Action Spectra of Non-Resonant Two-Photon (NRTP) Isomerization of *α,ω*-Diphenylpolyenes

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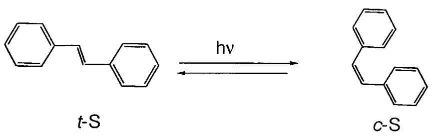
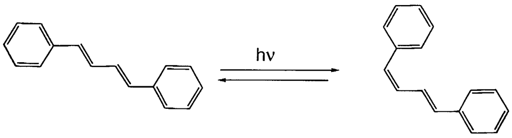
The efficiency of the non-resonant two-photon (NRTP) isomerizations of stilbenes and 1,4-diphenyl-1,3-butadienes were found to depend strongly on the wavelength of the laser pulses. The results not only confirm the 2^1A_g nature of the excited states responsible for the *cis-trans* isomerizations but also demonstrate that the action spectra of the NRTP reactions correspond to the two-photon allowed absorption bannds.

Much attention has been focused on the mechanistic aspects of photophysical and photochemical processes of α,ω-diphenylpolyenes.[1] In our recent studies of the non-resonant two-photon (NRTP) photochemistry,[2] it has been shown that the NRTP excitation of stilbenes with 532 nm laser pulses (the second harmonic of a Nd:YAG laser) induces only *cis-trans* isomerization; the cyclization to dihydrophenanthrene is completely suppressed, while it is a major side pathway of the common one-photon photoreaction of *cis*-stilbene (*c*-S).[2b] Recently experimental and theoretical studies indicate that the lowest one-photon allowed ^1B_u state and a two-photon-allowed ^1A_g state are very close in energy for many α,ω-diphenylpolyenes.[1] The NRTP results have given strong support for the mechanism proposed first by Orlandi and Siebrand,[3] where the photochemical *cis-trans* isomerization of stilbene occurs via the two-photon allowed excited state 2^1A_g. In this communication, we report wavelength dependence of the efficiency of the NRTP reactions of stilbenes and 1,4-diphenyl-1,3-butadienes. The results not only confirm the ^1A_g nature of the excited states responsible for the *cis-trans* isomerizations but also demonstrate that the action spectra of the NRTP reactions correspond to the two-photon allowed absorption bands. The present method to record the two-photon absorption spectrum, *i.e.* the two-photon reaction (TPR) method, is applicable to a non- or weekly fluorescent compound such as *c*-S.



t-S *c*-S (1)



tt-DPB *ct*-DPB (2)

The NRTP irradiation of *trans*-stilbene (*t*-S) using 450 nm – 540 nm laser pulses generated with an optical parametric oscillator (OPO), which was pumped by the third harmonic of a pulsed Nd:YAG laser, resulted in clean isomerization to the *cis*-isomer to reach the photostationary states after 9000 laser shots (*c*-S/*t*-S = 4/1). The whole feature of the isomerization was very similar to that investigated previously by using the 532 nm laser pulses.[2b] Figure 1 shows a plot of the initial rate of the *trans*-to-*cis* isomerization vs. a half of the wavelength of the incident laser pulses ($\lambda_t/2$).[4] The reaction efficiency estimated as the initial rate increased with decreasing wavelength from λ_t = 560 nm to reach the maximum at λ_t = 474 nm. The action spectrum should correspond to the two-photon absorption spectrum if the quantum yield of the NRTP reaction is independent on the wavelength.[4] The assumption is taken to be virtually valid, since the spectral feature is in good agreement with the two-photon absorption bands of *t*-S obtained by other methods, which gave the band maximum at 244[5a] and 232 nm.[5b] The small difference in the wavelength among the methods may be the reflection of the validity of the above assumption.

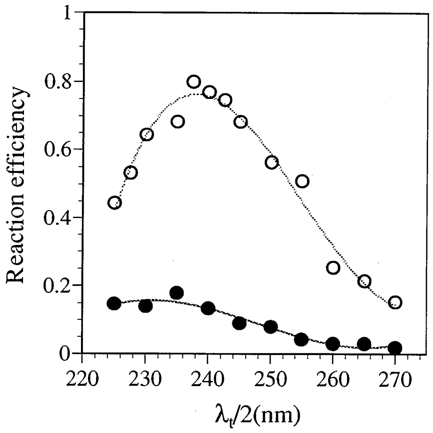


Figure 1. The wavelength dependence of the reaction efficiency of *trans*-to-*cis* (–O–) and *cis*-to-*trans* (–●–) isomerizations.

Among a number of experimental methods to obtain the two-photon absorption spectra, the following are the most common: (1) the two-photon fluorescence (TPF) method, where the intensity of the fluorescence from the lowest excited state generated via the two-photon absorption is monitored,[5a, 6] (2) the two-photon thermal lensing (TPTL) method [5b, 7] and (3) the multi-photon resonance ionization (MPRI) method.[8] Whereas the TPF method is the most convenient, it cannot be applied to weakly fluorescent compounds. The latter two methods have no such drawback but require some special techniques and equipments. The present TPR method is straightforward and applicable to non-fluorescent compounds, while relatively time-consuming.

The TPR method was also applied to the detection of the two-photon bands of *c*-S and *trans, trans*-1,4-diphenyl-1,3-butadiene (*tt*-DPB). As shown in Figure 1, the reaction efficiency of *c*-S reached to a maximum at around 230 nm ($\lambda_t/2$) by a similar method applied for *t*-S. The observed band would be assigned to the two-photon excited state of *c*-S, which has never been characterized by other methods until now.[9]

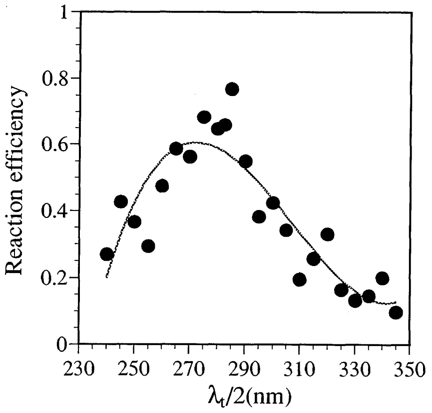


Figure2. The wavelength dependence of the reaction efficiency of the isomerization of *tt*-DPB to *ct*-DPB.

Irradiation of a hexane solution of *tt*-DPB with the 532 nm laser pulses at room temperature showed only the isomerization to *cis,trans*-1,4-diphenyl-1,3-butadiene (*ct*-DPB) and the photostationary state was reached with a *tt*-DPB/*ct*-DPB ratio of 35/65. The two-photon nature of the isomerization was confirmed by the square dependence of the yield of *ct*-DPB after correction of the backward reaction to *tt*-DPB on the laser intensity. On the other hand, the corresponding single-photon excitation using 266 nm laser pulses resulted in severe loss of the material balance due to several side reactions other than isomerization.[10] The highly selective isomerization of *tt*-DPB by the NRTP excitation is again indicative of the 2^1A_g nature of the excited state responsible for the *trans, trans*- to *cis, trans* isomerization. Figure 2 shows the wavelength dependence of efficiency of the formation of *ct*-DPB from *tt*-DPB. The spectrum with the band maximum at around 280 nm is in good accord with the two-photon absorption spectra taken by the TPF[12] and TPTL[13] methods.

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4 The reaction efficiency for the isomerization from *t*-S to *c*-S was estimated as the initial rate by analyzing the time profile of the formation of *c*-S. The yields of *c*-S were determined by capillary gas chromatography and/or HPLC. The reaction efficiency should depend on the condition of the applied laser pulses, the reaction quantum yield, and the two-photon absorptivity. Since throughout the experiments, the coherent lights (450 nm ~ 540 nm) of OPO are identical in pulse width (*ca.* 3 ns), density (1.8×10^{17} photons/cm^2), and energy (10 mJ/pulse), the efficiency corresponds directly to the two-photon absorptivity under the assumption of the independent reaction quantum yields on the wavelengths.

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