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Photochemical cyclization reaction in *cis*-tetramethoxystilbene

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Abstract

trans-3,3′,5,5′-Tetramethoxystilbene (TMST) underwent *cis–trans* isomerization on photoirradiation. However, *cis*-3,3′,5,5′-tetramethoxystilbene efficiently underwent cyclization reaction to give dihydrophenanthrene (DHP) type compounds followed by oxidation to give 2,4,5,7-tetramethoxyphenanthrene (TMP), but the isomerization to the *trans* isomer did not practically take place.

Keywords: Stilbenes; Photoisomerization; Photocyclization

1. Introduction

Photochemical *cis–trans* isomerization has been studied extensively [1–11]. On direct irradiation, *trans*-stilbene undergoes isomerization to give the *cis* isomer with the quantum yield of ca. 0.5 taking place in the excited singlet state deactivating from the perpendicular singlet excited state. *cis*-Stilbene undergoes either isomerization to the *trans* isomer or cyclization reaction to give dihydrophenanthrene (DHP) type compound in the excited singlet state with nearly equal probability [7,12].

We have recently synthesized photoresponsive stilbene dendrimers with benzylether type dendron on the *m*-position of the stilbene, where the core stilbene was derived from the 3,3′,5,5′-tetramethoxystilbene (TMST) [13,14]. As a 0th generation dendrimer, the photochemical behavior of TMST was needed.

Fischer and co-workers studied the photochemical and photophysical behavior of the *trans* isomer of 3,3′,5,5′-tetramethoxystilbene [15]. They reported that *trans*-TMST underwent *cis–trans* isomerization to give *cis*-TMST, and the resulted *cis*-TMST may undergo cyclization reaction to produce dihydrophenanthrene type compounds. However, Fischer and co-workers did not isolate the *cis* isomer as well as final product of the cyclization reaction, and therefore, the photochemical reaction of TMST proposed by Fischer is still uncertain.

As a reference, compounds of the photochemical properties of higher generation stilbene dendrimers, we are forced to prepare and isolate both *cis*- and *trans*-TMST and to study their photochemical behavior. We wish to report here the photochemical properties of pure *cis*- and *trans*-TMST and the photochemical product, 2,4,5,7-tetramethoxyphenanthrene (TMP). We have found that *cis*-TMST underwent efficient cyclization reaction, while the *trans* isomer underwent either fluorescence emission or isomerization to the *cis* isomer.

2. Experimental

2.1. Materials and solvents

3,5-Dimethoxybenzaldehyde was purchased from Tokyo Kasei Kogyo Corp. 3,5-Dimethoxybenzyltriphenylphosphonium bromide was prepared from 3,5-dimethoxybenzyl bromide and triphenylphosphine in benzene. Sodium methoxide was prepared from sodium and methanol. Dry THF, dry methanol and benzene were purchased from Wako Chemicals Corp. and used as received.

2.1.1. *cis- and trans-3,3′,5,5′-Tetramethoxystilbenes*

A solution of sodium methoxide (12.0 mmol) in methanol (50 ml) was added slowly to the mixture of 3,5-dimethoxybenzaldehyde (1.33 g, 8 mmol) and 3,5-dimethoxybenzyltriphenylphosphonium bromide (4.93 g, 10.0 mmol) in dry THF–dry methanol (70:30) under nitrogen and then the mixture was stirred for 2 h. The mixed solvent was evaporated and residue was dissolved to dichloromethane, then washed with water. Water layer was extracted with dichloromethane twice and combined organic layer was

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dried over Na_2SO_4. After filtration, dichloromethane was evaporated and residue was purified by silica-gel column chromatography eluting with hexanes and then gradually increasing portion of ethyl acetate (to hexanes–ethyl acetate, 3:1) to give both the *cis* isomer (1.35 g, 4.5 mmol, 56%) and the *trans* isomer (0.747 g, 2.49 mmol, 31%). NMR spectra of the *trans* isomer matched that reported previously [14].

2.1.2. *cis-3,3′,5,5′-Tetramethoxystilbene*

δ_H (400 MHz; $CDCl_3$; Me_4Si) 6.53 (2H, s, CH=CH), 6.44 (4H, d, *J*2.2, 2-H, 2′-H, 6-H and 6′-H), 6.32 (2H, t, *J*2.2, 4-H and 4′-H), 3.66 (12H, s, 4× MeO).

2.1.3. *2,4,5,7-Tetramethoxyphenanthrene*

Laser flash photolysis was performed to the solution of *cis*-3,3′,5,5′-tetramethoxystilbene (100 mg, 0.33 mmol) in benzene (10 ml) in quartz cell. The solution was bubbled with oxygen for 30 min (20 ml min^{-1}) before irradiation. Irradiation was stopped every 1 h, then bubbled oxygen for 30 min, and then started irradiation again. After total irradiation time reached 6 h, solution was evaporated. The residue was purified by column chromatography with eluting hexanes–ethyl acetate 3:1, followed by recrystallization from hexanes–ethyl acetate to give white crystal (Found: C, 72.37; H, 6.11. Calculated for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08%); δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.48 (2H, s, 9-H and 10-H), 6.81 (2H, d, *J*2.6, 1-H and 8-H), 6.72 (2H, d, *J*2.6, 3-H and 6-H), 3.98 (6H, s, 4-MeO and 5-MeO), 3.93 (6H, s, 2-MeO and 7-MeO).

2.2. *Measurements*

Absorption spectra were measured on a Shimazu UV-1600. Fluorescence spectra were measured on a Hitachi F-4000. Laser flash photolysis was performed by using an excimer laser (Lambda Physik LPX-100, 308 nm 20 ns FWHM) as an excitation light source and a pulsed xenon arc (Ushio UXL-159) was used as a monitoring light source. A photomultiplier (Hamamatsu R-928) and a storage oscilloscope (Iwatsu TS-8123) were used for the detection.

3. Results and discussion

3.1. *Absorption spectra*

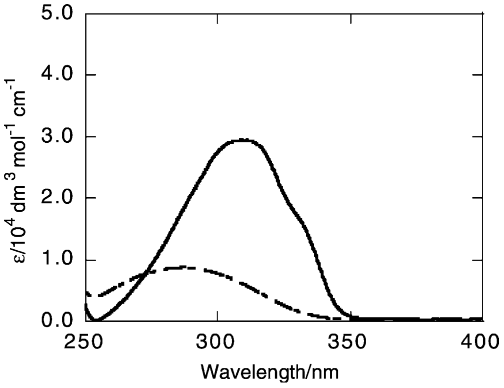


Fig. 1. Absorption spectra of *trans*-TMST (solid line) and *cis*-TMST (dot–dash line) in THF under argon atmosphere.

Fig. 1 shows the absorption spectra of *cis*- and *trans*-TMST in THF at room temperature. The absorption maximum of the *trans* isomer appears at 310 nm with molar extinction coefficient ($\varepsilon = 29500\,dm^3\,mol^{-1}\,cm^{-1}$) and that of the *cis* isomer is at 285 nm ($\varepsilon = 8700\,dm^3\,mol^{-1}\,cm^{-1}$). The *cis* isomer exhibited absorption maximum at shorter wavelength with smaller extinction coefficient than that of *trans* isomer since two aromatic rings and double bond take almost planar conformation in the *trans* isomer, whereas single bonds connecting two aromatic rings and double bond are twisted due to the steric hindrance in the *cis* isomer.

3.2. *Fluorescence spectra*

The fluorescence emission and the fluorescence excitation spectra of *trans*-TMST in THF were shown in Fig. 2. The fluorescence maximum of the *trans* isomer is observed at 380 nm. The solution of corresponding *cis* isomer also slightly emits the fluorescence (data not shown) due to trace amounts of contaminated *trans* isomer, which could not be detected by NMR spectroscopy. However, no fluorescence due to the singlet excited state of *cis*-TMST was observed. The fluorescence excitation spectrum of the *trans* isomer with fluorescence emission at 387 nm (Fig. 2) was similar to the corresponding absorption spectrum as shown in Fig. 1.

3.3. *UV irradiation of trans-TMST*

On irradiation with 310 nm light from the 150 W xenon lamp through the monochrometer in THF, *trans*-TMST

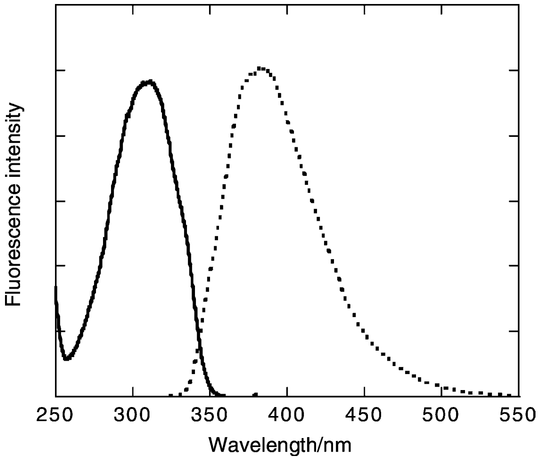


Fig. 2. Fluorescence (dotted line) and fluorescence excitation (solid line) spectra of *trans*-TMST in THF at room temperature under argon atmosphere.

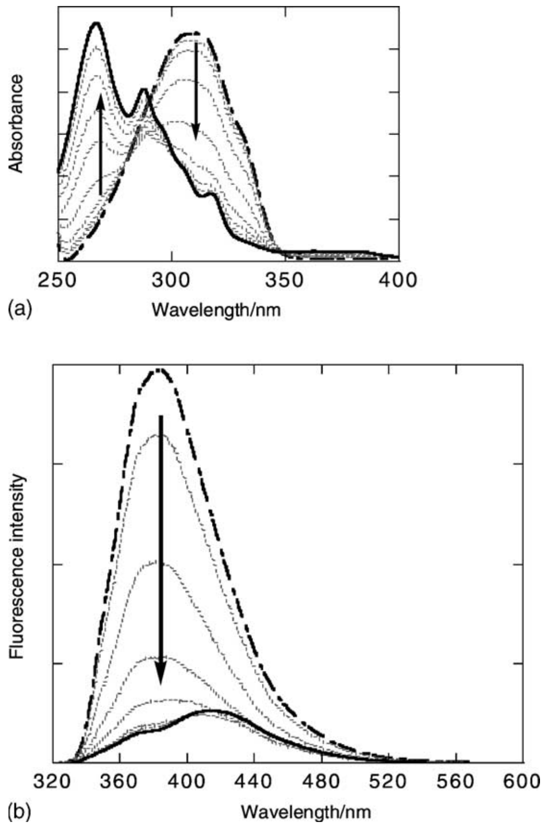


Fig. 3. (a) Change of absorption spectrum of *trans*-TMST on irradiation with 310 nm light in THF under argon atmosphere: before irradiation (dot–dash line) and after irradiation (solid line). (b) Corresponding fluorescence spectrum change of *trans*-TMST: before irradiation (dot–dash line) and after irradiation (solid line).

underwent intramolecular cyclization as well as *cis–trans* isomerization. Decrease of absorbance around 310 nm and spontaneous increase of absorbance around 260 nm in Fig. 3a suggest that major photoproduct is neither *cis*- nor *trans*-TMST but 2,4,5,7- tetramethoxyphenanthrene as a cyclization product because of the absorption spectrum. As shown in Fig. 3b, fluorescence emission at the emission maximum of 385 nm from the *trans*-TMST decreased with irradiation time and yielded new peak at the emission maximum of 415 nm due to the production of TMP. As described later, the structure of this photocyclization product TMP has been confirmed by ^{1}H NMR and elemental analysis.

3.4. *UV irradiation of cis-TMST*

As shown in Fig. 4a and b, irradiation of *cis*-TMST at 310 nm also gave the similar absorption and fluorescence spectra obtained from the irradiation of the *trans* isomer in Fig. 3a and b, which also suggests photocyclization reaction to give TMP as a major product. The time development of the photoisomerization and cyclization of *cis*-TMST was also followed by ^{1}H NMR (Fig 5a). On irradiation with 308 nm light from excimer laser under oxygen in benzene, one can actually find some *trans*-TMST in addition to the considerable increase of TMP. This result indicates efficient cyclization to give dihydrophenthrene type compounds followed by oxidation to give TMP rather than isomerization around the double bond. The reaction finally gave the TMP as a single photoproduct because photocyclization reaction is one-way via 2,4,5,7-tetramethoxydihydro-phenanthrene (TMDHP) as an intermediate, while *cis–trans* photoisomerization is reversible (Scheme 1). The time development of these three products upon irradiation was shown in Fig. 5b.

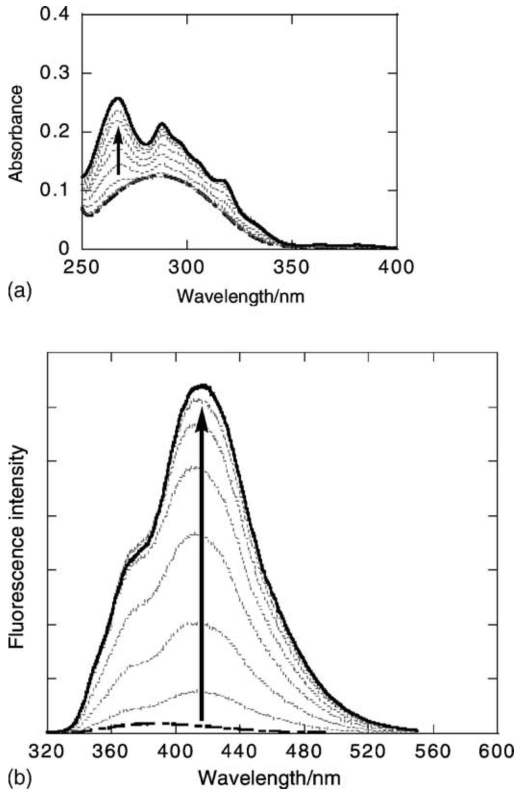


Fig. 4. (a) Change of absorption spectrum of *cis*-TMST on irradiation with 285 nm light in THF under argon atmosphere: before irradiation (dot–dash line) and after irradiation (solid line). (b) Corresponding fluorescence spectrum change of *cis*-TMST: before irradiation (dot–dash line) and after irradiation (solid line).

The UV absorption, fluorescence and fluorescence excitation spectra of pure TMP in THF were shown in Fig. 6. The fluorescence emission has been observed with fluorescence maximum at 420 nm. The fluorescence excitation spectrum is similar to the corresponding absorption spectrum.

When the same irradiation was performed under argon, the complex mixture was observed in NMR spectra as well as photocyclization product (data not shown). The complex mixture was probably produced from the dihydrophenanthrene type intermediate since oxidation of the intermediate does not take place smoothly under argon.

In parent stilbene, *trans* isomer undergoes either isomerization to give *cis* isomer with the quantum yield of 0.5 or fluorescence emission with the efficiency of 0.04, while *cis*

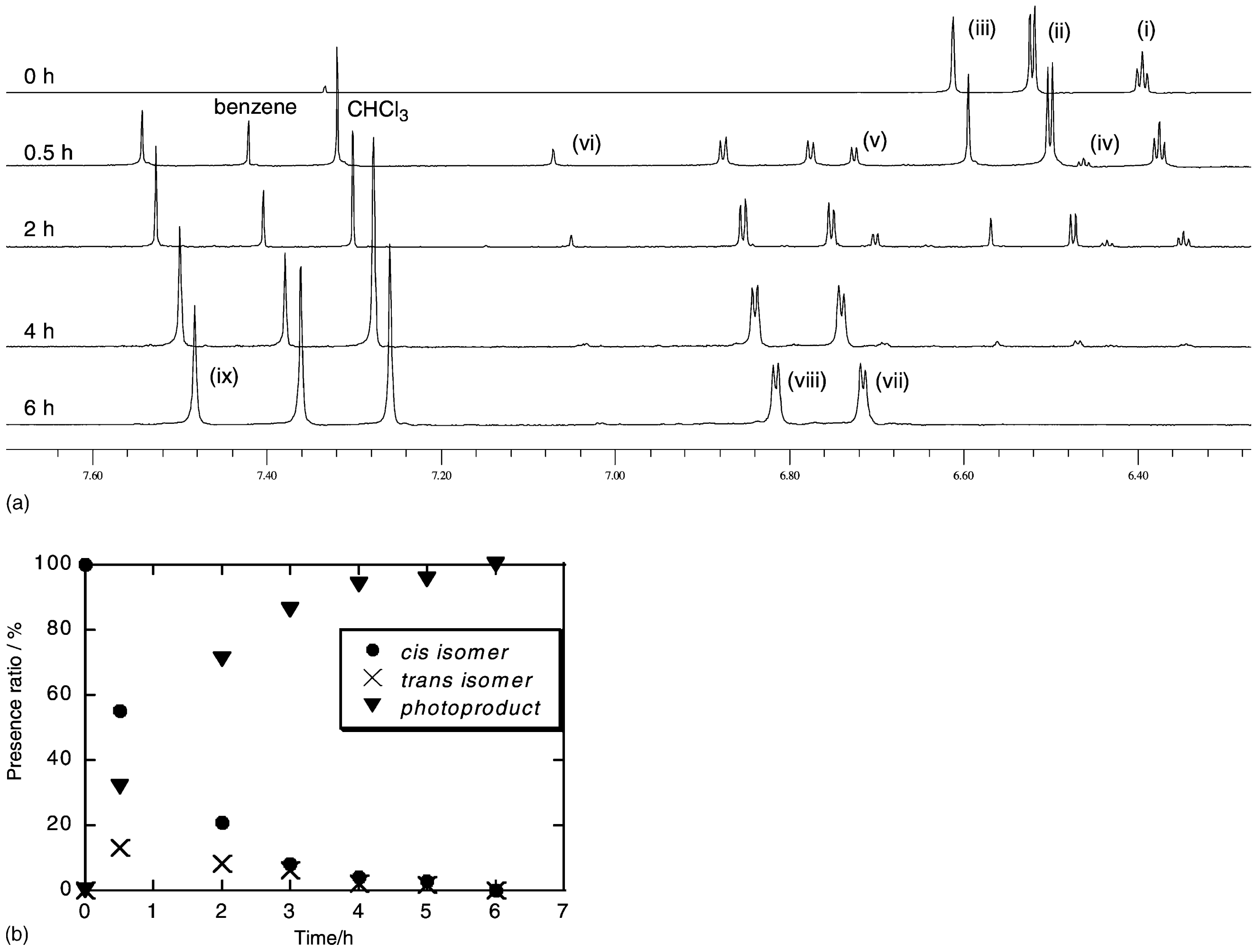


Fig. 5. Time development for *cis*-TMST on laser flash with 308 nm laser in benzene under oxygen atmosphere. (a) ^{1}H NMR spectrum change. (i–iii) *cis*-TMST, (iv–vi) *trans*-TMST, (vii–ix) TMP. (b) Ratio of *cis*- and *trans*-TMST and TMP.

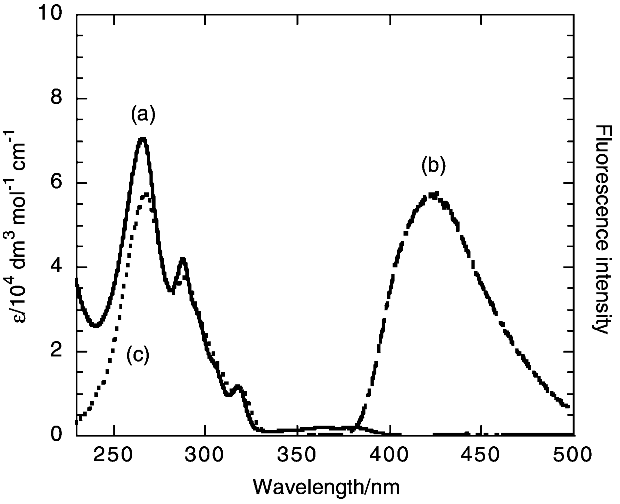


Fig. 6. (a) Absorption, (b) fluorescence and (c) fluorescence excitation spectra of TMP in THF at room temperature.

isomer undergoes either isomerization to the *trans* isomer with the efficiency of 0.35 or cyclization to give dihydrophenanthrene with the efficiency of 0.30 [7]. However, the cyclization product DHP quickly revert to give the *cis*

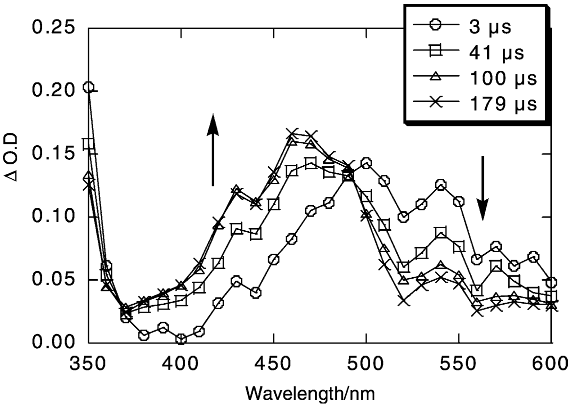
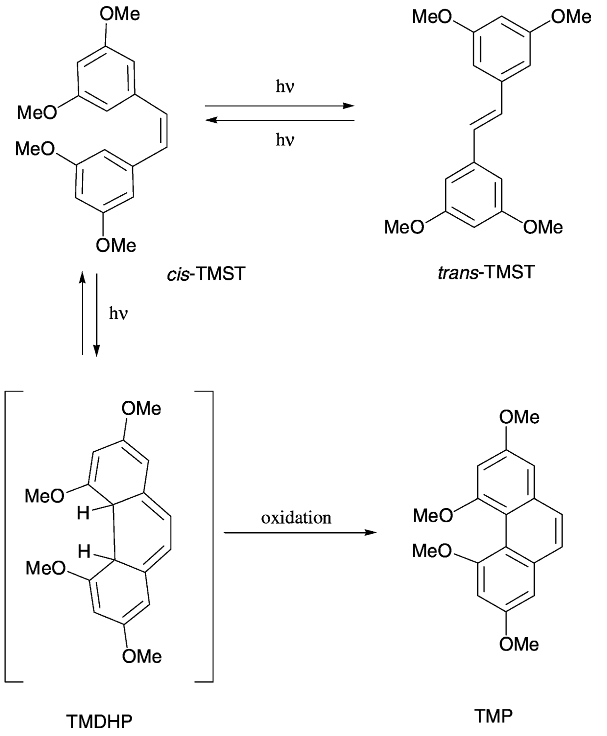


Fig. 7. Transient absorption spectra observed on laser flash photolysis with 308 nm laser beam in benzene under argon atmosphere.



Scheme 1. Photoisomerization and photocyclization of *cis*- and *trans*-TMST.

isomer and therefore, only *cis–trans* isomerization is usually observed in the isomerization of stilbene. In *cis*-TMST, the cyclization reaction seems much more efficient than the isomerization to the *trans* isomer.

3.5. The intermediate of photocyclization observed on laser flash photolysis

When *cis*-TMST is irradiated with pulsed excimer laser at 308 nm, one can observe transient spectra. These spectra were shown in Fig. 7. Just after the laser pulse, the transient spectrum with λ_{max} at 500–540 nm was observed. The transient spectrum gradually changed to give λ_{max} at 460 nm. These results indicate the conversion of the initial cyclization product (TMDHP$_1$) to the final cyclization product (TMDHP$_2$) with the time constant of 66 μs. The second intermediate, TMDHP$_2$ has a lifetime of approximately 15 min under argon at room temperature in benzene (Fig. 8). Laser photolysis of *trans*-TMST did not give any detectable transient spectra.

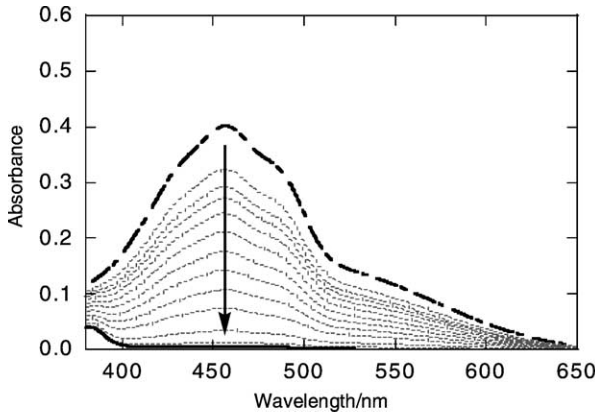


Fig. 8. Change of absorption spectrum of TMDHP after irradiation with 308 nm laser beam in benzene at room temperature under argon atmosphere.

3.6. Potential energy surfaces of isomerization and cyclization of TMST

Since no T–T absorption spectrum was observed on direct laser excitation of *cis* and *trans*-TMST, they did not undergo intersystem crossing to the triplet state. Therefore, the *cis–trans* isomerization as well as cyclization reaction proceeds in the singlet excited state. Thus, the potential energy surfaces of isomerization and cyclization reactions are shown in Fig. 9. The singlet excitation energies of *cis*-,

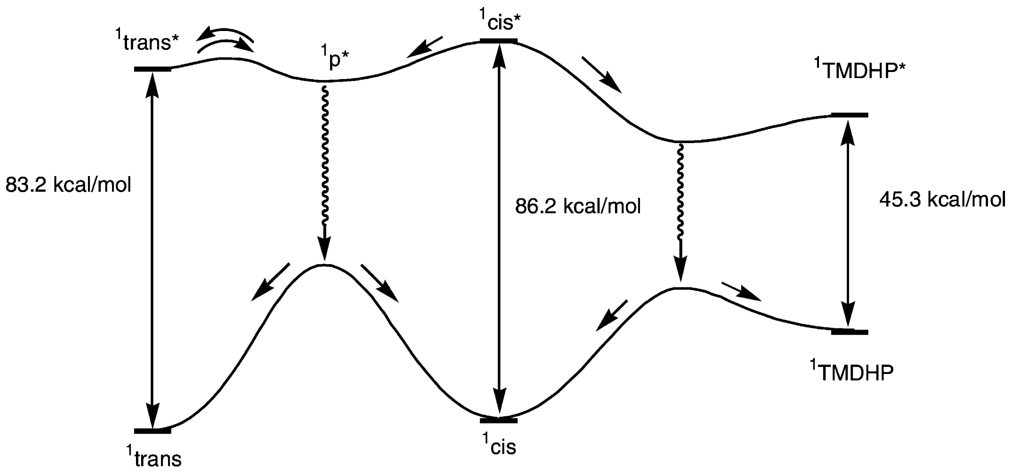


Fig. 9. Potential energy surface of photoisomerization and photocyclization of TMST.

trans-TMST, and TMDHP were estimated from the crossing point of the absorption spectrum and fluorescence spectrum or the absorption edge. These values are also included in Fig. 9.

4. Conclusion

trans- and *cis*-3,3′,5,5′-Tetramethoxystilbene underwent photocyclization to give 2,4,5,7-tetramethoxydihydro-phenanthrene as well as *cis–trans* photoisomerization as revealed by preparation and isolation of pure *cis*-TMST and TMP.

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