Selective Isomerization of *cis*-Stilbene by Non-Resonant Two-Photon Excitation

Takashi Miyazawa, Shin-ya Koshihara,[†] Yusaburo Segawa, and Mitsuo Kira*
Photodynamics Research Center, the Institute of Physical and Chemical Research (RIKEN),
19-1399, Koeji, Nagamachi, Aoba-ku, Sendai 980

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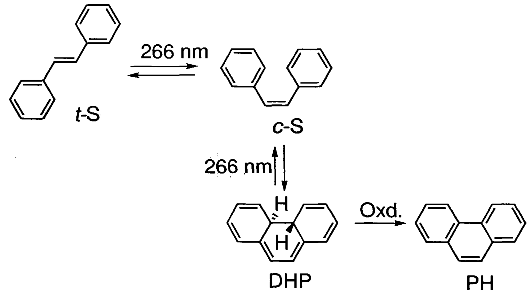
Non-resonant two-photon excitation induced dramatical change in the photoreaction pathways of stilbenes. Typically, irradiation of *cis*-stilbene with 532 nm laser pulses caused only isomerization to *trans*-stilbene in hexane at room temperature; the cyclization to dihydrophenanthrene was completely suppressed.

Photochemical processes are of great importance for synthesis of structurally interesting molecules, design for opto-electronic devices, and understanding the mechanism of eyesight. However, photoexcitation of a substance yields a number of photoproducts in general, and therefore, synthetic design by using photochemical processes is rather difficult. Typically, photolysis of stilbenes as the prototype of π-conjugated organic molecules has been known to induce both *cis-trans* isomerization and cyclization to 4a,4b-dihydrophenanthrene (DHP), which is easily oxidized to give phenanthrene (PH) (Eq. 1). Extensive studies on the photochemistry of stilbenes[1] have shown that the modification of the product distribution by changing the experimental conditions such as excitation wavelengths, temperatures, and solvents has been poorly successful. We have found that the non-resonant two-photon (NRTP) excitation induces dramatical change in the reaction pathways of stilbenes. Irradiation of *cis*-stilbene with 532 nm laser pulses caused only isomerization to *trans*-stilbene in hexane at room temperature; the cyclization to DHP was completely suppressed.[2]



(1)

In accordance with the previous studies of single-photon photoreactions of *cis*-stilbene (*c*-S),[3] irradiation of a hexane solution of *c*-S (purified by preparative glc, 6.62×10^{-3} M) at room temperature with a 266 nm light (the fourth harmonic of a Nd:YAG laser, 18 MW/cm^2, 5 ns width, 10 Hz) for 30 min (18,000 pulses) gave *c*-S, *trans*-stilbene (*t*-S), and PH in 39, 27, and 23 % yields, respectively, as determined by gas chromatography; no other product was detected by glc. Dependence of the product distribution on the number of irradiation pulses is shown in Figure 1.

Quite different results were obtained when *c*-S was irradiated with 532 nm laser pulses (the second harmonic of a Nd:YAG laser, 219 MW/cm^2, 6 ns width, 10 Hz) at room temperature. Irradiation of a hexane solution of *c*-S (6.62×10^{-3} M) with the 532 nm laser pulses produced a clean mixture of *c*-S and *t*-S without formation of phenanthrene as shown in Figure 2(a). After the irradiation of 90,000 shots, the mixture reached to the photostationary state, where the yields of *c*-S and *t*-S were 80 and 16 % . The yield of *t*-S after correction for the backward reaction from *c*-S to *t*-S with the Lamola's equation[4] increased in proportion to the square of the light intensity as shown in Figure 2(b).

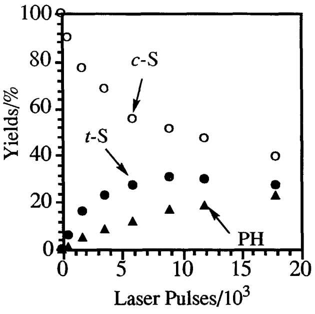


Figure 1. Time profile of the product distribution during irradiation of *cis*-stilbene with 266-nm laser pulses.

$$t\text{-S} \overset{532\ \text{nm}}{\rightleftarrows} c\text{-S} \overset{532\ \text{nm}}{\not\rightleftarrows} \text{DHP} \qquad (2)$$

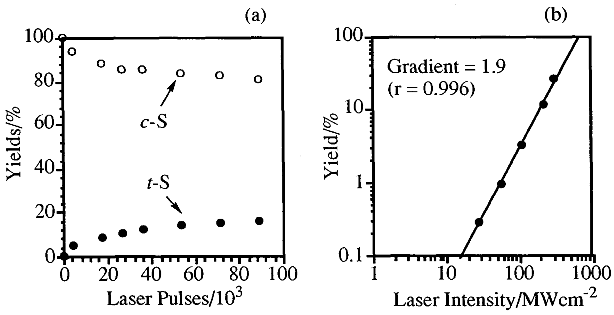


Figure 2. (a) Time profile of the product distribution during irradiation of *cis*-stilbene with 532-nm laser pulses. (b) Square dependence of the yield of *trans*-stilbene on the input power for two-photon induced isomerization of *cis*-stilbene.

The above results suggest that the NRTP excitation of *c*-S with 532 nm laser pulses induces *cis-trans* isomerization without cyclization to DHP. In addition to the nonlinear dependence of the photochemical conversion on the light intensity, the following findings support the above conclusion: (1) when the hexane solution of *c*-S was irradiated with two 532 nm pulsed laser beams with the intensity I_0 but having a time interval of 10 ns between the two pulses (*n* shots each), the efficiency of the *cis*-to-*trans* isomerization decreased to a half of that for the irradiation of *n* shots of a 532 nm laser beam with the intensity of $2I_0$. (2) Irradiation of the solution by using a CW Ar laser (514 nm, 2 W) gave no reaction, even though the integrated intensity of the Ar laser was larger than that of the 532 nm laser pulses, indicating that the reaction induced by the 532 nm laser pulses is due to neither heat up of the sample nor photoreactions induced by the direct singlet-triplet absorption.[5] At this moment, it may be difficult to completely eliminate the possibility that the apparent missing of DHP may be attributed to the facile backward reaction to *c*-S by the 532 nm laser pulses, since DHP has the absorption end at around 530 nm. However, this is unlikely, because formation of a significant amount of phenanthrene during irradiation of *c*-S with 266 nm laser pulses (18 MW/cm^2) was not suppressed, even when intense 532 nm laser pulses (219 MW/cm^2) were supplied at the same time.

As expected, the results of the NRTP photochemistry of *t*-S were quite parallel to those of *c*-S. Irradiation of a hexane solution of *t*-S (purified by recrystallization from ethanol followed by sublimation) with 532 nm laser pulses gave a simple mixture of *c*-S and *t*-S without formation of PH (Figure 3 (a)). Square dependence of the conversion on the light intensity was also observed for the isomerization from *t*-S to *c*-S (see Figure 3 (b)).

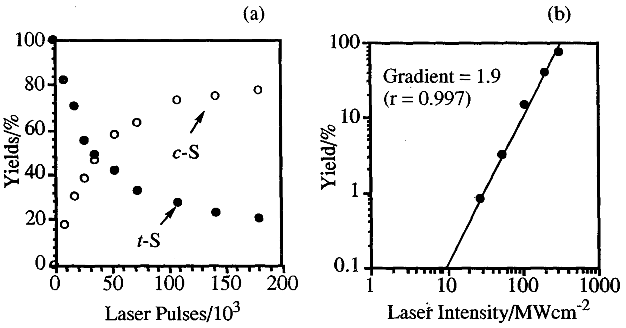


Figure 3. (a) Time profile of the product distribution during irradiation of *trans*-stilbene with 532 nm laser pulses. (b) Square dependence of the yield of *cis*-stilbene on the input power for two-photon induced isomerization of *trans*-stilbene.

The present results may allow the following speculation for the mechanism of the photoisomerizations of *c*-S. Thus, the *cis*-to-*trans* isomerization takes place from the two-photon allowed excited state, while the cyclization to DHP occurs from the one-photon allowed excited state. It is known that *t*-S has a low-lying two-photon-allowed excited state,[6] whereas the energy level of the corresponding state of *c*-S is not clear at present. The electronic nature of the two-photon-allowed excited state of *t*-S[7] and the role in the isomerization from *t*-S to *c*-S has been discussed at length.[8] On this basis, it is suggested that an excited state with A symmetry (a two-photon allowed state) of *c*-S is responsible for the isomerization to *t*-S. The excited state responsible for the cyclization to DHP may be the lowest excited singlet state of *c*-S with B symmetry.

Whereas further works are required for elucidation of the origin of the unique selectivity of the NRTP induced photoreactions, the NRTP method offers a novel and practical tool for controlling the photoreaction pathways even in the condensed phase at room temperature. Related works are now in progress.

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References and Notes

† Present address: Department of Applied Physics, Faculty of Science, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo, 152, Japan.

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