Solvent-dependent *cis-trans* Photoisomerization of *p*-Methoxy-*p*′-nitro-substituted *trans,trans,trans*-1,6-Diphenyl-1,3,5-hexatriene

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Irradiation of *p*-methoxy-*p*′-nitro-substituted 1,6-diphenyl-1,3,5-hexatriene induced *trans*, *trans*, *trans* → *cis*, *trans*, *trans* (*ttt* → *ctt*) isomerization in toluene, whereas in acetonitrile inefficient *ttt* → *ctt*, *tct* isomerization was observed. The results are explained in terms of weakly polar nature of twisted excited states.

cis-trans Photoisomerization of conjugated polyenes is considered to proceed via double-bond twisted excited states (p^*), by analogy of stilbene. Studies of these states are important in relation to the initial step in vision.[1,2] The electronic structures of p^* have been understood, in most cases, in terms of charge separation induced by double-bond twisting at excited states ('sudden polarization effect'[2] or 'the theory of biradicaloid states'[3]). However, due to complex nature of polyene isomerization, only a limited number of experimental examples have been reported. This prevents full understanding of the electronic nature of p^*.

In our previous work, we have shown that *p*,*p*′-diformyl-substituted 1,6-diphenyl-1,3,5-hexatriene (DPH) undergoes *trans*, *trans*, *trans* → *cis*, *trans*, *trans* (*ttt* → *ctt*) selective and efficient isomerization in polar solvents such as acetonitrile (AN) and methanol, but as the solvent polarity decreases, the efficiency of isomerization is strongly reduced.[4] Also for other symmetrically disubstituted DPHs with electron-accepting (A) or electron-donating (D) groups, similar solvent effects were observed.[5] The results for A–A and D–D derivatives can be explained by highly polar, zwitterionic nature of p^*.

We report here the photoisomerization of *ttt*-1-(*p*-methoxyphenyl)-6-(*p*-nitrophenyl)-1,3,5-hexatriene (*ttt*-**1**). Although fluorescence properties of D–A-substituted DPHs have already been reported,[6] their photoisomerization behavior is not known at present. In contrast to the cases for symmetrically substituted DPHs, the isomerization of *ttt*-**1** occurred in a low polar solvent more efficiently than in a polar solvent. The results can be understood by assuming that p^* has a weakly polarized 'dot-dot' structure.[3]

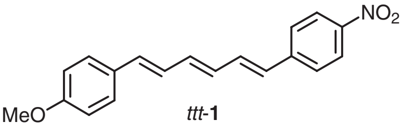
ttt-**1**

Table 1 summarizes the isomer ratios at the photostationary state (pss), quantum yields of *ttt* → *ctt* and *ttt* → *trans*, *cis*, *trans* (*tct*) isomerization ($\phi_{ttt\text{-}ctt}$ and $\phi_{ttt\text{-}tct}$, respectively), and fluorescence quantum yields (ϕ_f) and lifetimes (τ_s) for *ttt*-**1**[7] in toluene (Tol) and AN. On direct irradiation of an argon-degassed solution of *ttt*-**1** in Tol (2–5×10^{-5} mol dm^{-3}), its UV–vis spectrum changed rapidly with an isosbestic point at 360 nm to reach a pss (Figure 1). The irradiated sample was analyzed by a reverse-phase HPLC with a multi-channel photodetector. The photoproduct was shown by UV–vis spectrum to be *ctt*-**1** (1-*ctt*-**1** or 5-*ctt*-**1**), and no *tct*-**1** was detected in the reaction mixture.[8] Comparison of the ^{1}H NMR spectrum of the photoproduct with those for the *ctt* isomers of *p*, *p*′-dinitro- and *p*, *p*′-dimethoxy-substituted DPHs (**2** and **3**, respectively) allows a tentative assignment of the product to 1-*ctt*-**1**.[9] Triplet sensitized irradiation of *ttt*-**1** in Tol using tetraphenylporphine sensitizer gave *tct*-**1** exclusively; the pss mixture contained *ttt*-**1** (94%) and *tct*-**1** (6%). Thus it is clear that the isomerization induced by direct irradiation in Tol proceeds via singlet excited states. In contrast to the observations in Tol, the isomerization in AN was inefficient (Table 1). The solvent effects on the isomerization of *ttt*-**1** are found to be reverse to those for symmetrically substituted DPHs.[4,5] The HPLC analysis showed the presence of *tct* and *ctt* isomers in the pss mixture.

Table 1. Photochemical data for *ttt*-**1**

	Isomer ratio at pss/%[a]						
Solvent	*ttt*	*ctt*	*tct*	$\phi_{ttt\text{-}ctt}$	$\phi_{ttt\text{-}tct}$	ϕ_f	τ_s/ns
Tol	73	27	n.d.[b]	0.10	0.00	0.41	1.5
AN	91	2	7	5×10^{-4}	8×10^{-4}	0.035	<0.3[c]

[a]Irradiation wavelength: 419 ± 10 nm in Tol and 411 ± 10 nm in AN. [b]Not detected. [c]Shorter than the time resolution of our single-photon counting apparatus.

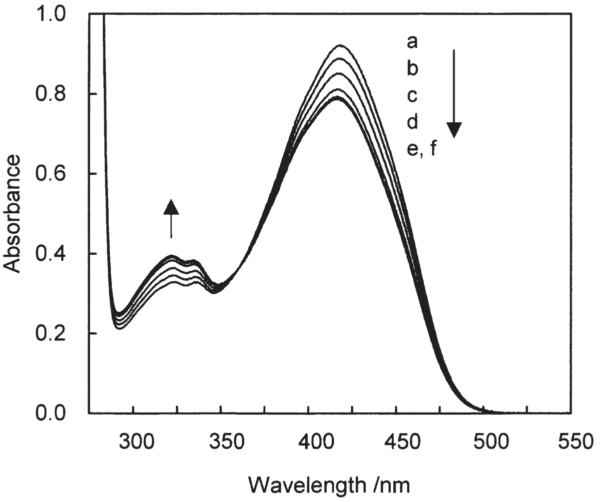

Figure 1. Changes in UV–vis spectra on irradiation of *ttt*-**1** in Tol. Irradiation wavelength: 419 ± 10 nm. Irradiation time: (a) 0, (b) 2, (c) 8, (d) 30, (e) 60, and (f) 120 s.

Table 2. Absorption and emission maxima of *ttt*-**1**

Solvent	$\lambda_{\rm abs}$/nm	$\lambda_{\rm em}$/nm
MCH	440, 413,[a] 391, 314	458, 489,[a] 517, 563
Tol	419,[a] 323	533
DCM	419,[a] 325	696
AN	411,[a] 323	735

[a] Main peak.

Similarly to other D–A-substituted DPHs,[6] the fluorescence emission maximum ($\lambda_{\rm em}$) of *ttt*-**1** was highly solvent-dependent, whereas the absorption maximum ($\lambda_{\rm abs}$) for the main peak was not significantly affected by the solvent polarity (Table 2). In methylcyclohexane (MCH), the fluorescence spectrum showed a vibrational structure and was almost a mirror image of the structured absorption at wavelengths longer than 350 nm, indicating that the emission originates from the singlet excited state of the *ttt* isomer, *ttt**. On the other hand, the emission spectra in dichloromethane (DCM) and AN were strongly red-shifted and structureless, which were considered to be the emission from intramolecular charge transfer state (CT*).[6] Although the excited states responsible for fluorescence emission in Tol are not determined at present, the moderately red-shifted $\lambda_{\rm em}$ suggests the presence of an equilibrium between *ttt** and CT*.

Within the model of 'the theory of biradicaloid states,' the twisted states *p** for push-pull ethylenes or D–A stilbenes are expected to have weakly polarized 'dot-dot' structures.[3] In this model, the pre-twisting planar states are rather more strongly polarized by strong conjugation between D and A substituents. If we assume a similar weakly polarized structure of *p** for the present compound, we can easily understand the observed solvent effects on the photoisomerization of *ttt*-**1**. In Tol, *p** is stabilized while the pre-twisting state(s) (*ttt** and/or CT*) is unstabilized, leading to a small activation energy ($\Delta E_{\rm a}$) for twisting. The formation of the 1-*ctt* isomer may possibly be related with a small electron density of the C1–C2 double bond relative to that for the C5–C6 bond in the pre-twisting excited state(s). It is likely that twisting occurs more easily around double bonds with less electron density. In AN, on the other hand, CT* is expected to be strongly stabilized, resulting to the increase in $\Delta E_{\rm a}$. It should be noted, however, that the decrease in the isomerization quantum yield with increasing solvent polarity was not accompanied with the increase in $\phi_{\rm f}$ and $\tau_{\rm s}$ (Table 1). The very low energy of CT* (735 nm, 39 kcal/mol; 1 cal = 4.184 J) in AN probably increases the efficiency of internal conversion (IC) from CT*.[10] The efficient IC from CT*, which competes with conversion to *p** and fluorescence emission, would reduce not only the isomerization yields but also $\phi_{\rm f}$.

Photochemical and photophysical properties of D–A-substituted stilbenes have been extensively studied.[11–13] For *p*-dimethylamino-*p*′-cyano derivative, it is reported that $\Delta E_{\rm a}$ for $t \rightarrow c$ isomerization increases considerably with increasing solvent polarity.[12] The results were explained in terms of strongly polar nature of pre-twisting state CT* as compared to *p** and the transition state for CT* → *p** conversion. The photoisomerization of *trans*-*p*-methoxy-*p*′-nitro-stilbene (*t*-**4**) is also shown to be much more efficient in low polar solvents than in highly polar solvents.[13] In this case, however, the isomerization occurs via triplet states as a result of nitro substitution. In spite of having the same substituents as *t*-**4**, *ttt*-**1** underwent no triplet isomerization on direct irradiation in Tol. This suggests that triplet *p** is in equilibrium with the triplet state of the *ttt* isomer, and that the energy minimum occurs at a twisting angle of less than 90° for *p** on the triplet potential surface.

For *trans*, *trans*-1,4-diphenyl-1,3-butadiene system, Rettig et al. have reported the photoisomerization of *p*-dimethylamino-*p*′-cyano-substituted derivative in polar solvents.[14] The isomerization behavior in low polar solvents is not reported; however, from the increase in $\phi_{\rm f}$ and $\tau_{\rm s}$ with increasing solvent polarity, the authors expected the isomerization to be more efficient in low polar solvents, and interpreted the results by assuming a 'dot-dot' character of *p**.

In our present study, it is found that *ttt*-**1** isomerized to *ctt*-**1** in Tol, whereas the isomerization in AN was inefficient. The highly solvent-dependent photochemical behavior can be explained in terms of weakly polar nature of *p**.[15]

References and Notes

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7 Triene *ttt*-**1** was prepared by the Wittig reaction of *p*-methoxycinnamaldehyde and the triphenylphosphonium salt of *p*-nitrocinnamylbromide. The crude product was a mixture of *ttt*-**1** and *tct*-**1**, which was recrystallized from Tol to give pure *ttt*-**1** (mp 183–184 °C).

8 *ttt*-**1**: UV–vis/nm (AN) $\lambda_{\rm abs}$ (ε/mol^{-1}dm^{3}cm^{-1}) 411 (6.08×10^4), 323 (2.62×10^4). *ctt*-**1**: 400 (4.5×10^4), 320 (5.2×10^4). *tct*-**1**: 410 (3.9×10^4), 315 (3.3×10^4).

9 1-*ctt*-**1** (tentative): ^{1}H NMR (Tol-d_8) δ 7.82 (2H, d, $J =$ 9.2 Hz, arom., *p*-$NO_2C_6H_4$)), 3.29 (3H, s, OCH_3). 1-*ctt*-**2**: 7.83 (2H, d, $J = 8.9$, arom., 6-(*p*-$NO_2C_6H_4$)), 7.79 (2H, d, $J = 8.9$, arom., 1-(*p*-$NO_2C_6H_4$)). 1-*ctt*-**3**: 3.30 (3H, s, OCH_3, 1-(*p*-$OMeC_6H_4$)), 3.33 (3H, s, OCH_3, 6-(*p*-$OMeC_6H_4$)).

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