 

# Effect of Methoxy Substituents on the Excited State Properties of Stilbene

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Excited state properties of stilbenes having methoxy substituents at the ortho position of the phenyl ring have been studied and the remarkable methoxy substituent effect to suppress the fluorescence quantum yield depending on the number of methoxy substituent was observed. The fluorescence quantum yield of the trans isomer decreased with increasing number of methoxy substituents and 0.54 for *trans*-**1**, 0.13 for *trans*-**2**, and 0.011 for *trans*-**3** in benzene.

Many studies have been reported concerning the photochemical isomerization and fluorescence properties of stilbene and its analogues.[1–8] The excited singlet state of stilbene undergoes isomerization around the C=C double bond to achieve the perpendicular excited singlet state ($^1$p*) which deactivates to give the perpendicular ground state ($^1$p) finally giving the ground state cis ($^1$c) and trans isomers ($^1$t). In *trans*-stilbene the main deactivation process from the excited singlet state (96%) is the above-mentioned isomerization around the C=C double bond in the excited singlet state to give $^1$p* followed by isomerization to $^1$c with a quantum yield of ca. 0.5.[1,2] In addition to deactivation by isomerization in the excited singlet state of *trans*-stilbene, nearly 4% of the excited singlet state deactivates by fluorescence emission, but no intersystem crossing to the triplet excited state has been observed. Singlet *cis*-stilbene undergoes either isomerization around the double bond to give perpendicular singlet excited state ($^1$p*) with 70% efficiency and cyclization to give dihydrophenanthrene type compounds with 30% efficiency accompanied by very small fluorescence emission in the range of $10^{-2}$%.[3] The introduction of electron-donating or electron-withdrawing groups affects the properties of the singlet excited state. For example, substitution of a nitro group at the para position of a phenyl ring accelerates the intersystem crossing to the triplet state and therefore, both singlet and triplet excited states are responsible for the isomerization.[7,8] On the other hand, electron-donating group such as amino groups at the ortho or meta position of the phenyl ring increase the lifetime of the excited singlet state of stilbene to give 3.7 and 7.5 ns for *o*- and *m*-aminostilbene[9,10] respectively, compared to the parent compounds stilbene (60 ps) and *p*-aminostilbene (100 ps).

Thus, the introduction of electron-donating groups to the phenyl ring of stilbene seems to increase the fluorescence quantum yield and fluorescence lifetime.[11–13] In our previous experiments, introduction of a methoxy substituent at the 4 meta position of the phenyl ring also increased the excited state lifetime of stilbene to give 3 ns in hexane.[12] The lifetime increased with increasing polarity of solvent to give 10 ns in tetrahydrofuran (THF) and 17 ns in acetonitrile. Thus, even the excited state of symmetrically substituted stilbene was strongly influenced by the solvent and consequently the photophysical characteristics were investigated.[11]

Since no systematic study has been reported on the effect of electron-donating substituents on the photochemical and photophysical properties of stilbene, it is worth studying the effect of methoxy substituents at different positions of the phenyl ring. Thus, compounds with methoxy substituents at the ortho position (Figure 1) were prepared and their excited state properties were investigated. The remarkable effect of methoxy substituents to decrease the quantum yield of fluorescence emission with increasing the number at the ortho position of the phenyl ring was observed.

## Results

The absorption spectra of methoxy-substituted stilbene in benzene are summarized in Figure 2. The absorption maximum ($\lambda_{max}$) is observed at 330, 324, and 315 nm for *trans*-2,2′-dimethoxy- (**1**), *trans*-2,2′,6-trimethoxy- (**2**), and *trans*-2,2′,6,6′-tetramethoxystilbene (**3**), respectively. The maximum wavelength of the absorption spectra shifted to shorter wavelength with increasing number of methoxy substituents and the absorption edge tends to shift to shorter wavelength with increasing number of methoxy substituent. The maximum wavelength of fluorescence emission ($\lambda_{max}$(f)) also shifted to shorter wavelength with increasing number of methoxy substituent as shown in Figure 3. The $\lambda_{max}$(f) value is 372, 366, and 361 nm for *trans*-**1**, *trans*-**2**, and *trans*-**3**, respectively. The Stokes shift between the maximum wavelength of absorption and fluorescence spectra was calculated to be ca. 3500 cm$^{-1}$ for *trans*-**1**, -**2**, and -**3**. The maximum wavelength of the fluorescence excitation spectra seems to be similar among these compounds. The singlet excitation energy ($E_S$) was calculated from the crossing point of the fluorescence and absorption spectra to be 330, 332, and 336 kJ mol$^{-1}$ for *trans*-**1**, -**2**, and -**3**, respectively. These values are 8–17 kJ mol$^{-1}$ lower that of *trans*-**4** (347 kJ mol$^{-1}$),[14] but are 33–38 kJ mol$^{-1}$ lower than that of *trans*-stilbene (370 kJ mol$^{-1}$).[1d,3] The fluorescence quantum yield ($\Phi_f$) is determined to be

Published on the web November 12, 2008; doi:10.1246/bcsj.81.1500

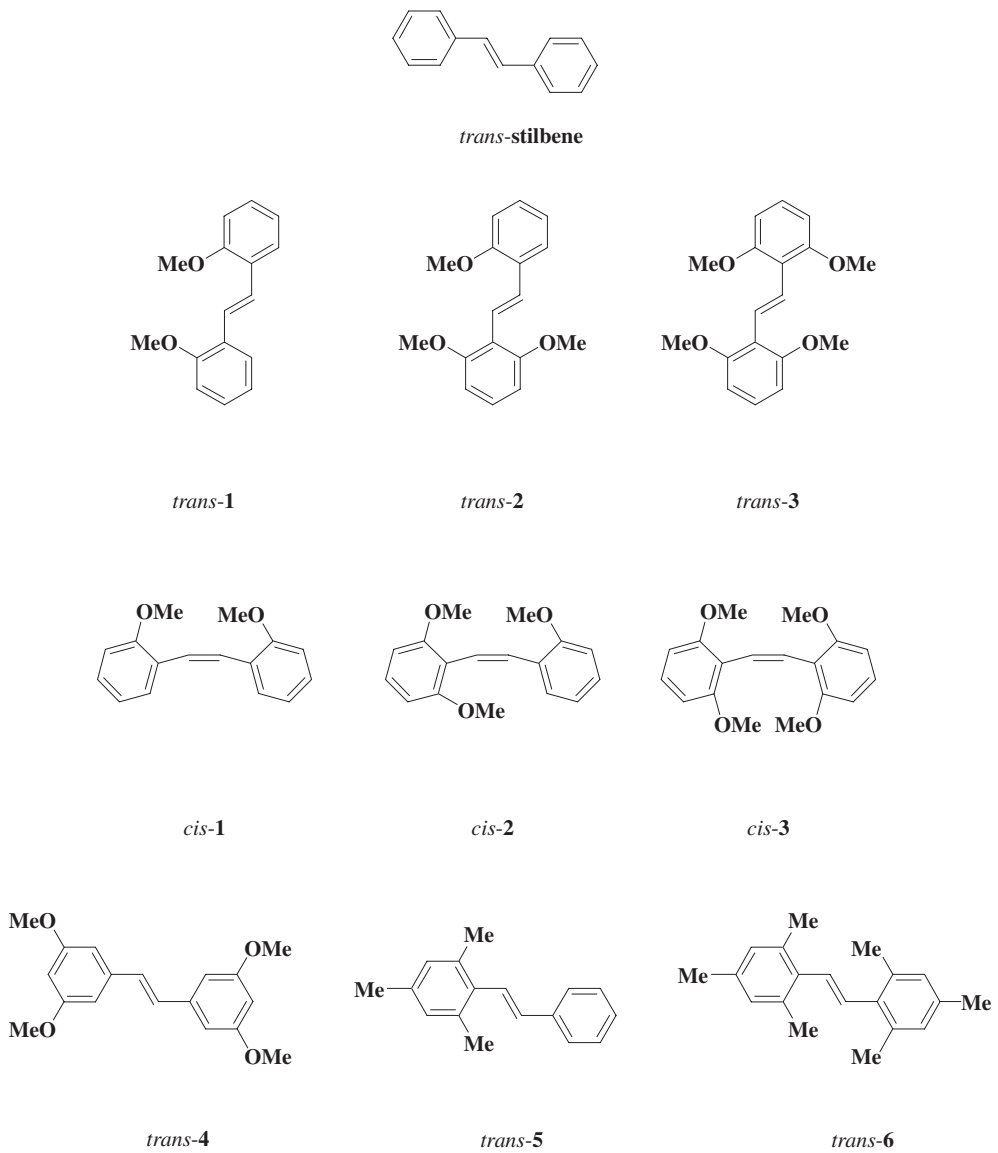


**Figure 1.** Structure of stilbenes.

0.54, 0.13, and 0.011 for *trans*-**1**, *trans*-**2**, and *trans*-**3**, respectively. The fluorescence lifetime of *trans*-**1** was observed to be 0.5 ns in THF solution at room temperature. However, we could not determine the fluorescence lifetime of *trans*-**2** and -**3** due to the detection limit of our instrument (ca. 0.4 ns) indicating that the singlet lifetime of *trans*-**2** and -**3** is considerably shorter than 0.4 ns.

The absorption maximum of the cis isomer shifted to shorter wavelength 309, 297, and 291 nm in the order of *cis*-**1**, -**2**, and -**3** (Figure 2). The decrease in wavelength indicates that the increase in number of methoxy substituents decreases the wavelength of absorption maximum probably due to the increase of the steric effect to inhibit planarity and conjugation. If we compare the absorption spectra of *cis*- and *trans*-**3**, the absorption maximum was shifted to shorter wavelength by ca. 25 nm for *cis*-**3** compared to *trans*-**3**. Different from the trans isomers, we could not observe fluorescence spectra for all cis isomers of **1**–**3** in THF at room temperature.

Figure 4 shows the data for crystallographic analysis of *trans*-**3**,[15] where the dihedral angle between the benzene ring and C=C double bond is determined to be 16°.

Figure 5 shows the time dependence of the absorption spectra upon irradiation starting from *trans*-**3**. The photostationary state isomer composition $([t]/[c])_{pss}$ was determined in benzene to be 35.1/64.9, 13.9/86.1, and 17.3/82.7 for *trans*-**1** (330 nm excitation), *trans*-**2** (324 nm excitation), and *trans*-**3** (316 nm excitation), respectively. The $([t]/[c])_{pss}$ value of **3** slightly depends on the solvent polarity to give 14.2/85.8 in THF and 13.6/86.4 in acetonitrile. The $([t]/[c])_{pss}$ is correlated to the ratio of the extinction coefficient of cis and trans isomers and the quantum yield of isomerization from trans-to-cis ($\Phi_{t\text{-}c}$) and cis-to-trans ($\Phi_{c\text{-}t}$).

$$([t]/[c])_{pss} = (\varepsilon_c/\varepsilon_t)(\Phi_{c\text{-}t}/\Phi_{t\text{-}c}) \quad (1)$$

The molar extinction coefficients of *cis*- and *trans*-**1** at 330 nm are determined to be 5900 and 18600 $M^{-1}\,cm^{-1}$, respectively. The values of *cis*- and *trans*-**2** are 5200 and 21800 $M^{-1}\,cm^{-1}$, respectively and those of *cis*- and *trans*-**3**

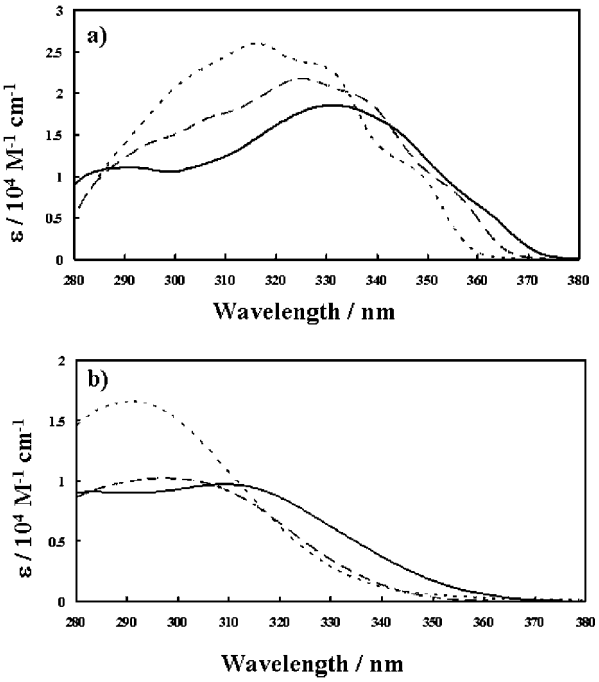


**Figure 2.** (a) Absorption spectra of *trans*-**1**, -**2**, and -**3** in benzene. (b) Absorption spectra of *cis*-**1**, -**2**, and -**3** in benzene.

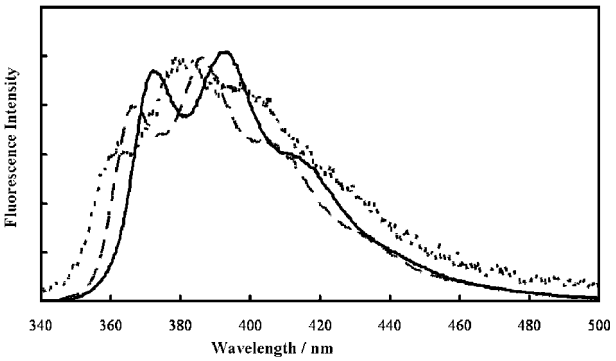


**Figure 3.** Fluorescene spectra of *trans*-**1**, -**2**, and -**3** in benzene.

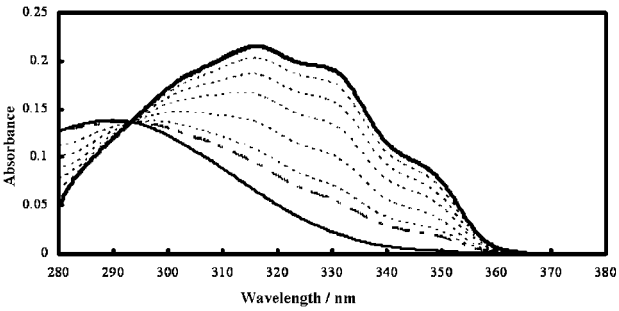


**Figure 5.** Spectral change on photoirradiation of *trans*-**3** with photoisomerization.

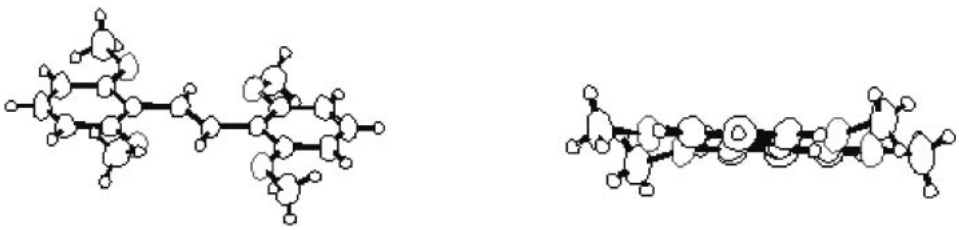

**Figure 4.** X-ray crystal structure of *trans*-**3**.

are 7600 and 26000 $M^{-1}\,cm^{-1}$, respectively. The quantum yields of trans-to-cis isomerization ($\Phi_{t\text{-}c}$) were determined to be 0.20, 0.40, and 0.45, respectively for **1**, **2**, and **3**. Thus, one can calculate the quantum yields of cis-to-trans isomerization ($\Phi_{c\text{-}t}$) to be 0.34, 0.28, and 0.32, for **1**, **2**, and **3**, respectively. The above observed and estimated values are summarized in Table 1.

## Discussion

The absorption spectra and fluorescence spectra of *trans*-**1**, -**2**, and -**3** appeared at longer wavelength than *trans*-stilbene. These results indicate that the methoxy substituent lowers the singlet excitation energy by electronic effect.

The fluorescence quantum yield of the trans isomer decreased with increasing number of methoxy substituents with values of 0.54 for *trans*-**1**, 0.13 for *trans*-**2**, and 0.011 for *trans*-**3** in benzene (Table 1). One should mention this strong substituent effect on the fluorescence quantum yield of stilbene derivatives. In the case of methoxy substitution at the meta position (3,3′,5,5′-tetramethoxystilbene, **4**), the excited singlet lifetime increased to 10 ns in THF, where the quantum yield of fluorescence emission is observed to be 0.4.[12] The 50 fold decrease of the fluorescence emission in *trans*-**3** compared to *trans*-**1** might be caused by congestion of the molecular structure of the tetramethoxystilbene and/or electronic effects of methoxy substituents to increase the deactivation from the excited singlet state. We should discuss these possibilities.

It has been reported that the methyl substituent at the ortho position accelerates the isomerization around the double bond to give a quantum yield of isomerization as high as 0.47 and 0.48 and a quantum yield of fluorescence emission as small as 0.003 and <0.001 for *trans*-2,4,6-trimethylstilbene (**5**) and *trans*-2,2′,4,4′,6,6′-hexamethylstilbene (**6**), respectively.[5] In this case, even the trans isomers of **5** and **6**, the single bond connecting the phenyl ring and the C=C double bond takes similar arrangement to the *cis*-stilbene due to the steric effect of the methyl group at the ortho position, which appears in the similarity of the absorption spectra of *trans*-**5** and *trans*-**6** to that of *cis*-stilbene.[5]

The molecular congestion is reflected in the absorption spectra as observed in **5** and **6**. Although the spectral profile of the absorption spectra is similar among *trans*-**1**, -**2**, and -**3**,

**Table 1.** Absorption Fluorescence, and Isomerization Properties of Stilbene and Its Derivarives **1**–**6** in Benzene

| Compound | $\lambda_{max}$/nm ($\varepsilon/10^4$ M$^{-1}$ cm$^{-1}$) | | | $\Phi_f$ | $\Phi_{t\text{-}c}$ | $\Phi_{c\text{-}t}$ | $E_s$ /kJ mol$^{-1}$ | $([t]/[c])_{pps}$ |
|---|---|---|---|---|---|---|---|---|
| *trans*-Stilbene[a)] | 295 | 315 | 330 | 0.035 | 0.52 | 0.35 | 370 | |
| *trans*-**1** | 330 (1.86) | 345 (1.48) | 360 (0.62) | 0.54 | 0.20 | 0.34[d)] | 330 | 35.1/64.9[e)] |
| *trans*-**2** | 325 (2.18) | 340 (1.84) | 350 (0.95) | 0.13 | 0.40 | 0.28[d)] | 332 | 13.9/86.1[f)] |
| *trans*-**3** | 315 (2.60) | 330 (2.31) | 345 (1.18) | 0.011 | 0.45 | 0.32[d)] | 336 | 17.3/82.7[g)] |
| *trans*-**4**[b)] | | 310 | | 0.24 | 0.31 | 0.39 | 347 | |
| *trans*-**5**[c)] | | 285 | | 0.003 | 0.47 | 0.40 | | |
| *trans*-**6**[c)] | | 260 | | <0.001 | 0.48 | | | |

a) In pentane, Refs. 1–3. b) Ref. 12. c) In methylcyclohexane:isohexane = 2:1, Ref. 5. d) Estimated from $\Phi_{t\text{-}c}$ and $([t]/[c])_{pps}$ using eq 1. e) Irradiated at 330 nm. f) Irradiated at 325 nm. g) Irradiated at 315 nm.

the absorption maximum and the absorption edge shifts to a shorter wavelength in the order of *trans*-**1**, -**2**, and -**3**. Even the absorption spectra of *trans*-**3** is observed in a considerably longer wavelength region than that in *trans*-stilbene indicating the importance of electronic effects of methoxy substituents on the absorption and fluorescence profiles to give a bathochromic shift. The inverse correlation of the absorption spectra with the number of methoxy substituent may be due to the compromise of the electronic and the steric effects by increasing the methoxy substituent at the ortho position. Thus, the presence of steric congestion induces the breaking of the conjugation of the whole molecular structure to some extent in *trans*-**3**. Actually, slight deviation from the planar conformation of *trans*-**3** is supported by the crystallographic analysis (Figure 4),[15] where the structure has dihedral angles between the phenyl and the double bond planes of 16°.

As discussed above the decrease in the quantum yield of fluorescence emission in *trans*-**3** should be the consequence of the increase of the rate constant of deactivation from the excited state by way of trans–cis isomerization around the C=C double bond. Actually, the quantum yield of trans-to-cis isomerization of **3** is determined to be $0.45 \pm 0.05$, indicating that the efficiency of twisting around the double bond in the excited state is $0.9 \pm 0.1$ ($2 \times (0.45 \pm 0.05)$). The quantum yield of trans-to-cis isomerization is 0.20 and 0.40, respectively for **1** and **2**. In addition, the singlet excitation energy increased in the order of *trans*-**1** (330 kJ mol$^{-1}$), *trans*-**2** (322 kJ mol$^{-1}$), and *trans*-**3** (336 kJ mol$^{-1}$). These results are in accordance with the finding that *trans*-**3** with the highest excitation energy gave quite low quantum yield of fluorescence emission compared to *trans*-**1** and -**2** and considerably high quantum yield of trans-to-cis isomerization. One could imagine the change of the molecular structure in solution, where the single bond between the aromatic ring and C=C double bond has some twist angle and the $\pi$ conjugation of the molecule seems to be diminished in *trans*-**3**. Anyhow, the small increase of the singlet energy in *trans*-**3** may decrease the activation barrier of rotation around the double bond from $^1$t* to $^1$p* and increase the deactivation rate constant by way of isomerization. The introduction of a methoxy substituent at the ortho position could cause the bathochromic shift in absorption spectra as observed in the meta substituted compound *trans*-**4**. Actually, the absorption spectra of *trans*-**1** appeared at longer wavelength than *trans*-stilbene. However, the increase of the methoxy substituent at the ortho position shifted the absorption spectra to the shorter wavelength region as observed in *trans*-**2** and *trans*-**3**. These results indicate that the introduction of the methoxy group resulted in bathochromic shift as observed in *trans*-**1**, but further introduction of a methoxy substituent at the ortho position might be a compromise of the bathochromic effect of the methoxy substituent and the steric effect. Thus, finally, in *trans*-**3**, the steric effect prevails over the bathochromic effect by increasing the twist angle between the benzene ring and the C=C double bond to give twist angle of 16°.

In summary, stilbene derivatives with methoxy substituents at three and four ortho positions were successfully prepared and for the first time it is reported that methoxy substituents highly decrease the fluorescence quantum yield even though the molecular structure is assumed to be almost planar and does not seem to take a congested structure. In addition, it is notable in the present findings that the difference in the effect of ortho methoxy substituents from those at the meta position where the fluorescence quantum yield and fluorescence lifetime increased with the introduction of methoxy substituents. These remarkable findings of the effect of methoxy substituents at the ortho position will contribute the understanding of the photochemical properties of substituted stilbenes as a most fundamental compound for photochemical reaction.

## Experimental

***trans*-3.** The methoxy-substituted *trans*-stilbenes were prepared by Wittig reaction.[16] Their structures were identified by NMR spectroscopy and elemental analysis.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 683164 for compound *trans*-**3**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/consts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

To a suspension of NBS (1.4 g, 7.6 mmol) and AIBN (12.5 mg, 0.08 mmol) in carbon tetrachloride (10 mL) was added a solution of 2,6-dimethoxytoluene (1 g, 6.6 mmol) in $CCl_4$ (3 mL) at room temperature. The reaction mixture was stirred for 24 h at rt and

heated under reflux for 24 h. Then the reaction mixture was extracted with $CH_2Cl_2$. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. Purification by column chromatography (silica gel, $CH_2Cl_2$:hexane = 1:1) gave 2,6-dimethoxybenzyl bromide. A solution of benzyl bromide (1 equiv) and triphenylphosphine (1 equiv) in benzene (10 mL) was heated at reflux. After stirring for 1 day, the mixture was concentrated and filtered to get phosphorus compound. To a suspension of 60% NaH (in oil) in THF (20 mL) was added phosphorus compound (493.4 mg, 1.00 mmol) at 0 °C followed by stirring for 1 h at room temperature. To the solution was added 2,6-dimethoxybenzaldehyde (166.2 mg, 1.00 mmol) in THF (10 mL). After stirring for 1 day at room temperature, the mixture was poured into water and extracted with $CH_2Cl_2$. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and evaporated. The crude product (512.1 mg) was purified by recrystallization from hexane and $CH_2Cl_2$ to obtain a solid trans isomer (140.6 mg). Mp: 142–143 °C; $^1$H NMR ($CDCl_3$, 500 MHz, TMS): $\delta$ 7.73 (2H, s), 7.12 (2H, t, $J$ = 8.35 Hz), 6.57 (4H, d, $J$ = 8.35 Hz), 3.87 (12H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 158.4, 127.4, 124.0, 116.6, 104.1, 55.9. Anal. Found: C, 71.68; H, 6.57%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

***trans*-1:** Mp: 102–103 °C; $^1$H NMR ($CDCl_3$, 500 MHz, TMS): $\delta$ 7.65 (2H, d, $J$ = 7.65 Hz), 7.47 (2H, s), 7.24–7.21 (2H, m), 6.97 (2H, t, $J$ = 7.49 Hz), 6.89 (2H, d, $J$ = 8.22 Hz), 3.88 (6H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 156.7, 128.3, 127.1, 126.3, 123.5, 120.6, 110.8, 55.6. Anal. Found: C, 79.94; H, 6.97%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

***trans*-2:** Mp: 78–79 °C; $^1$H NMR ($CDCl_3$, 500 MHz, TMS): $\delta$ 7.87 (1H, d, $J$ = 16.8 Hz), 7.64 (1H, d, $J$ = 7.64 Hz), 7.39 (1H, d, $J$ = 16.8 Hz), 7.19 (1H, t, $J$ = 7.75 Hz), 7.13 (1H, t, $J$ = 8.35 Hz), 6.95 (1H, t, $J$ = 7.29 Hz), 6.86 (1H, d, $J$ = 8.20 Hz), 6.56 (2H, d, $J$ = 8.35 Hz), 3.86 (6H, s), 3.85 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 158.6, 156.8, 128.6, 128.0, 127.8, 127.2, 126.3, 120.7, 120.4, 115.4, 110.8, 104.0, 55.8, 55.6. Anal. Found: C, 75.56; H, 6.72%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

***cis*-1.** The methoxy-substituted *cis*-stilbenes were prepared by irradiation with 365-nm light each *trans*-stilbene. The product was purified by column chromatography and recrystallization from $CH_2Cl_2$. Mp: 82–82 °C; $^1$H NMR ($CDCl_3$, 500 MHz, TMS): $\delta$ 7.19–7.10 (4H, m), 6.86 (2H, dd, $J$ = 0.82, 8.24 Hz), 6.69 (2H, dt, $J$ = 0.99, 7.58 Hz), 6.76 (2H, s), 3.83 (6H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 156.8, 129.8, 128.1, 126.1, 125.4, 119.8, 110.3, 55.3.

***cis*-2:** Mp: 66–67 °C; $^1$H NMR ($CDCl_3$, 500 MHz, TMS): $\delta$ 7.20–7.00 (2H, m), 6.95–6.90 (2H, m), 6.84 (1H, dd, $J$ = 0.81, 8.10 Hz), 6.61 (1H, t, $J$ = 7.56 Hz), 6.52 (1H, d, $J$ = 12.29 Hz), 6.46 (2H, d, $J$ = 8.37 Hz), 3.84 (3H, s), 3.55 (6H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 157.3, 156.1, 128.2, 128.0, 127.7, 127.2, 120.9, 119.5, 115.1, 109.8, 103.5, 55.4, 55.3.

***cis*-3:** Mp: 134–135 °C; $^1$H NMR ($CDCl_3$, 500 MHz, TMS): $\delta$ 7.07 (2H, t, $J$ = 8.30 Hz), 6.71 (2H, s), 6.42 (4H, d, $J$ = 8.30 Hz), 3.52 (12H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 157.4, 127.6, 123.8, 117.7, 103.3, 55.2.

This work was supported by a Grant-in-Aid for Science Research in a Priority Area "New Frontiers in Photochromism (No. 471)" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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