Because of a non-crossing rule, the actual correlations are those given by the solid lines, and the high barrier prevents the conrotatory cyclization in the ground state. On the other hand, there is no such high barrier in conrotatory isomerization between the open-ring and the closed-ring forms in the S_1 state. This leads the conrotatory cyclization to be allowed photochemically.

Though proceeded very slowly at room temperature, the closed-ring form of MTMA is expected to be continuously converted thermally to the open-ring form, the more stable isomer. In thermal conversion of the closed-ring form to the open-ring form, the interatomic distance between carbons 6 and 10 of MTMA is supposed to change from 1.52 Å to 4.00 Å. Shown in Figure 6 are the molecular energy (a) and the rotational angle of thienyl rings (b) in the ground state as a function of interatomic distance (C_6-C_{10}). Anti-parallel conformation was assumed for the open-ring form, and at each given interatomic distance (C_6-C_{10}), a full geometry optimization was proceeded. Figure 6 shows that the molecular energy increases continuously as the atomic distance deviates from that of the stable isomer, and eventually leads to an avoided crossing. The crossing point is 226 kJ/mol higher in energy than the open-ring form and 160 kJ/mol higher in energy than the closed-ring form, respectively. Figure 6 also shows that the rotational angle of the thienyl ring

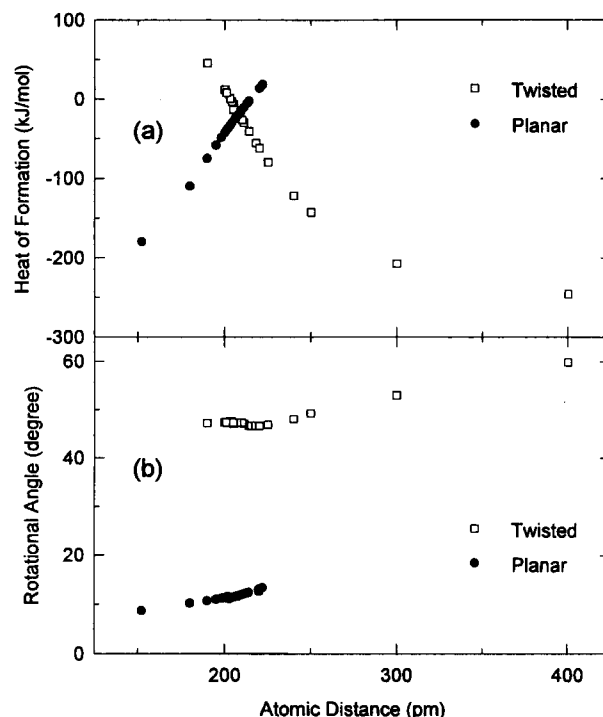


Figure 6. (a) Molecular energy as a function of the interatomic distance, C_6-C_{10} , in the ground state. (b) Rotational angle of the thienyl rings as a function of the interatomic distance. No constraint was given other than the interatomic distance in the geometry optimization.

remains almost unchanged while the molecular energy increases as much as 240 kJ/mol. This suggests that in thermochromic conversion, initially the thienyl rings maintain essentially the original configuration, and in order to complete the reaction, extra torque to the thienyl rings in the conrotatory direction is later necessary. Both the high activation energy and the structural requirement for the conversion lead thermochromic reaction to be effectively prohibited.

The molecular structure of MTMA in the S_1 state is also examined. The closed-ring form in the S_1 state has a more twisted structure in comparison with the structure of the closed-ring form in the ground state; the rotational angle of the thienyl rings in the S_1 state is 18.7° compared to 8.7° in the ground state. In the S_1 state, the open-ring form of MTMA also has three pairs of conformations, one parallel and two anti-parallel pairs (Figure 7), however, they show large differences in the rotational angles of thienyl rings. Especially anti-parallel conformation *b* has less twisted structure (37.2°) in comparison with that in the ground state (60.6°). After absorption of a photon, the difference in the rotational angle of thienyl rings will create a torque to the rings. For the anti-parallel conformation *b* of the open-ring form and the closed-ring form, the induced conrotatory motion of thienyl rings occurs in the favorable direction for photochromic reaction. This is considered as another evidence that only the anti-parallel conformation *b* is responsible to cyclization.

Variations of molecular characteristics during cyclization of MTMA in the S_1 state are investigated. The two thienyl

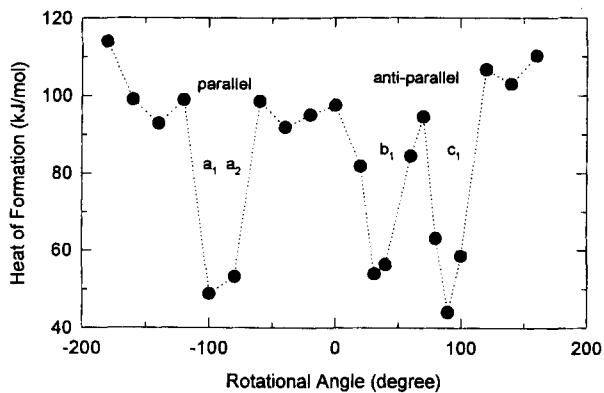


Figure 7. Molecular energy as a function of the rotational angle of thienyl ring in the S_1 state. The rotational angle shown in this figure is that of one of the two thienyl rings, which was fixed at a given value while full geometry optimization was carried out.

rings are assumed to be in the anti-parallel orientation before conrotatory rotation, and the interatomic distance between carbons 6 and 10 is varied from 2.16 Å to 1.56 Å. Shown in Figure 8 is the molecular energy as a function of the interatomic distance. The molecular energy varies smoothly in the course of reaction. At the top of the curve, the transition state, where one of the force constants has a negative value, is located. The height of the energy barrier of cyclization in the S_1 state is 33.2 kJ/mol, and that of ring-opening 13.2 kJ/mol, both of which are much smaller than the heights of the energy barriers in the course of interconversion between the parallel and anti-parallel conformations. The low reaction energy barrier and smooth variation of geometry in the course of reaction is considered as the origin of the high reactivity and reversibility of the photochromic reaction of MTMA in the excited state. In previous studies on isomerization of arylethenes and fulgide derivatives, it has been demonstrated that the quantum efficiency increases with photon energy as much as four folds.¹⁵ The excess vibronic energy appears to be utilized to overcome the energy barrier for the photochromic reaction.

Shown in Figure 9 is the simplified potential energy diagram of MTMA in the ground and the S_1 states. The energy minima represent the open-ring and the closed-ring

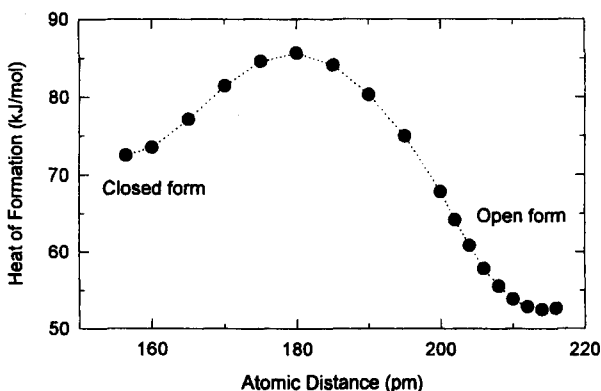


Figure 8. Molecular energy as a function of the interatomic distance, C_6-C_{10} , in the S_1 state. No constraint was given other than the interatomic distance in the geometry optimization.

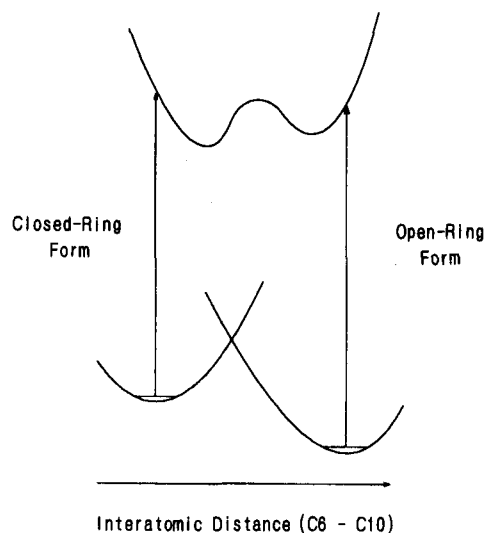


Figure 9. Simplified potential energy diagram for the ground and the S_1 states of MTMA.

forms of MTMA. In the S_1 state, MTMA forms a double-well potential in which the photochromic isomers easily interconvert over the relatively low energy barrier, resulting in the high photoreactivity and reversibility of MTMA. Whereas in the ground state, an avoided crossing at high energy is found between the states of the open-ring and the closed-ring forms, resulting in the high thermostability. The locations of energy minima in the S_1 state do not exactly coincide with those in the ground state, but shifted toward the energy minimum of the other form. As a result, absorption of a photon generates a conrotatory rotation of thienyl rings.

It has been reported that the quantum efficiency of cyclization of arylethene derivatives including MTMA strongly depends on the polarity of solvents; the quantum efficiency of cyclization decreases as much as 40 times in polar solvents, whereas the quantum yield of ring-opening does not show noticeable change.¹⁸ The fluorescence decay curve of MTMA can not be reproduced with a single-component decay model, but with a multicomponent one, where interconversion of the components is negligible. The contribution of slow decaying component of fluorescence increases with increasing solvent polarity, and large Stokes shift has been observed from the open-ring form in polar solvents. In an effort to explain these experimental results, Irie and Sayo proposed two molecular structures in the excited state, a planar structure with a relatively low dipole moment and a twisted structure with a large dipole moment due to intramolecular charge-transfer.¹⁸ The Franck-Condon state conformation of MTMA is assumed to be in between planar and twisted geometries. In less polar solvents, the excited state stabilizes to a planar conformation with a low dipole moment, whereas in more polar environment, the Franck-Condon state converts to the charge separate state. In the charge separate state, the planes of the thienyl rings are perpendicular to the plane of the maleic anhydride moiety; the perpendicular geometry is disadvantageous to cyclization and the radiative transition to the ground state is forbidden.¹⁸

Among the three different pairs of conformations of the open-ring form in the S_1 state, anti-parallel conformation *b*, presumably responsible for cyclization, has a lower dipole moment in comparison with other conformations of the open-ring form (Table 1). Under more polar environment, anti-parallel conformation *b* is expected to become less stable. Both the parallel conformation and anti-parallel conformation *c* show higher dipole moments and their thienyl rings are almost perpendicular to the maleic anhydride moiety. These molecular characteristics in the excited state are consistent with those previously proposed by Irie and Sayo,¹⁸ however, it is still less certain that the difference in dipole moment of 4.6 Debye alone can account for the large solvent effects including the dramatic variation of quantum efficiency as much as forty times. More careful studies are necessary for the molecular characteristics in the excited state, particularly the charge-transfer state, originally introduced to explain the remarkable effects of solvent polarity. Based upon the results of this study, direct observation of the photochromic reaction of MTMA in time domain is planned, which will provide more information about the molecular characteristics in the course of the photochromic reaction.

Conclusions

A semi-empirical MO study has been carried out for MTMA. For the open-ring form, there are three (one anti-parallel and two parallel) pairs of conformations in the ground state, each pair consisting of the two mirror images. The conformations have similar energies, and interconversion between the anti-parallel and the parallel conformations is hampered due to a high energy barriers for rotation of a thienyl ring. On the other hand, conversions between the parallel conformations as well as between the anti-parallel conformations are relatively facile, and as a result, they become indistinguishable in a slow time scale. It explains the fact that the previous NMR results of the open-ring form of MTMA can be accounted for by assuming only two configurations (parallel and anti-parallel). It is believed that anti-parallel conformation *b* is responsible for cyclization, due to the appropriate structure for the reaction. High thermostability of MTMA has been attributed to an avoided crossing at high energy found in the ground states of the open-ring and the closed-ring forms.

In the S_1 state, there are the same number of conformations as in the ground state. The rotational angles of thienyl rings in the excited state show substantial differences from those in the ground state. The differences will cause rotation of the thienyl rings after absorption of light. In case of anti-parallel conformation *b*, the light-induced rotation occurs in the favorable direction for cyclization. The S_1 states of the open-ring and the closed-ring forms of MTMA compose a double well potential, each well representing a photochromic isomer. Photoreactivity of MTMA can be traced to the low energy barrier and smooth variation of molecular structure in the course of reaction. The activation energy is estimated to be 33.2 kJ/mol in cycli-

zation and 13.2 kJ/mol in ring-opening. The previously reported large change of quantum yield with wavelength suggests that excess vibronic energy can be the source of the activation energy. The large solvent effects of MTMA can be partly explained with the relatively low dipole moment of anti-parallel conformation *b* in the S_1 state.

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