

# Ultrafast Dynamics of Photochromic Systems

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## I. Introduction

Photochromism is defined as a reversible transformation in a chemical species between two forms, and in these reversible processes, at least one pathway is induced by photoexcitation. As a result of different molecular structures between these two forms, the two isomers differ from one another in various properties such as the absorption spectra, refractive indices, dielectric constants, etc. Several excellent reviews describing these properties are found in the cited publications<sup>1–4</sup> and other articles in the present issue.

The instant property changes that occur only by photoirradiation without processing have been attracting much attention, and their application into various optoelectronic devices, such as optical memory, photooptical switching, and display, have been proposed. For application to the actual photonic devices, the photochromic systems require several conditions: (1) thermal stability of both isomers, (2) low fatigue (can be cycled many times while maintaining performance), (3) rapid response, (4) high sensitivity, (5) nondestructive readout capability.

For construction of photochromic systems fulfilling the conditions given above, the quick response (rapid

reaction) is of crucial importance. This is because the reaction in the excited state generally occurs in competition with various processes such as the radiative transition (fluorescence and phosphorescence), nonradiative transition (internal conversion and intersystem crossing), quenching reactions by other molecules, etc. Hence, the large rate constant of the photochromic reaction is indispensable for an increase in the reaction yield and a decrease in undesirable competitive subreaction processes which leads to a decrease in durability. In addition, the high reaction yield as a result of the large rate constant is directly related to the high sensitivity and the quick response of the system.

Ultrafast laser spectroscopy is one of the most powerful tools for the direct elucidation of the reaction profiles of the photochromic systems. This technique provides detailed information on reaction kinetics and mechanisms, which is of fundamental importance for smart design of photochromic materials with improved properties.

Although more than 100 years have passed since the discovery of photochromism, research has been concentrated on a relatively small number of compounds. In the present article, we concentrate on the temporal response of mainly four photochromic systems by introducing investigations in which ultrafast laser spectroscopy has been applied: azobenzenes, spiropyrans, fulgides, and diarylethenes. The photochromic properties of azobenzenes arise from the *cis*–*trans* isomerization of the N=N bond. The bond rearrangement induced by the photoexcitation is responsible for the property change of spiropyran derivatives. On the other hand, electrocyclic reactions occurring in the excited states of fulgides and diarylethenes are the origin of the photochromism in these systems. Azobenzene and spiropyran derivatives are regarded as the “first generation” of the photochromic systems where one of the two reactions is thermally induced. On the other hand, fulgides and diarylethenes are rather new systems with thermally irreversible photochromic properties.

## II. Experimental Techniques for the Detection of Ultrafast Dynamics

Since the pioneering work of the flash photolysis by Norrish and Porter in 1949,<sup>5</sup> time-resolved detection of transient chemical species has been utilized as a powerful tool in the elucidation of the photo-

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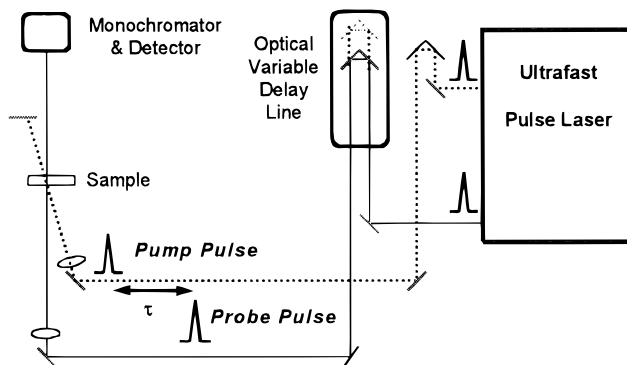
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chemical reactions. We can now access the femtosecond time region ( $10^{-15}$  s) with the aid of ultrafast laser technology. Along with the developments in the time resolution, a number of the methods of detection have been presented, such as time-resolved transient absorption spectroscopy in the UV, visible, and IR regions, time-resolved detection of emission, time-resolved Raman spectroscopy, etc.<sup>6</sup>

Also, for the photochromic processes, similar apparatus have been used. The pulsed excitation of the



**Figure 1.** Schematic diagram of ultrafast transient absorption spectroscopy.

system determines the time origin of the reaction. The subsequent reaction profiles are probed by various kinds of detection methods as mentioned above. Among the many detection methods, the time-resolved transient absorption measurement in the visible and UV regions has been utilized as a principal tool in the investigation of the photoinduced dynamic behaviors because of its wide applicability. Usually transient absorption spectroscopy can cover a number of chemical species such as excited molecules, ions, ion radicals, and neutral radicals. We can assign the species by comparing their spectra with reference ones which were measured for the corresponding chemical species selectively prepared by appropriate methods. Analysis of the time dependence of the transient spectra provides the reaction scheme of the photoinduced processes as well as quantitative information (reaction yields) of the transient species if the extinction coefficients of the transient species are known. This information, as observed by transient absorption spectroscopy, is usually indispensable for the rational interpretation of the results obtained by other techniques that provide more detailed information of some specific species. For example, time-resolved fluorescence detection gives more detailed kinetic information on the excited singlet state but no information on the chemical species produced by the reaction in the excited singlet state.

Also, for direct detection of the photochromic reactions, transient absorption spectroscopy and its kinetic measurements have been used as a central method. In general, transient absorption spectroscopy yields the temporal evolution of "transient" spectra representing the pump-pulse-induced absorption changes of the sample. The individual spectra, taken at a certain time delay after the excitation by the pump-pulse, may provide information on the properties of transient species. On the other hand, the transients, detected at a fixed wavelength, display the rise and decay curves of the pump-pulse-induced absorption changes and thereby the dynamics of photophysical and photochemical processes.

A basic diagram of the ultrafast absorption spectroscopy setup is given in Figure 1. In the time range of less than a few hundreds of picoseconds, measurement by using a combination of photodetectors and oscilloscopes is no longer adequate to resolve the time profile of the transient species. Hence, in performing

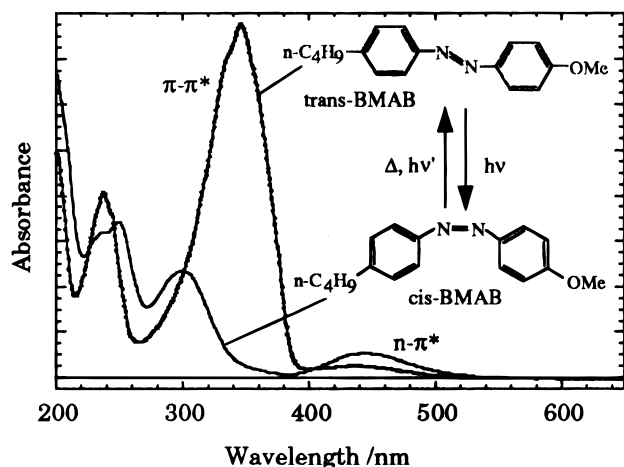
measurements with picosecond and femtosecond time resolution, it is necessary to employ two optical pulses of very short duration, one of which is an exciting (pump) pulse and the other is a monitoring (probe) pulse. These two pulses travel different paths before arriving at the sample position, and the interval time,  $\tau$ , between these two pulses can be varied by mechanically changing one of the optical path lengths (optical variable delay line). These two pulses are usually provided by one laser beam in order to attain an accurate relative timing. In these measurements, the time resolution is basically determined by the pulse duration of the laser pulse.

### III. Direct Detection of Photochromic Reactions

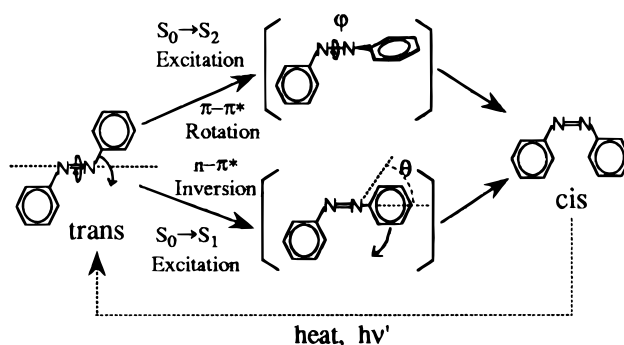
#### A. Isomerization of Azobenzene Derivatives

Azobenzene derivatives have been widely investigated as promising systems for various applications such as switching elements for microelectronics, high-density data storage, and nonlinear optics.<sup>7–9</sup> The systems used for these applications are liquid crystals, thin polymer films, Langmuir–Blodgett films, etc. In these systems, the physical and optical properties such as the absorption spectrum, dipole moment, refractive index, and molecular conformation can be reversibly changed through the *trans*–*cis* isomerization of azobenzene. Azobenzene has lone pair electrons on the nitrogen atoms, and thus the  $n\text{--}\pi^*$  electronic transition is observed in addition to the  $\pi\text{--}\pi^*$  transition, which may result in isomerization dynamics different from those of stilbene.<sup>10</sup> Representative absorption spectra of *trans* and *cis* forms of an azobenzene derivative (4-butyl-4'-methoxyazobenzene, BMAB) are illustrated in Figure 2.

The  $n\text{--}\pi^*$  transition of *trans*-azobenzene is centered at  $\sim 440$  nm and formally symmetry forbidden with a molar extinction coefficient ( $\epsilon$ ) of approximately  $400 \text{ M}^{-1} \text{ cm}^{-1}$ . This value is relatively large for the forbidden transition, which is interpreted in terms of vibronic coupling between the  $n\text{--}\pi^*$  and  $\pi\text{--}\pi^*$  states.<sup>11</sup> On the other hand, the  $n\text{--}\pi^*$  absorption of *cis*-azobenzene is an allowed transition with  $\epsilon \approx 1500 \text{ M}^{-1} \text{ cm}^{-1}$  at  $\sim 440$  nm. The  $\pi\text{--}\pi^*$  transition



**Figure 2.** Absorption spectra of *trans*- and *cis*-(4-butyl-4'-methoxyazobenzene) (abbreviated as BMAB) in *n*-hexane.



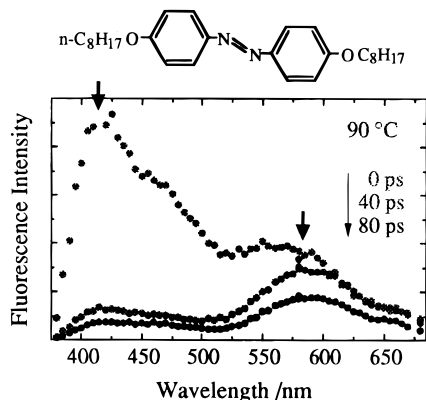
**Figure 3.** Proposed reaction mechanism of photoisomerization of *trans*-azobenzene. Wavelength dependence on the mechanism is written.

of *trans*-azobenzene is centered at 320–350 nm with  $\epsilon \approx 2\text{--}3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , and the  $\pi\text{--}\pi^*$  transition of the *cis* form has a peak shorter than that of the *trans* form ( $\epsilon \approx 7\text{--}10 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 260–300 nm).

It has been proposed that the photoisomerization of azobenzene depends on the excitation wavelength as shown in Figure 3.<sup>11,12</sup> The *trans*–*cis* isomerization proceeds through an inversion mechanism under  $n\text{--}\pi^*$  excitation, whereas the rotational mechanism operates under  $\pi\text{--}\pi^*$  excitation similar to the isomerization of stilbene. In the inversion mechanism, a linear geometry in the transition state is not involved because it is higher in energy than a semilinear geometry as given in Figure 3.<sup>11</sup> In addition, no influence of oxygen or heavy atom was observed in the photoisomerization reaction of azobenzene,<sup>13</sup> suggesting the singlet pathway of photoisomerization. The quantum yields of the *trans*–*cis* isomerization of restricted azobenzenes such as azobenzenophanes were examined under  $n\text{--}\pi^*$  and  $\pi\text{--}\pi^*$  excitation conditions.<sup>14</sup> Only the inversion mechanism can be expected in azobenzenophanes because of the steric hindrance. The quantum yield of the *trans*–*cis* isomerization was found to be 0.24 and 0.21 for  $n\text{--}\pi^*$  and  $\pi\text{--}\pi^*$  excitations, respectively, which is similar to that of azobenzene (0.23) for  $n\text{--}\pi^*$  excitation. This suggests that the isomerization of *trans*-azobenzene under  $n\text{--}\pi^*$  excitation proceeds via an inversion mechanism as azobenzenophanes do. In *trans*-azobenzene and its derivatives without any restrictions, the quantum yields of the *trans*–*cis* isomerization for  $\pi\text{--}\pi^*$  excitation are always smaller ( $\sim 0.1$ ) by a factor of 2,<sup>13–17</sup> indicating the violation of Kasha's rule. This may be an indication of a rotational mechanism operating for the *trans*–*cis* isomerization of azobenzene for  $\pi\text{--}\pi^*$  excitation, which is supported by the molecular orbital calculations.<sup>11,12,18</sup> On the other hand, for the *cis*–*trans* thermal isomerization of diazene, ab initio molecular orbital calculations based on the CIPSI algorithm (6-331 + G (3df,2p) basis set) have been carried out to estimate the isomerization mechanism.<sup>19</sup> The inversion transition state is a little smaller (6–7 kcal/mol) in energy than the rotation, which indicates the competition of inversion and rotation in azo compounds derived from diazene.

Femtosecond spectroscopic studies and the analysis of resonance Raman excitation profiles have been performed to estimate the photoisomerization mechanism of azobenzene for both  $n\text{--}\pi^*$  and  $\pi\text{--}\pi^*$  excita-





**Figure 4.** Time-resolved fluorescence spectra of the liquid crystalline *trans*-azobenzene derivative, 4,4'-dioctyloxyazobenzene (abbreviated as *trans*-8AB8), at 90 °C. The spectrum at  $\sim 420$  nm is due to  $S_2$  fluorescence, whereas the spectrum at  $\sim 590$  nm is due to  $S_1$  fluorescence from a J-like aggregate of *trans*-8AB8.

tion conditions.<sup>20–26</sup> The details of direct observation of the isomerization dynamics are given in the following sections, and the violation of Kasha's rule is also discussed on the basis of femtosecond laser spectroscopy.

### 1. Fluorescence of Azobenzene Derivatives

The  $n-\pi^*$  ( $S_1$ ) state of *trans*-azobenzene is generally nonfluorescent because of the forbidden transition and isomerization reaction in the  $S_1$  manifold.<sup>11</sup> Struve first examined the fluorescence dynamics from the  $S_1$  state in 1977.<sup>29</sup> It was found that the  $n-\pi^*$  luminescence of *trans*-azobenzene appeared in a longer wavelength region (600–800 nm) in cyclohexane and decayed with a lifetime of  $\sim 25$  ps at 700 nm by a picosecond Nd:glass laser and an optical Kerr gate method using  $CS_2$ . However, the luminescence spectrum was extremely broad and structureless in the observed wavelength region.

Shimomura and Kunitake reported the strong enhancement of the fluorescence of azobenzene-containing amphiphiles at  $\sim 600$  nm in the aqueous bilayer systems.<sup>30</sup> This finding was interpreted in terms of head-to-tail chromophore orientation of azobenzene derivatives to form J-like aggregates, although the fluorescence was considered to have  $\pi-\pi^*$  ( $S_2$ ) character. Recently, we examined the fluorescence properties of an azobenzene liquid crystal, 4,4'-dioctyloxyazobenzene (8AB8), as a function of temperature by picosecond single-photon timing spectroscopy.<sup>31</sup> As illustrated in Figure 4, time-resolved fluorescence spectra of *trans*-8AB8 have a peak at  $\sim 590$  nm in addition to the  $\pi-\pi^*$  ( $S_2$ ) fluorescence observed at  $\sim 420$  nm. This observation is very similar to that reported by Shimomura and Kunitake.<sup>30</sup> The fluorescence spectrum at  $\sim 590$  nm was assigned to be  $S_1$  fluorescence of a J-like aggregate of 8AB8, and its lifetime was estimated to be 150–180 ps.<sup>31</sup> On the other hand,  $\pi-\pi^*$  fluorescence of *trans*-8AB8 monomer showed very rapid decay similar to the instrument response function ( $\sim 30$  ps fwhm) with a lifetime shorter than 2 ps. The fluorescence spectrum and lifetime of *trans*-8AB8 from the  $\pi-\pi^*$  ( $S_2$ ) state are similar to those observed

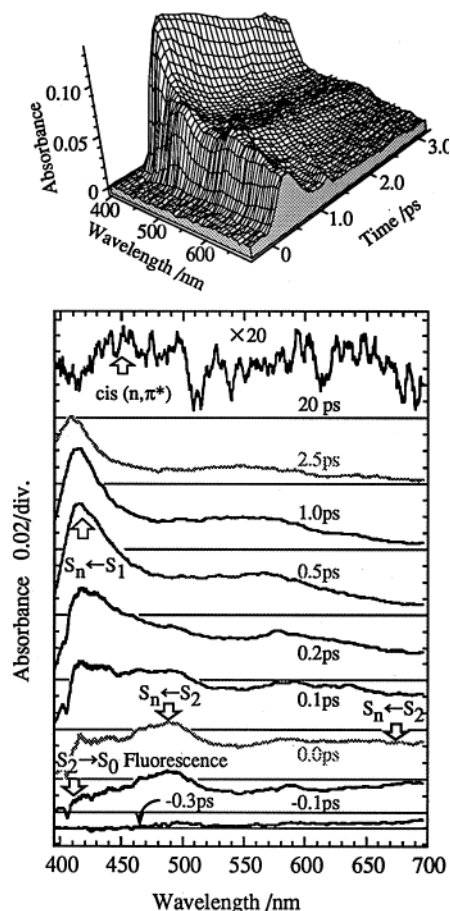
in solution where the fluorescence spectrum has a peak at  $\sim 400$  nm,<sup>31</sup> although spectral broadening was clearly observed in the crystalline phase (Figure 3). The lifetime of the  $\pi-\pi^*$  ( $S_2$ ) state for *trans*-BMAB in *n*-hexane was estimated to be  $\sim 250$  fs by femtosecond transient absorption spectroscopy.<sup>23</sup>

From a historical point of view, Morgante and Struve reported the fluorescence dynamics of *trans*-azobenzene from the  $\pi-\pi^*$  ( $S_2$ ) state by a picosecond Nd:glass laser and an optical Kerr gate method and estimated the lifetime to be  $\sim 5$  ps,<sup>32</sup> although they have not reported the fluorescence spectrum. The fluorescence spectrum from the  $S_2$  state of *trans*-azobenzene derivatives and their quantum yields were examined by Hamai and Hirayama.<sup>33</sup> They reported that the fluorescence spectrum from the  $S_2$  state has a maximum at 385 nm with  $\Phi_f \approx 1.7 \times 10^{-5}$  for *trans*-azobenzene and a maximum at  $\sim 410$  nm with  $\Phi_f \approx 0.9 \times 10^{-5}$  for 1-methoxy *trans*-azobenzene. The  $S_2$  lifetime of *trans*-azobenzene was also estimated to be ca. 60 fs using the Strickler–Berg equation. On the other hand, an  $S_2$  lifetime of  $\sim 250$  fs was evaluated from  $\Phi_f \approx 1 \times 10^{-4}$  by Monti et al.<sup>18</sup> The experimental data for *trans*-BMAB with a fluorescence maximum at  $\sim 400$  nm and a lifetime of  $\sim 250$  fs<sup>23</sup> are in good agreement with the reported and estimated values of the  $S_2$  fluorescence of *trans*-azobenzene.

The observation of the  $S_2$  fluorescence of azobenzene derivatives is direct evidence of the violation of Kasha's rule. In addition to the radiative transition, the nonradiative process from the  $S_2$  to  $S_0$  state may also exist as a competitive process with internal conversion from the  $S_2$  to  $S_1$  states. These radiative and nonradiative transitions from the  $\pi-\pi^*$  ( $S_2$ ) to the ground states result in the lower quantum yield of *trans*–*cis* isomerization from the  $\pi-\pi^*$  ( $S_2$ ) state than that from the  $n-\pi^*$  ( $S_1$ ) state, even if we only consider the isomerization of azobenzene in the  $S_1$  manifold.

### 2. Femtosecond Dynamics of Azobenzene Derivatives

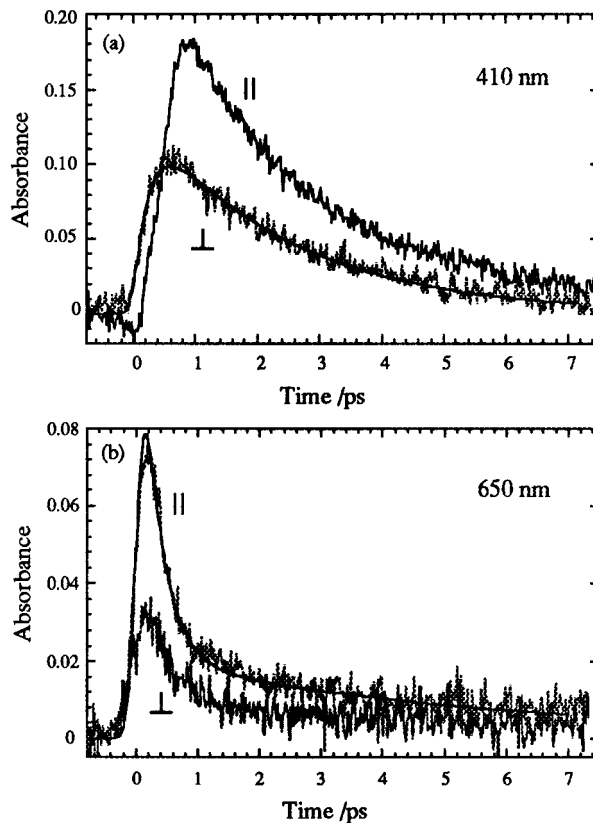
Femtosecond pump–probe experiments of *trans*-azobenzene were carried out by Lednev et al. under the  $\pi-\pi^*$  ( $S_2$ ) excitation condition.<sup>20</sup> The transient absorption spectrum of *trans*-azobenzene in *n*-hexane, obtained 0.47 ps after the excitation, appears in the range from 370 to 450 nm and has a peak at 390 nm with a main decay component of  $0.9 \pm 0.2$  ps. First, they assigned this spectrum to absorption from the  $S_2$  state of *trans*-azobenzene and later to the  $S_1$  state.<sup>24</sup> A long-lived component existing for 13–16 ps is also observed, which is explained by relaxation from the intermediate to the ground state of *trans*-azobenzene. In the case that *trans*-azobenzene is excited at 503 nm to the  $n-\pi^*$  ( $S_1$ ) state, the absorption spectrum has a peak at  $\sim 400$  nm in *n*-hexane and decays with a single exponential with a lifetime of  $\sim 2.5$  ps.<sup>24</sup> When *trans*-azobenzene was excited at 420 or 390 nm, an additional fast component of  $\sim 0.6$  ps was observed. Nägele et al. also examined the *trans*–*cis* isomerization of azobenzene under  $n-\pi^*$  excitation at 435 nm, and the decay constants observed at 440–750 nm were found to be



**Figure 5.** Transient absorption spectra of a *trans*-azobenzene derivative, *trans*-BMAB, in *n*-hexane excited at  $\sim 360$  nm ( $\pi$ - $\pi^*$  ( $S_2$ ) excitation).

$\sim 320$  fs and 2.1 ps.<sup>21</sup> They considered that the fast component of  $\sim 320$  fs is due to the rate of *trans*-*cis* isomerization and the 2 ps component to the diffusion-type motion along the  $S_1$  potential energy surface that escaped from the reactive pathway. The lifetime of 2.1–2.5 ps is very similar to our experimental results obtained for relaxation of the  $n$ - $\pi^*$  ( $S_1$ ) state of an azobenzene derivative, *trans*-BMAB, in *n*-hexane prepared from excitation to the  $\pi$ - $\pi^*$  ( $S_2$ ) state followed by internal conversion.<sup>23</sup>

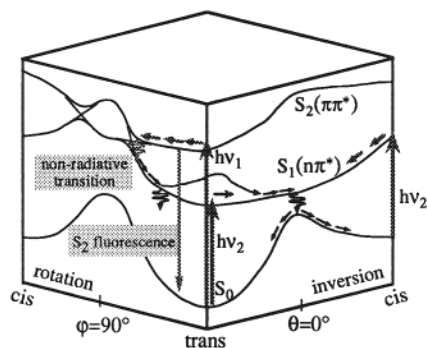
Figure 5 illustrates the transient absorption spectra of *trans*-BMAB in *n*-hexane excited at 360 nm ( $\pi$ - $\pi^*$  ( $S_2$ ) state). The spectrum just after the excitation has a peak at  $\sim 490$  nm and a very broad absorption in the longer wavelength region. The rapid decay component observed in this wavelength region is  $\sim 250$  fs, which is due to the  $S_n \leftarrow S_2$  absorption of *trans*-BMAB. The stimulated fluorescence from the  $\pi$ - $\pi^*$  ( $S_2$ ) state with a maximum at  $\sim 400$  nm overlaps the transient absorption ranging from 390 to 470 nm. The disappearance of the  $S_n \leftarrow S_2$  absorption bands is followed by the appearance of an intense absorption band at  $\sim 415$  nm and a shoulder at  $\sim 550$  nm with a rise time of  $\sim 250$  fs that can be assigned to the  $S_n \leftarrow S_1$  absorption of *trans*-BMAB. The relaxation time of *trans*-BMAB in the  $n$ - $\pi^*$  ( $S_1$ ) state was estimated to be  $\sim 2.3$  ps. After the disappearance of this band, a weak absorption spectrum with a maximum at  $\sim 450$  nm, corresponding to the difference spectrum of  $n$ - $\pi^*$  absorption of *cis*- and



**Figure 6.** Polarization absorption dynamics of *trans*-BMAB in *n*-hexane observed at 410 ( $S_n \leftarrow S_1$  absorption) and 650 nm ( $S_n \leftarrow S_2$  absorption). The difference of the rise part at 410 nm originates from the spectral overlap of a stimulated fluorescence from  $S_2$  state.

*trans*-BMAB in the ground state, can be observed and remains for long time.

The presence of stimulated fluorescence from the  $\pi$ - $\pi^*$  ( $S_2$ ) state, its relaxation dynamics, and the formation of the  $n$ - $\pi^*$  ( $S_1$ ) state of *trans*-BMAB were confirmed by the polarization transient absorption as shown in Figure 6. The rising part of the parallel component at 410 nm was clearly delayed for 200–300 fs from the perpendicular component, which is most likely due to overlap of the stimulated fluorescence from the  $\pi$ - $\pi^*$  ( $S_2$ ) state. On the other hand, no difference was observed at 650 nm. The polarization dynamics at 410 nm have rise and decay components of  $\sim 250$  fs and 2.3 ps, respectively. The rise dynamics at 410 nm are in good agreement with the decay observed at 650 nm, indicating formation of the  $n$ - $\pi^*$  ( $S_1$ ) state with a time constant of  $\sim 250$  fs. This time constant is almost independent of the solvents, whereas the relaxation time of the  $n$ - $\pi^*$  ( $S_1$ ) state of *trans*-BMAB depends on the solvent viscosity:  $\sim 10$  ps in ethylene glycol.<sup>23</sup> The isomerization dynamics of stilbene, in which the rotation mechanism operates, is known to be dependent on the solvents.<sup>10,34</sup> If the rotation mechanism plays an important role for the  $\pi$ - $\pi^*$  ( $S_2$ ) state of *trans*-azobenzene, the relaxation time of *trans*-azobenzene in the  $\pi$ - $\pi^*$  ( $S_2$ ) state should depend on the solvents and the lifetime should be on the order of picoseconds. These results suggest that the isomerization of azobenzene derivative, *trans*-BMAB, mainly proceeds from the  $n$ - $\pi^*$  ( $S_1$ ) state along the inversion coordi-



**Figure 7.** Schematic representation of the potential energy surfaces of azobenzene for both rotation and inversion pathways.<sup>18,12,21</sup>  $h\nu_1$  corresponds to excitation to the  $S_2$  state and  $h\nu_2$  to the  $S_1$  state.

nate even in excitation to the  $\pi-\pi^*$  ( $S_2$ ) state. The schematic illustration of the potential energy surfaces is given in Figure 7. When *trans*-azobenzene is excited to the  $\pi-\pi^*$  ( $S_2$ ) state, deactivation of the  $\pi-\pi^*$  state occurs via rotational motion and reaches to the  $n-\pi^*$  state with a lifetime of  $\sim 250$  fs. The  $S_2 \rightarrow S_1$  internal conversion competes with the radiative and nonradiative processes to the  $S_0$  state, which may result in the lower isomerization quantum yields in the *trans*-*cis* isomerization of azobenzene for the  $\pi-\pi^*$  ( $S_2$ ) excitation than for the  $n-\pi^*$  ( $S_1$ ) excitation.

For the isomerization dynamics of *cis*-azobenzene, Nägele et al. recently reported the femtosecond transient absorption dynamics in ethanol under excitation to the  $n-\pi^*$  ( $S_1$ ) state with the frequency doubled output pulses of a Ti:Sapphire laser ( $\sim 435$  nm, 100 fs).<sup>21</sup> It was found that the strong absorption increase at the *trans* product band ( $\sim 360$  nm) was observed after the decay of the 170 fs kinetic component and the excited-state absorption at  $\sim 563$  nm decayed with a 170 fs transient in addition to the 2 ps and 10–20 ps components. The 2 ps component was attributed to the diffusion-type motion along the  $S_1$  potential energy surface that escaped from the reactive pathway. These observations indicate that the ultrafast *cis*-*trans* photoisomerization proceeds with a 170 fs time constant. The ultrafast isomerization reaction of excited *cis*-azobenzene is interpreted in terms of the barrierless isomerization through the inversion pathway as indicated in Figure 7.<sup>12,18,21</sup> The potential energy surface clearly shows the barrierless process in the inversion pathway, while a large barrier exists for the rotational mechanism in the  $S_1$  manifold. On the other hand, the slower isomerization rate ( $\sim 320$  fs in ethanol given by Nägele et al.,<sup>21</sup> 2.3 ps in *n*-hexane given by Azuma et al.,<sup>23</sup> 2.5 ps in *n*-hexane by Lednev et al.<sup>24</sup>) of *trans*-azobenzene in the  $S_1$  state indicates the smoothly sloping pathway in the inversion process as compared to *cis*-azobenzene. The inversion mechanism for  $n-\pi^*$  excitation was also suggested from the simulation calculation of resonance Raman excitation profiles and the  $n-\pi^*$  absorption spectrum by using the time-dependent wave packet propagation technique.<sup>26</sup>

For the isomerization dynamics of aminoazobenzene derivatives, 4-(4'-aminophenylazo)benzoic acid sodium salt (APB) in ethanol was investigated by exciting the  $\pi-\pi^*$  transition using femtosecond

pump-probe spectroscopy.<sup>22</sup> The  $n-\pi^*$  and  $\pi-\pi^*$  states are in close proximity in energy for APB, which is characteristic for aminoazobenzene derivatives. Three different kinetic processes were revealed: a weak component in the  $\sim 100$  fs regime, a strong absorption change of  $\sim 0.9$  ps time scale, and an additional component of  $\sim 12$  and 280 ps. The 0.9 ps component was assigned to the decay process from the excited state to the ground state and indicative of the very rapid photoisomerization from the *trans* to the *cis* form. A weak, ultrafast 100 fs process is considered to be an initial reactive motion out of the initial Franck-Condon regime. The additional longer component of  $\sim 12$  ps is due to the cooling of the vibrationally hot ground state.

Since the photochromic reaction is similar to the nonradiative transition, in a sense, the electronic excitation energy should be converted into thermal energy through the vibrational and translational motions. The formation of a vibrationally hot ground state in the photochromic product has been commonly observed in various kinds of photochromic reactions triggered by bond cleavage in spirooxazine or spiro-pyran<sup>27,28</sup> and *cis*-*trans* isomerization in azobenzene.<sup>25</sup>

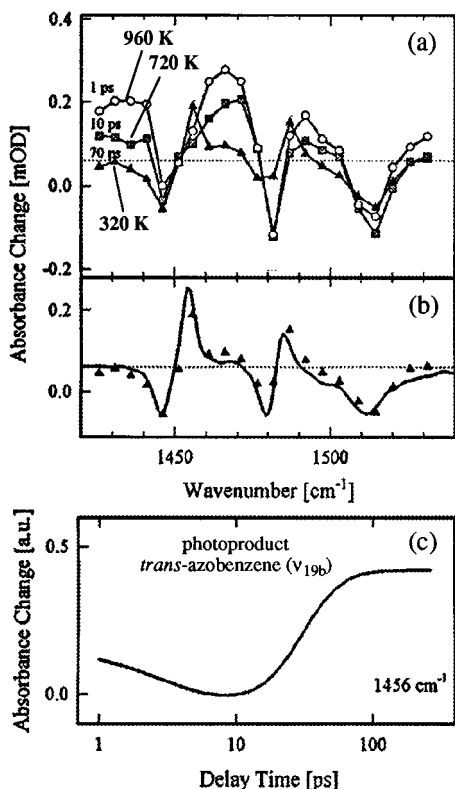
Hamm et al. examined the vibrational cooling after photoisomerization of *cis*-azobenzene to the *trans* form by femtosecond infrared spectroscopy.<sup>25</sup> As shown in the previous section, the excited *cis*-azobenzene in the  $n-\pi^*$  state reaches the ground state in less than 200 fs,<sup>21</sup> transferring most of the electronic excitation energy into the vibrational degrees of freedom and forming the vibrationally hot ground state of *trans*-azobenzene.

Figure 8 illustrates time-resolved IR spectra of *cis*-azobenzene excited at 435 nm. Just after the excitation, the transient difference spectrum is very broad with positive and negative contributions that are due to transient product and bleaching of *cis*-azobenzene (1446, 1481, and 1515  $\text{cm}^{-1}$ ). The spectrum at 70 ps is almost the same as the steady-state difference spectrum, indicating the formation of ground-state cold *trans*-azobenzene ( $\nu_{19b} = 1456$   $\text{cm}^{-1}$  and  $\nu_{19a} = 1484$   $\text{cm}^{-1}$ , Figure 8b). Taking into account the anharmonicity of the molecule and the thermal Boltzmann distribution, transient IR spectra and temporal evolutions of absorbance change at a selected wavelength obtained by pump-probe experiments were simulated as a function of temperature. In the modeling, the intramolecular temperature was estimated to be 960, 720, and 320 K for 1, 10, and 70 ps, respectively.<sup>25</sup> The time scale of cooling through intermolecular energy transfer to the surrounding solvent is approximately 20 ps. The cooling process should be observed also in the *trans*-*cis* photoisomerization of azobenzene.

## B. Bond Cleavage of Spiropyran and Spirooxazine Derivatives

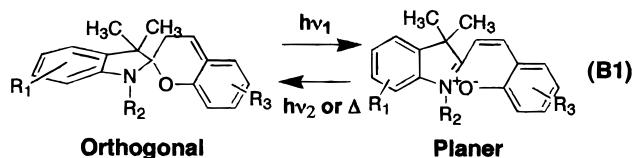
Spiro-pyrans belong to a class of photochromic compounds that have been intensively studied<sup>35</sup> since the pioneering work by Fisher and Hirshberg in 1952.<sup>36,37</sup> Upon ultraviolet irradiation, the bond between the spiro carbon and oxygen undergoes fission,





**Figure 8.** (a) Transient difference spectra of *cis*-azobenzene measured at 1, 10, and 70 ps after excitation at 435 nm ( $n-\pi^*$  ( $S_1$ ) state excitation). The respective spectra were simulated with a model calculation with a thermal energy distribution and an exponential temperature decrease from 100 to 300 K.<sup>25</sup> The spectra were simulated at 960 K (1 ps), 720 K (10 ps), and 320 K (70 ps). (b) The spectrum at 70 ps is comparable with the steady-state difference spectrum between *cis*- and *trans*-azobenzene. (c) Simulation of the temporal evolution at 1456  $\text{cm}^{-1}$ , corresponding to the formation of *trans*-azobenzene ( $\nu_{19b}$  band).<sup>25</sup> The thermal Boltzmann distribution and the contribution of anharmonicity induce the spectral shift in the difference spectrum and thus the nonexponential behavior of the absorption change at a selective vibrational frequency. (Reprinted with permission from ref 25. Copyright 1997 American Institute of Physics.)

thus facilitating the structural change needed to form merocyanines. Most of merocyanines are thermally unstable, leading to the back reaction to the spiro form even in the dark.



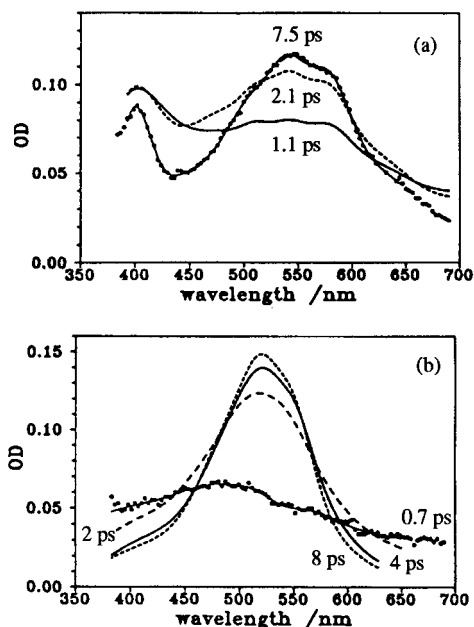
Merocyanines have a characteristic absorption band in the visible wavelength region due to the extended conjugation of the  $\pi$ -electron system as compared to that of the spiro form with an orthogonal geometry. Thus, the large amount of light-induced absorption change makes it easy to analyze the primary photochromic processes by time-resolved laser spectroscopy. 1',3',3'-Trimethylspiro-[2*H*-1-benzopyran-2,2'-indoline] (BIPS) and its derivatives have been extensively studied by nanosecond–femtosecond laser spectroscopy to elucidate the complex photo-

chromic reactions.<sup>28,38–55</sup> The nitro substitution on the benzopyran ring of BIPS (6-nitro-BIPS) was also found to increase the quantum yield of photocoloration and the thermal stability of merocyanine at the cost of photochemical stability.<sup>35</sup> On the other hand, spirooxazines, related compounds of spiroopyrans, are well characterized by their high degree of tolerance to photolysis in comparison to their spiroopyran counterparts, showing almost no signs of degradation after hundreds of photochromic cycles.<sup>56,57</sup>

The C–O bond cleavage between the spiro carbon and oxygen, believed to occur in the picosecond to subpicosecond time region, is assumed to lead to the formation of a primary photoproduct, called X, with an orthogonal parent geometry, followed by a geometrical change to the planar merocyanine forms. In 1982, Krysanov and Alfimov were the first to examine the photochromism of the 6-nitro-BIPS derivative by picosecond transient absorption spectroscopy using a mode-locked Nd:phosphate glass laser (8 ps fwhm).<sup>39</sup> They proposed that in the ring-opening reaction the planar colored merocyanine form is formed in less than 10 ps, which competes with the ultrafast intersystem crossing to the triplet state followed by the formation of nonplanar *cis*-cisoid intermediate X with an absorption maximum at  $\sim 440$  nm. This rationalization is based on nanosecond spectroscopic data that show the existence of a long-lived primary photoproduct X at  $\sim 450$  nm,<sup>40</sup> fluorescence quenching of 6-nitro-BIPS, and a singlet and triplet energy level diagram ( $S_1$  ( $\pi-\pi^*$ ) >  $T_1$  ( $n-\pi^*$ )). In the back reaction from merocyanine to spiroopyran, an intermediate X was not observed in contrast to the previous work.<sup>40</sup>

The participation of the triplet pathway in the photochromic reaction of the 6-nitro-BIPS derivatives was shown by triplet sensitization<sup>41</sup> and transient absorption spectroscopy.<sup>42,43,45,48</sup> According to Lenoble and Becker, the triplet excited state of spiroopyran for 6-nitro-BIPS ( $^3A^*$ ) leads to the nonplanar *cis*-cisoid intermediate X in its triplet excited state ( $^3X^*$ ) in 10 ns.  $^3A^*$  is also shown to go directly to the transoid merocyanine (B) on a time scale of 10 ns, while only  $^3X^*$  forms aggregates with B. As indicated previously, the typical merocyanine absorption band at 540 nm for 6-nitro-BIPS is observed on a time scale of 10 ps after excitation.<sup>39</sup> The formation time of merocyanine for 6-nitro-BIPS was estimated to be  $\sim 20$  ps in *n*-pentane by femtosecond transient absorption spectroscopy.<sup>28</sup> These data suggest that for nitro-substituted spiroopyrans, merocyanines are formed both from singlet and triplet manifolds.

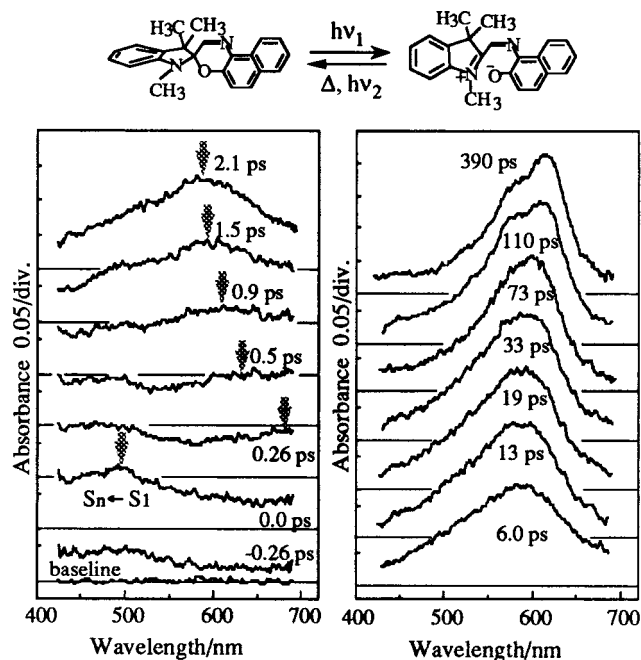
In contrast to the nitro-substituted spiroopyran derivatives, indolinospiroopyrans without nitro substitution show photochromism only in the excited singlet manifold, which was confirmed by analyzing the oxygen effect on transient absorption.<sup>44</sup> This is very similar to spirooxazines, in which the absence of any oxygen effects on the formation and the decay rates of merocyanine have been reported together with the lack of any transient species in the triplet state.<sup>58,59</sup> It is also reported that well purified and freshly prepared spirooxazines are nonfluorescent. The formation of merocyanine occurs entirely from the excited singlet state of spirooxazine, and its lifetime is expected to be extremely short in the course of the photochromic reaction.



**Figure 9.** Transient absorption spectra of BIPS (a) and naphtho-BIPS (b) in *n*-pentane at 22 °C. The delay times after excitation are given in the figure. (Reprinted with permission from ref 28. Copyright 1991 American Chemical Society.)

In 1987, the dynamics of the photochromic reactions of a spirooxazine derivative were examined by Schneider et al.<sup>60,61</sup> using pump-probe experiments with a 5 ps pulse duration at a fixed detection wavelength. They concluded that the hypothetical nonplanar photoproduct X was formed promptly (shorter than 2 ps) followed by the reaction to yield the planar form. They reported that the latter reaction occurs on the 2–12 ps time scale depending on the solvent. Ernsting et al. have studied the primary photochromic processes of BIPS and naphtho-BIPS by femtosecond transient absorption spectroscopy (260 fs at ~308 nm).<sup>28,51,52</sup>

Figure 9 shows the representative transient absorption spectra of BIPS and naphtho-BIPS in *n*-pentane.<sup>28</sup> In the initial time region, the spectrum covers the entire visible wavelength range, with an unpronounced maximum at ~400 nm. Further increase of the delay time shows the rise of absorption typical for the merocyanine products. Rise times of merocyanine absorption bands were faster than that of 6-nitro-BIPS and estimated to be ~0.9 ps for BIPS and ~1.4 ps for naphtho-BIPS. The spectra at respective delay times were fitted by a sum of Gaussian functions using the positions of bands obtained from the microsecond spectrum. The spectrum at ~40 ps delay time and later are similar to the spectrum recorded in the microsecond time range, although the initial spectra are widely spread. This broadening is due to the formation of ground-state merocyanine isomers with a high internal vibrational temperature, in which most of the excitation photon energy is converted into thermal energy by C–O bond cleavage. The internal temperature is estimated to be 940 K,<sup>28</sup> which may result in the distribution of merocyanine isomers. The vibrational energy is then transferred to the translational energy to the surrounding medium on a time scale on the order of 10 ps.

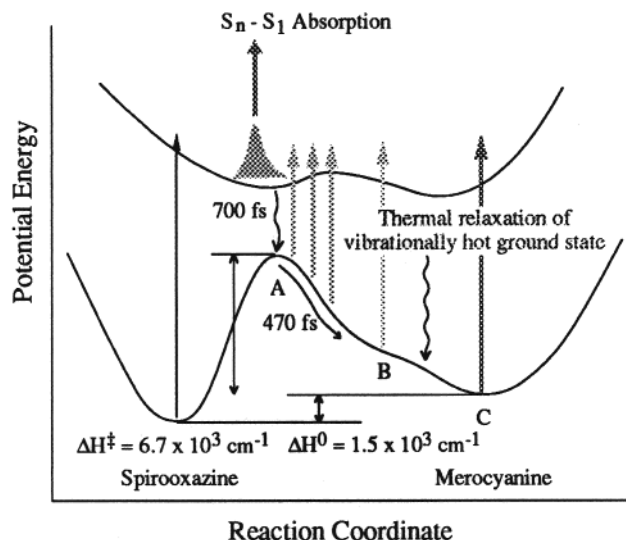


**Figure 10.** Transient absorption spectra of spirooxazine in 1-butanol excited at ~360 nm. Initially, the spectrum with a peak at ~590 nm obtained at a few picoseconds delay time, corresponding to merocyanine absorption, is very broad. This spectrum becomes sharp with time up to a few tens of picoseconds. The process is due to the vibrational energy transfer from the vibrationally hot merocyanine in the ground state to the surrounding medium.

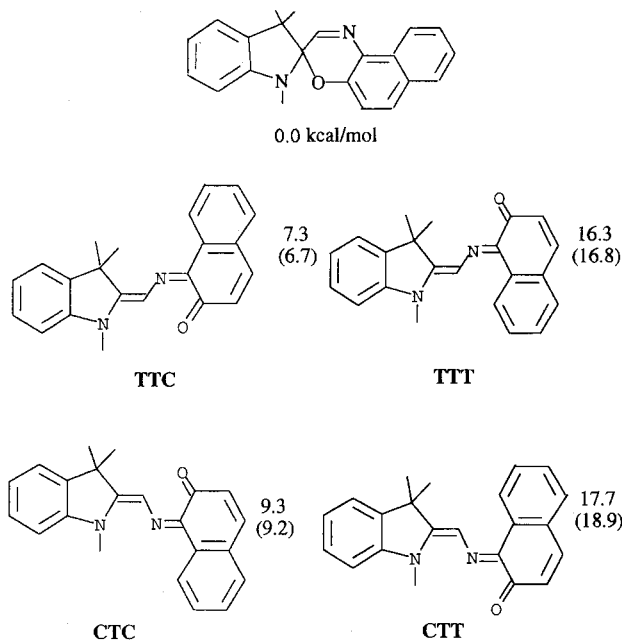
However, evidence for the existence and spectral properties of the primary photoproduct X are not so clear even in the experiments given above. Tamai and Masuhara examined the femtosecond dynamics of C–O bond cleavage of a spirooxazine, 3',3'-dimethyl-1'-methylspiro [2*H*-naphtho [1,2-*e*]-1,4-oxazine-2,2'-indoline], by transient absorption spectroscopy.<sup>27</sup> Figure 10 illustrates the transient absorption spectra of spirooxazine in 1-butanol. The spectrum with a peak at around 490 nm appears just after the excitation, which can be assigned to the  $S_n \leftarrow S_1$  absorption of the oxazine chromophore because of the spectral similarity with phenanthrene and its derivatives. As time progresses, a broad absorption band from 550 to 700 nm is formed and the peak of this broad band appears to be blue-shifted by more than 3000  $\text{cm}^{-1}$ . This broad spectrum was assigned to be due to the nonplanar primary photoproduct X. After 2 ps, the spectrum has a peak at ~580 nm corresponding to that of merocyanine in nonpolar solvents such as cyclohexane (578 nm).<sup>59</sup> Further spectral shift and spectral narrowing to the relaxed form of merocyanine can be seen after few hundreds of picoseconds. From the analysis of rise and decay dynamics, the rate constants of C–O bond cleavage and relaxation from the transition state to a metastable merocyanine were estimated to be approximately 700 and 470  $\text{fs}^{-1}$ , respectively.

A schematic potential energy curve for the spirooxazine photochromic reaction is illustrated in Figure 11. The standard enthalpy  $\Delta H^\ddagger$  and the activation enthalpy  $\Delta H^\ddagger$  in the ground state are also given in the figure.<sup>58</sup> The C–O bond cleavage followed by the formation of metastable (B) to the stable merocyanine





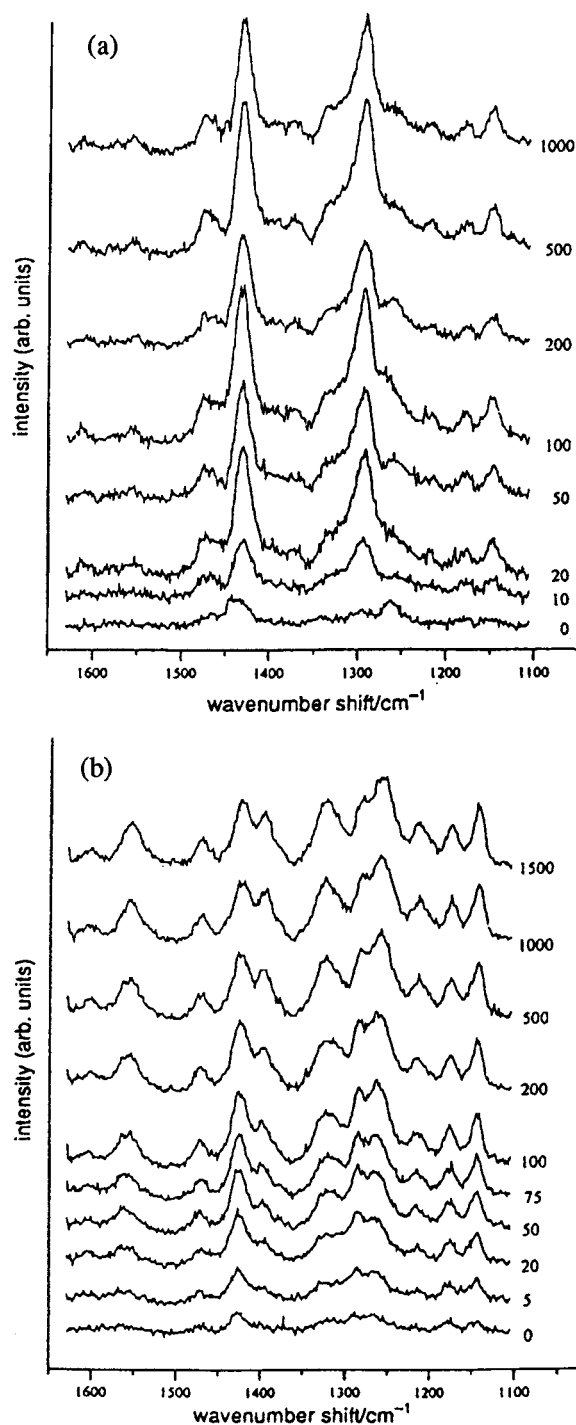
**Figure 11.** Schematic potential energy curve of photochromic reaction in spirooxazine.  $\Delta H^\ddagger$  and  $\Delta H^0$  of the photochromic reaction in the ground state are also given in the figure.



**Figure 12.** Thermodynamic relative stabilities of spirooxazines. Various configurations of merocyanines are given with the relative energies of heat of formation.<sup>62</sup>

(C) is well characterized by the spectral shape of the transient absorption. The formation of vibrationally hot merocyanines is also indicated as a spectral broadening of merocyanine absorption on a time scale of a few picoseconds after excitation.

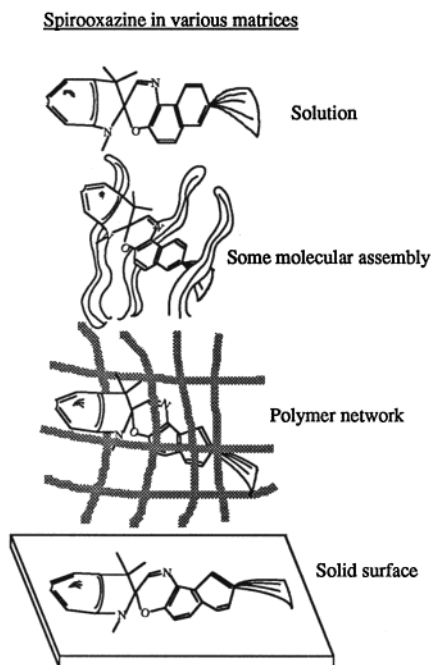
Since a number of isomers exist for merocyanines, it is very important to know what structure is the most stable conformation. Molecular orbital calculation and NMR–NOE experiments have been done to estimate the most stable structure of spirooxazine.<sup>62</sup> The TTC structure was found to be the most stable conformation of spirooxazine as illustrated in Figure 12.<sup>62</sup> Time-resolved Raman spectroscopy measurements were performed to obtain information on the structure of merocyanines.<sup>49,50,63,64</sup> Takahashi et al. examined BIPS photochromism using nanosecond time-resolved resonance Raman spectroscopy and



**Figure 13.** (a) Picosecond time-resolved resonance Raman (PTR<sup>3</sup>) spectra of a spirooxazine derivative, NOSI-2, in cyclohexane. (b) PTR<sup>3</sup> spectra of NOSI-2 in 1-butanol. Delay times are given in the figure. (Reprinted with permission from ref 64. Copyright 1993 Royal Society of Chemistry.)

concluded that the transient species involved the polar TTC configuration in aliphatic hydrocarbons, while in polar solvents, CTT and CTC configurations with larger dipole moments were more stable than TTC.<sup>49,50</sup>

The dynamics of the photochemical formation of merocyanines of spironaphthooxazine derivatives were examined in various solvents by picosecond time-resolved resonance Raman (PTR<sup>3</sup>) and picosecond transient absorption techniques.<sup>64</sup> The primary



**Figure 14.** Schematic illustration of the effect of matrixes, such as solution, some molecular assembly, polymer network, and solid surface, on photochromic reactions of spirooxazines. (Reprinted with permission from ref 66. Copyright 1993 Bunshin Shuppan.)

photochemical step occurs on a subpicosecond time scale followed by the formation of a cisoid intermediate over the next 6–30 ps. The rate of isomerization from cisoid to transoid isomers depends on both solvent viscosity and polarity. As illustrated in Figure 13, PTR<sup>3</sup> spectra of the spironaphthooxazine derivative in cyclohexane and 1-butanol are very different in the temporal evolution of spectral shape.<sup>64</sup> From the analysis of PTR<sup>3</sup> spectra it was found that in 1-butanol there are at least three different transient species to give the final isomeric distribution over the first few nanoseconds, whereas a single species is detected in cyclohexane after the first 200 ps of the reaction. The presence of various merocyanine intermediates derived from spironaphthooxazines was also examined by picosecond fluorescence spectroscopy.<sup>65</sup> The decay curves of merocyanines were expressed with a sum of two or three exponential decay functions with  $\tau_1 = 10\text{--}60$  ps,  $\tau_2 = 0.5\text{--}1$  ns, and  $\tau_3 = 1\text{--}2$  ns, which were ascribed to the different fluorescing merocyanine isomers.

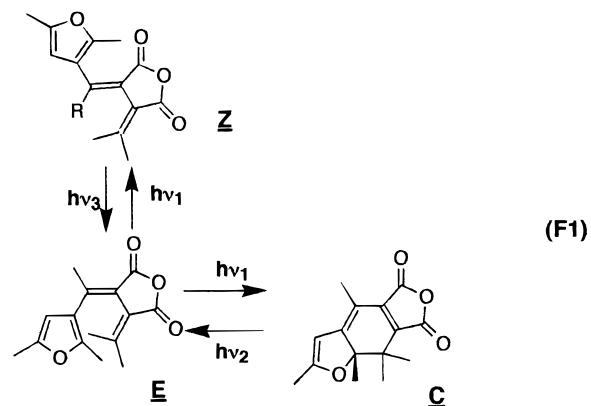
Finally, the effect of surrounding matrixes on the photochromism of spiropyran will be summarized. This has been extensively studied and is well reviewed in ref 66. In the polymer matrix, Horie et al. examined the photochromic reaction of 6-nitro-BIPS and decoloration of merocyanine in polycarbonate film by transient absorption spectroscopy.<sup>46</sup> They found that the formation of merocyanine proceeds within several nanoseconds and even at temperatures below the  $\gamma$ -transition temperature corresponding to the onset of phenyl ring rotation of polycarbonate film, which indicates the importance of free volume in the matrix polymer. Figure 14 is an illustration characterizing the effect of matrixes on photochromic reactions of spirooxazines.<sup>66</sup> On solid surfaces, polymer networks, or very viscous environ-

ments, photochromic reactions of spiropyran to form merocyanines following structural change from cisoid-open forms to stable transoid forms are rather difficult, although the initial C–O bond cleavage may occur even in the unfavorable environments. The most suitable environment for photochromic reactions is a solution phase or some matrix with a large free volume. For ultrafast photochromic switching by using spiropyran, the following are important: design of a matrix to have enough free volume and the reaction to occur only in the singlet manifold.

### C. Electrochemical Reactions of Fulgides

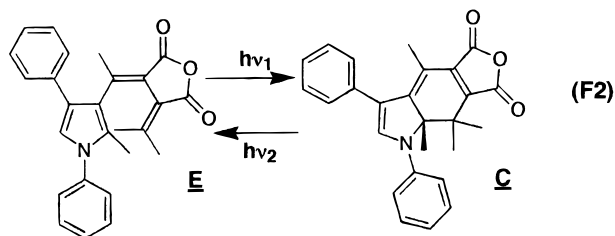
The photochemical reaction of phenyl-substituted bismethylene succinic anhydrides was discovered by Stobbe almost 100 years ago.<sup>67</sup> Santagio and Becker presented persuasive evidence that this photochemical reaction arose from the formation of intramolecular rearrangement of chemical bonds.<sup>68</sup>

Since Heller and co-workers reported 2-[1-(2,5-dimethyl-3-furyl) ethylidene]-3-isopropylidenesuccinic anhydride (**F1**) as a thermally irreversible photochromic compound,<sup>69</sup> a number of fulgides have been synthesized. Although both of the isomers are thermally stable in **F1**, the undesirable *E*–*Z* isomerization, which reduces the *E*–*C* reaction (photocyclization leading to the coloration) yield, takes place as a competitive reaction.

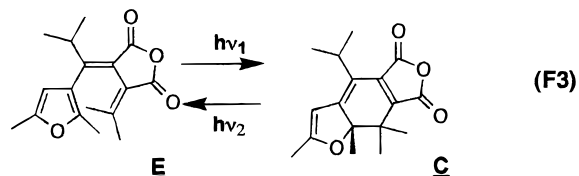


Lenoble and Becker applied nanosecond laser spectroscopy for several fulgides and found that the photochemical conversion occurs within their time resolution (1 ns).<sup>70</sup> Ilge et al. reported that the photoisomerization about the ethylenic bonds of 2,3-bis(4-alkoxybenzylidene)succinic anhydride occurs within 5 ps.<sup>71</sup> They also reported that production of the closed form of 2-(phenylbenzylidene)-3-isopropylidenesuccinic anhydride takes place within 6 ps in toluene solution.<sup>72</sup>

Yu et al. applied nanosecond laser spectroscopy at 248 nm for the *E*-( $\alpha$ )-(1,4-diphenyl-2-methyl-3-pyrrolyl)ethylidene (isopropylidene) succinic anhydride (**F2**) in cyclohexane and acetonitrile.<sup>73</sup> In addition to the rapid appearance of the closed form within the time resolution of their apparatus (ca. 20 ns), it was observed that the triplet state of the open form of **F2** decays in the microsecond region together with the increase in the absorption of the closed form. They concluded that the ring-cyclization reaction occurs both in the singlet and triplet states.



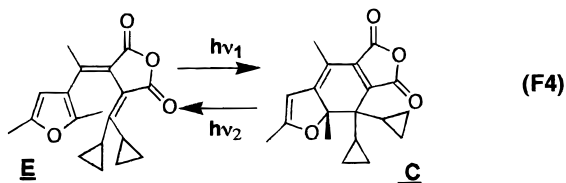
Kurita et al. applied picosecond transient absorption spectroscopy for the photocyclization reaction of 2-[1-(2,5-dimethyl-3-furyl)-2-methylpropylidene]-3-isopropylidenesuccinic anhydride (**F3**) in polymer matrixes.<sup>74</sup> Introduction of the isopropyl group pre-



vents the *E*-*Z* isomerization reaction in this compound. The open form (**E**) has almost no absorption in the visible region, while the closed form (**C**) has an absorption maximum at 500 nm.

They measured the transient absorption spectra of the open form of **F3** in PMMA, polystyrene, nitrocellulose polymer matrixes following the picosecond (22 ps fwhm) 355 nm laser excitation. They found the rapid appearance of the closed form in the transient absorption after the excitation. From the deconvolution analyses of the rapid growth of the closed form, the time constant of 10 ps was obtained for the ring-closing reaction in these three matrixes. By taking into account the difficulty of discrimination of similar relaxation processes such as vibrational cooling, small geometrical changes in polymer matrixes, and the intrinsic reaction of the closed form formation, they concluded that the ring-closing reaction took place very rapidly (<10 ps) even in the rigid polymer matrixes.

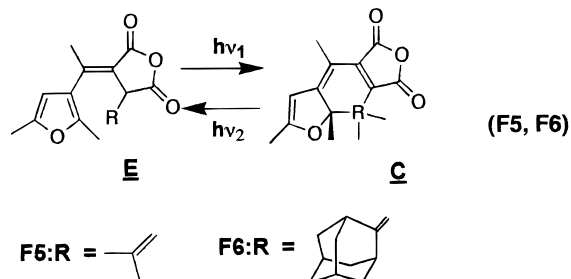
By the direct detection of the change of the refractive index arising from the ring-closing reaction of a fulgide (**F4**), the reaction rate constant was estimated by Martin et al.<sup>75</sup> They employed picosecond 340 nm



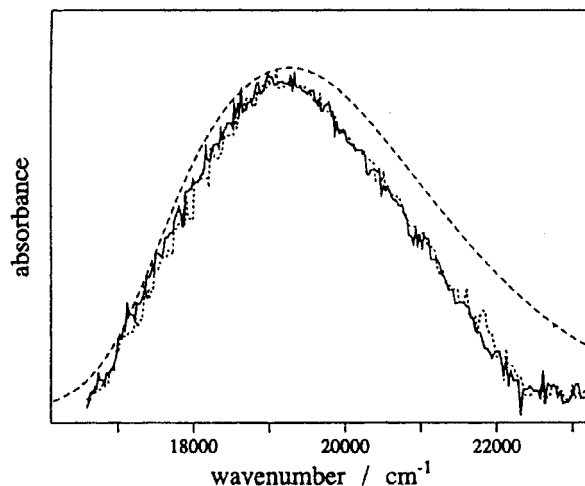
laser pulses with a 6 ps fwhm to create a grating in the sample through simultaneous excitation of the sample by the two laser pulses with an angle  $\theta$ , which induces interference of the light and leads to the grating-like creation of the closed form. The probe light at 680 nm was guided into the exposed position of the sample with a Bragg angle, and diffracted light intensity was detected as a function of time after the excitation. Although the closed and open forms do not have an absorption at 680 nm, the refractive index change arising from the production of the closed form

contributes to the diffraction of light. By using this technique, they obtained a 40 ps time constant for the ring-closing reaction of **F4** both in PMMA matrix and in toluene solution.

Handschuh et al. studied the dynamics of furyl fulgides (**F5** and **F6**) by applying femtosecond time-resolved spectroscopy.<sup>76</sup> They employed 392 nm-

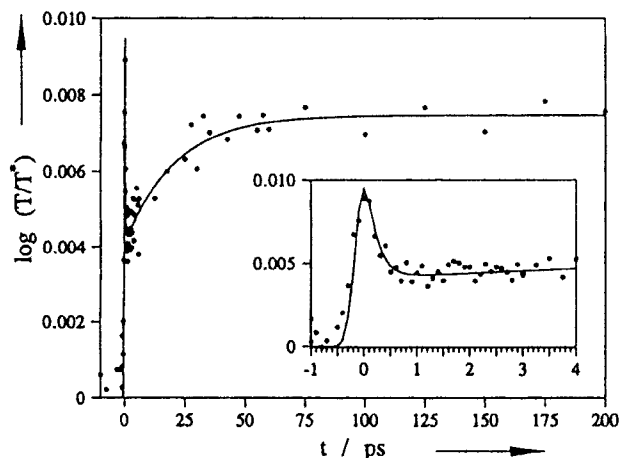


femtosecond laser pulses for the excitation of E forms of **F5** and **F6** in toluene and acetonitrile. For the detection of the dynamics, the time evolution of transient absorption spectra was monitored. They observed rapid decay of the transient absorption with a time constant <1 ps following excitation with a 200 fs laser pulse and the appearance of the C form absorption after this rapid decay as shown in Figures 15 and 16. The increase of the C form absorption continued in the several tens of picosecond time region and reached a plateau value. On the basis of these experimental results, they concluded that the ring-closing reaction has two channels: a very rapid one taking place within 1 ps and a rather slow one in the several tens of picoseconds region. They proposed that the rapid reaction channel competes with the recovery of the ground state and the production of the intermediate state, which undergoes the ring-closing reaction in the several tens of picoseconds time region. The contribution of the rapid reaction channel to the total production of the C form was almost 50% for both compounds in both solutions.



**Figure 15.** Absorption spectra of **F6**, 1.5 ps (solid line) and 900 ps (dotted line), after pulse excitation of **F6E** and cw absorption of **F6C** (broken line) in toluene (295 K).



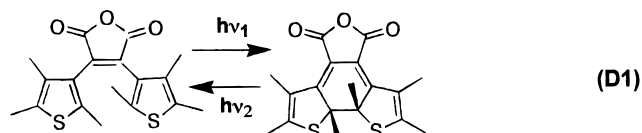


**Figure 16.** Time evolution of the transient absorption at  $\nu = 19\,200\text{ cm}^{-1}$  after pulse excitation of **F6E** in toluene (295 K): experimental data (closed circle) and fitted model curve (solid line). Notice stretched abscissa insert. (Reprinted with permission from ref 76. Copyright 1997 American Chemical Society.)

#### D. Electrocyclic Reactions of Diarylethene Derivatives

Diarylethenes with heterocyclic rings have been developed as new types of thermally irreversible and fatigue-resistant photochromic compounds by Irie and co-workers.<sup>2,77</sup> Some of these compounds have no thermochromicity even at 300 °C, the colored forms are stable for more than three months at 80 °C, and the cyclization and ring-opening cycles can be repeated more than  $10^4$  times while keeping adequate photochromic functions.<sup>2,78</sup> In addition to these excellent properties, it has been found recently that several diarylethenes undergo photochromic reaction even in the crystalline phase.<sup>78,79</sup>

Picosecond transient absorption spectroscopy was applied to the direct elucidation of photochromic reactions of 1,2-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**D1**) in the solution phase.<sup>80</sup> The absorp-



tion maximum of the closed form is at ca. 560 nm, while the open form has an absorption band in the wavelength region <450 nm. The ring-closing reaction was investigated by picosecond transient absorption spectroscopy with a 355 nm laser pulse with a 22 ps fwhm. From the analysis of the time evolution of the spectra following the excitation of the open form of **D1** in *n*-hexane solution, a very rapid ( $\leq 8$  ps) reaction channel was found in the ring-closing reaction. This time constant was much faster than the fluorescence lifetime of the open form of **D1** in *n*-hexane solution (350 ps). The above result indicates that the ring closure can take place in the relaxation processes to the relaxed fluorescent state from the excited Franck-Condon state, in addition to the reaction in the fluorescent state. The former pathway was confirmed to be the major reaction pathway.

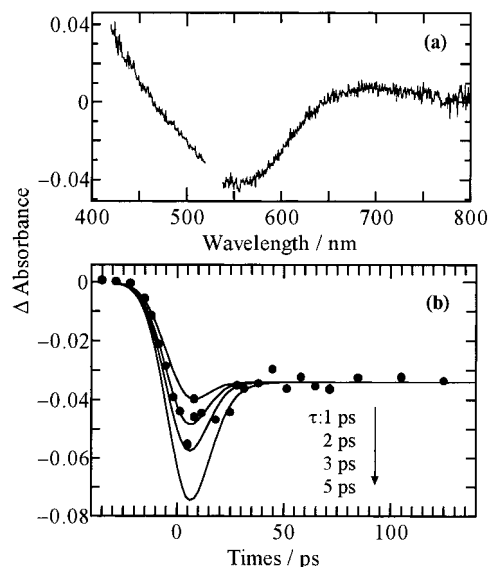
For the photochromic reaction of **D1** and its analogues, it was confirmed that the photocyclization yields decreased with an increase of the solvent polarity.<sup>81</sup> The fluorescence properties of the open form in various solvents strongly suggested that two conformations exist in the excited state: a planar conformation and another one in which the thiophene rings deviate from the planar conformation relative to the maleic anhydride moiety. The state energies of these two conformations are dependent on the solvent polarity. From the above relation between the reaction yield of the ring closure and the fluorescent properties, it was suggested that the twisted conformation with the intramolecular CT character was stabilized with the increase in the solvent polarity, which led to the decreased chance for the cyclization.<sup>81</sup> Actually, direct detection of the ring-closing reaction in THF solution of **D1** revealed a smaller intensity of the closed form absorption in the transient absorbance in several nanoseconds time regions. In addition, the appearance of the absorption signal around 560 nm (the closed form) in the few tens of picoseconds time region is also much smaller than that in *n*-hexane.<sup>80</sup> This result indicated that not only the reactions in the fluorescent state but also the reaction during the relaxation to the fluorescent state are solvent-dependent.

In relation to the mechanisms of this ultrafast photocyclization reaction, it should be noted here that Petek and co-workers reported ultrafast photochemical reactions of *cis*-stilbene in solutions as well as in inert gas clusters.<sup>82-84</sup> On the basis of the experimental results by direct measurements of reaction dynamics and those of precise laser spectroscopies of the related compounds, they proposed that the  $S_1$  state of *cis*-stilbene immediately after the excitation (the wave packet) undergoes the cyclization reaction to yield dihydrophenanthrene, in competition with the relaxation to the configuration from which it decays nonradiatively to *cis*- and *trans*-stilbenes.

Along with their investigations, the experimental results on the ring closure of **D1** were interpreted in the following manner. Since the Stokes shift between the absorption and fluorescence of the open form of **D1** is rather large and solvent dependent, some conformational rearrangement seems to be responsible for the relaxation process in the  $S_1$  potential surface to produce the fluorescent state which has a large dipole moment. During this relaxation process in the  $S_1$  state, some of the **D1** may undergo the cyclization reaction and others relax to the fluorescent state. The reorientation of the surrounding polar solvent stabilizes the  $S_1$  state rather strongly and makes it difficult for the fluorescent state to be activated to the reactive state to undergo the ring closure.

The picosecond transient absorption spectroscopy was applied also to the ring-opening reaction of **D1** in solutions.<sup>80</sup>

Figure 17a shows the time-resolved transient absorption spectrum of the closed form of **D1** in benzene solution observed 20 ps after the excitation with a picosecond 532 nm laser pulse with a 15 ps fwhm.



**Figure 17.** (a) Transient absorption spectrum of the closed form of **D1** in benzene solution, observed 20 ps after the excitation with a picosecond 532 nm laser pulse. (b) Time profile of transient absorbance at 550 nm. Solid lines are calculated curves by taking into account the pulse widths of the exciting and the monitoring lights and the quantum yield of the ring-opening reaction.

The negative absorption was assigned to the bleaching of the closed form. The time profile of the absorption signal at 550 nm is shown in Figure 17b, indicating that the slight recovery of the bleaching of the closed form immediately after the excitation is followed by the constant value. In the time region at and after ca. 40 ps from the excitation, no evolution of the spectra was observed. The residual absorption spectra are almost identical with the difference spectrum between the closed and the open forms. The solid lines in this figure are the calculated curves by taking into account the pulse durations of the exciting and monitoring pulses and the quantum yield of the ring-opening reaction. The time constants for the recovery of the negative absorption are indicated in the figure. The calculated curves with time constants of 2–3 ps reproduce the experimental results, indicating that the ring-opening reaction took place with a time constant of <2–3 ps. Similar time profiles and ultrafast reactions with a time constant of <2–3 ps were also observed in *n*-hexane and THF solutions.<sup>80</sup>

Recently, it was found that some of diarylethenes undergo ring-closing and ring-opening reactions even in the crystalline phase.<sup>78,79</sup> To one of the special classes of these diarylethenes, **D2**, picosecond transient absorption spectroscopy was applied.<sup>85</sup>

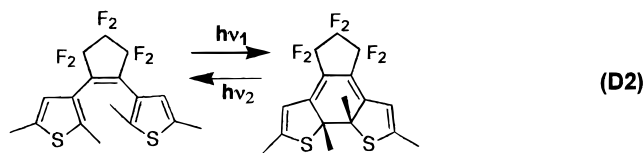
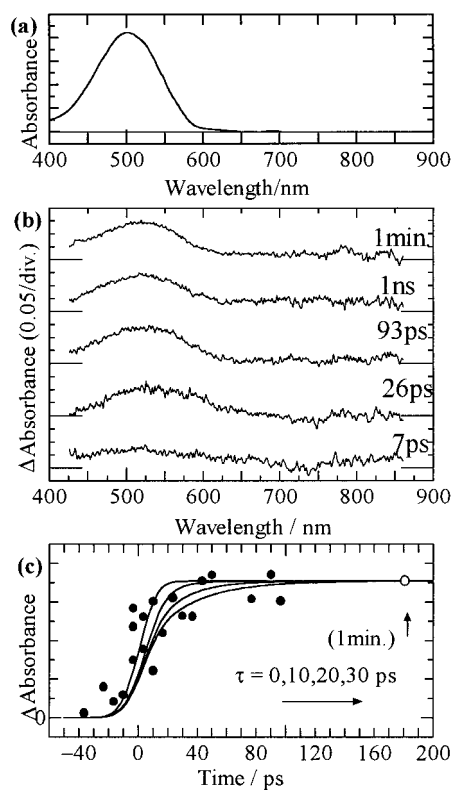


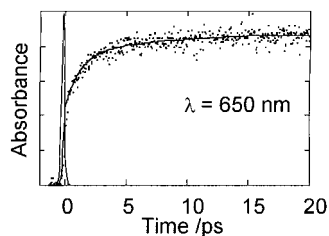
Figure 18a shows a steady-state absorption spectrum of **D2** in cyclohexane solution after irradiation with UV light. Since the open form of DMTF has no absorption in the visible region, the absorption with a maximum at 505 nm is due to the closed form of



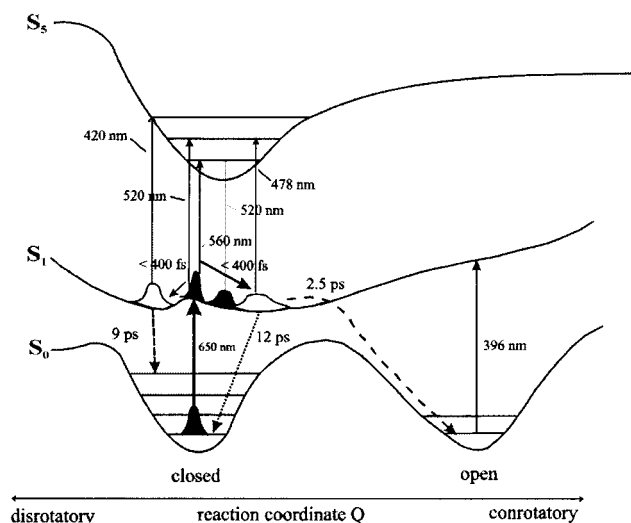
**Figure 18.** (a) Steady-state absorption spectrum of the closed form of **D2** in cyclohexane solution. (b) Time-resolved transient absorption spectra of the microcrystalline phase of open form **D2**, excited with a picosecond 355 nm laser pulse. (c) Time profile of the transient absorbance of the microcrystalline phase of the open form of **D2**, excited with a picosecond 355 nm laser pulse and monitored at 505 nm. Solid lines were convolution curves calculated on the basis of the pulse widths of pump and probe lights and the time constants.

**D2.** The formation time of the ring-closing reaction of **D2** in cyclohexane solution was estimated to be <10 ps by analysis of the time profile of the transient absorbance at 505 nm of **D2** excited with a picosecond 355 nm laser pulse with a 15 ps pulse width.<sup>85</sup>

The dynamic behaviors in the crystalline phase were also investigated by picosecond transient absorption spectroscopy.<sup>85</sup> To avoid integration of the closed form on the solid-state sample, the irradiation was performed only once for a certain position of microcrystal samples and the position was changed after every exposure. The transient absorption spectra following excitation of the open form by a 355 nm laser pulse with a 15 ps pulse width (Figure 18b) show the rapid appearance of the closed form immediately after the excitation. In Figure 18c, the time profile of the transient absorbance at 505 nm is exhibited. Although it was rather difficult to obtain a high S/N ratio in the time profile owing to the limitation in the exposure condition, it is clearly indicated that the ring-closing reaction takes place within ~10 ps. From these experimental results, no appreciable difference in the ring-closure response time was observed between solution and crystalline phases. These results indicate that the cyclization is a downhill process, and the steep slope of the reaction surface<sup>86</sup> from the excited open-ring state to the closed-ring ground state enables the reaction to



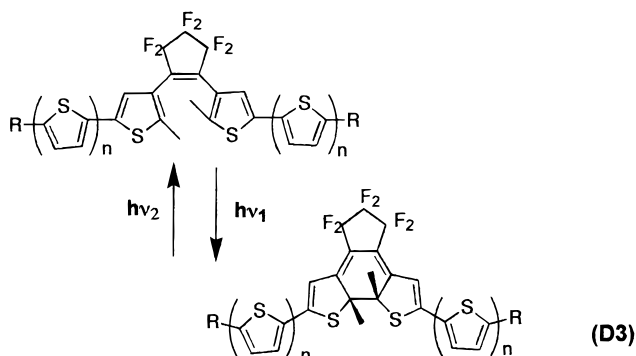
**Figure 19.** Time profile of the transient absorbance at 650 nm of **D3**, excited with a 200 fs 360 nm laser pulse.



**Figure 20.** Schematic illustration of the  $S_0$ ,  $S_1$ , and  $S_5$  potential energy surfaces along the reaction coordinate and description of the initial vibrational relaxation dynamics, photophysical decay processes, and the ring-opening reaction kinetics. (Reprinted with permission from ref 89. Copyright 1998 Elsevier.)

proceed even in the crystalline phase as well as in high viscous solutions.

Combination of a diarylethene structure with photoconductive groups has a potential application as a molecular switch. **D3** is one of the molecules having this function. The ring-closing reaction turns on the

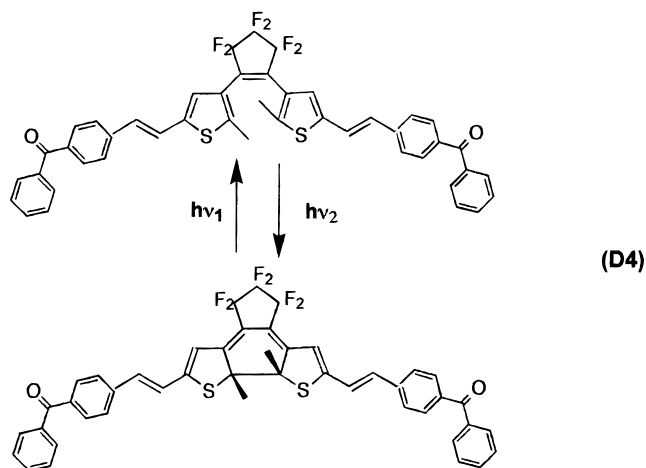


conduction between two thiophene oligomers, and the ring opening turns it off. Femtosecond laser spectroscopy was conducted for **D3** with  $n = 1$  in the solution phase by employing a 360 nm, 200 fs laser pulse.<sup>87</sup>

The closed form of **D3** has an absorption maximum around 620 nm, while the open form has no absorption in the region  $> 400$  nm. From the time profile of the transient absorbance at 650 nm (Figure 19), it

was revealed that the closed form appears in the several picosecond time region. Analysis of the transient absorption spectra and their time evolution leads to the conclusion that some intermediate species are formed within 100 fs, followed by closed form formation with the time constant of  $\sim 1.1$  ps.

Ern et al. applied femtosecond time-resolved transient absorption spectroscopy for the direct elucidation of the ring-opening process of benzoyl-phenylthienyl-substituted 1,2-bis[2-methyl-thien-3-yl]perfluorocyclopentene (**D4**) in dichloromethane solution.<sup>88</sup>



They used 120 fs laser pulses at 650 nm for the excitation of the closed form of **D4**, and a white light continuum for the monitoring light was employed for the detection of transient absorption spectra. By analyzing the time evolution of the spectra, they proposed that the closed form of **D4** relaxes to a conrotatorily or a disrotatorily twisted equilibrium structure within 500 fs after the excitation. They also proposed that the former structure constitutes the prestate for the ring-opening state while the latter just returns to the ground state as shown in Figure 19.

From the time profiles of the transient absorbance at several wavelength points, they estimated the time constant of the ring-closing process from the conrotatorily twisted state to be 2.1 ps and the decay time of the disrotatorily twisted state to be 9 ps.

#### IV. Future Prospects

As mentioned above, it has been revealed from direct application of ultrafast laser spectroscopy that a number of photochromic reactions take place very rapidly. In addition, with an increase in the time resolution of the detection, the extremely rapid channels of the photochromic reaction prior to or comparable with the relaxation to the equilibrium excited state have been found in several systems. The time region of these ultrafast reaction processes is on the order of a few picoseconds or shorter. Although these rapid reactions occur much faster than the usual lifetime of the singlet excited states of several to tens of nanoseconds, the reaction yields are less than unity. This fact indicates that it is necessary for improvement of the photochromic properties to



control the branching of the reaction channels in the ultrafast time region immediately after the excitation. Although many papers on the investigation by means of time-resolved laser spectroscopy have been published as briefly introduced here, the number of results with subpicosecond and femtosecond resolution is not large. Ultrafast laser spectroscopy in the femtosecond time region can provide important information for the elucidation of the modes regulating this branching ratio.

In relation to this, the ring-closing reactions of some photochromic compounds have been recognized as concerted reactions based on the Woodward–Hoffmann rule. In the excited state, the reaction process has no intermediate and produces stereospecific products. Actually, the molecular structures of the products (the closed forms) have given the indication that the conrotatory reaction is the above process. On the other hand, it has recently been reported that the diradicals play an important role in a cyclobutane ring-opening reaction by the photo-induced elimination of CO from cyclobutanone and related precursors.<sup>89</sup> This result suggests that the photochromic reaction may take place via some intermediates. Direct detection with higher time resolution is expected to reveal entire reaction profiles in the photochromic reaction, and elucidation of factors regulating the rapid reaction are of importance for the construction of highly efficient photochromic molecular systems.

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