A Heavy-Atom Effect on the *cis-trans* Photoisomerization of Bisformyl-Substituted *trans,trans,trans*-1,6-Diphenyl-1,3,5-hexatriene

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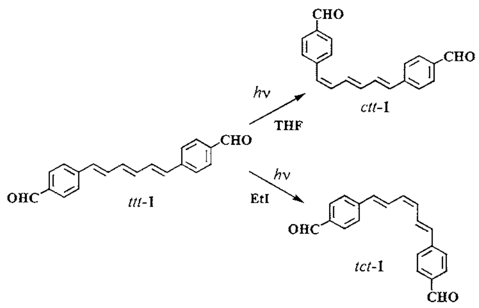
On irradiation of *p,p'*-bisformyl-substituted *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene in ethyl iodide, *trans,trans,trans* → *trans,cis,trans* isomerization was predominantly observed, which is in contrast to stereoselective *trans,trans,trans* → *cis,trans,trans* isomerization in common organic solvents.

The electronically excited-state properties of α,ω-diphenylpolyenes have been extensively studied because of their significance as model compounds not only for biological systems like rhodopsin and carotenes, but also for conjugated polymers exhibiting high electroconductivities and nonlinear optical activities.[1,2] Among these polyenes, *trans,trans,trans*-1,6-diphenyl-1,3,5- hexatriene (*ttt*-DPH) is of particular interest since it is the shortest chromophore in this series that has ^1A_g state as its lowest excited singlet state.[3] In comparison to numerous studies of spectroscopic properties, however, *cis-trans* photoisomerization of *ttt*-DPH has received less attention. Direct and sensitized irradiations of *ttt*-DPH produce complex mixtures which consist of the *ttt*, *cis,trans,trans* (*ctt*), *trans,cis,trans* (*tct*) and *cis,cis,trans* (*cct*) isomers.[4,5]

In the course of our study on the synthesis of a new conjugated polymer, we have found that a model compound *ttt*-1,6-bis (*p*-formylphenyl)-1,3,5-hexatriene (*ttt*-**1**) showed very simple photochemical behavior.[6] In contrast to the nonstereoselective photoisomerization of *ttt*-DPH, *ttt*-**1** isomerized in common organic solvents such as acetonitrile and methanol to give the *ctt* isomer stereoselectively without formation of any sizable amounts of other isomers or other photoproducts.[7-9] We now report that *ttt*-**1** is irradiated in a heavy-atom solvent ethyl iodide (EtI) to give the *tct* isomer predominantly, which was not detected in the photoreaction mixture obtained after irradiation in common organic solvents.

Irradiation of an argon-degassed solution of *ttt*-**1** in THF (3 x 10^{-5} mol dm^{-3})[10] with light of wavelengths 420 ± 7 nm gave a photostationary mixture containing only *cis-trans* isomers as monitored by a reverse-phase HPLC with a multi-channel photodetector.[11] No significant change was observed in the total amount of the isomers. Geometries of the *cis-trans* isomers were determined to be *ttt* and *ctt* by comparing ^{1}H NMR and UV-vis absorption spectra with those of the authentic samples described previously.[7] The *tct* isomer could not be detected. On the contrary, irradiation of *ttt*-**1** in EtI under similar conditions gave a photostationary mixture composed of the *ttt*, *tct*, and a trace amount of the *ctt* isomers. The *tct* isomer[12] was identified by comparing ^{1}H NMR and UV-vis absorption spectra with those of authentic *tct*-DPH[7] prepared chemically by Wittig reaction. The stereoselectivity in isomerization of *ttt*-**1** thus changed remarkably with changing the solvent from THF to EtI. Table 1 summarizes quantum yields of the *ttt* → *ctt* and *ttt* → *tct* isomerizations, $\phi_{ttt\text{-}ctt}$ and $\phi_{ttt\text{-}tct}$ respectively, in THF-EtI mixed solvents containing various amounts of EtI. With increasing EtI concentration, [EtI], a large decrease in $\phi_{ttt\text{-}ctt}$ was observed. On the other hand, changes in $\phi_{ttt\text{-}tct}$ were not clear at least in the range of [EtI] studied due to large experimental errors because of uncertainty in the determination of the small amount of *tct*-**1**. It is obvious, however, that $\phi_{ttt\text{-}tct}$ was enhanced in EtI compared to the value in THF. Thus the dependence of $\phi_{ttt\text{-}tct}$ on [EtI] differed entirely from that of $\phi_{ttt\text{-}ctt}$. Since the dielectric constant and viscosity of THF are practically the same as those of EtI, the observed decrease in $\phi_{ttt\text{-}ctt}$ and increase in $\phi_{ttt\text{-}tct}$ with increasing [EtI] should be a result from an enhanced S → T intersystem crossing efficiency due to a heavy-atom effect of EtI.



To obtain spectroscopic evidence for the enhancement of intersystem crossing efficiency due to EtI, fluorescence quantum yields, ϕ_f, excited singlet lifetimes, τ_s, and T-T transient absorption spectra of *ttt*-**1** were measured in THF-EtI solvents. The data shown in Table 1 indicate that ϕ_f and τ_s decreased monotonically as [EtI] increased. As illustrated in Figure 1, on the other hand, T-T absorption intensities were enhanced with increasing [EtI]. The enhancement of S → T intersystem crossing efficiency by EtI was thus established by the fluorescence and T-T absorption measurements.[13] The rate constant, k_q^s, for the quenching of singlet excited state of *ttt*-**1** by EtI was determined to be 4.6 x 10^8 $M^{-1}s^{-1}$ from the slope of the Stern-Volmer plot based on ϕ_f measurements, $k_q^s \tau_s = 0.43$ M^{-1}, and $\tau_s = 0.94$ ns in THF. A value

Table 1. Isomerization and fluorescence quantum yields and excited singlet lifetimes of *ttt*-**1** in THF-EtI mixed solvents

[EtI] / M	$\phi_{ttt\text{-}ctt}$ [a]	$\phi_{ttt\text{-}tct}$ [a]	ϕ_f [b]	τ_s / ns [b]
0.00	0.17	0.000	0.36	0.94
0.38	0.13	0.008	0.32	0.85
0.94	0.11	0.010	0.25	0.67
1.56	0.10	0.009	0.21	0.56
3.13	0.070	0.005	0.16	0.35
12.50	0.002	0.032	0.035	0.14

[a] Irradiation wavelength: 420 ± 7nm. [b] Excitation wavelength: 420 nm.

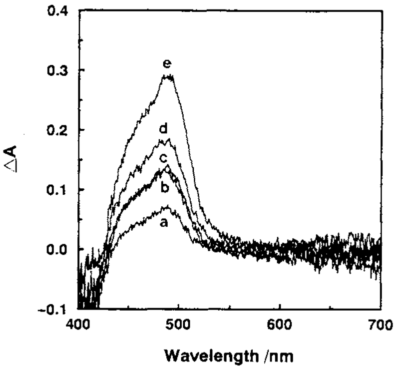


Figure 1. T-T transient absorption spectra of *ttt*-**1** in THF-EtI mixed solvents. [EtI]: a) 0.00, b) 0.38, c) 0.94, d) 1.56 and e) 3.13M. Excitation wavelength: 355 nm. Delay time: 50 ns. Gate width: 20 ns.

of $k_q^{s} = 5.5 \times 10^8\ M^{-1}s^{-1}$ obtained from a Stern-Volmer plot analog[14] based on the T-T absorption measurements agreed roughly with that from ϕ_f measurements. More importantly, the slope of the Stern-Volmer plot based on $\phi_{ttt\text{-}ctt}$ measurements, 0.41 M^{-1}, is in fairly good agreement with that of the plot based on ϕ_f measurements. The fact that EtI quenches the fluorescent state with the same efficiency as it inhibits the *ttt* → *ctt* isomerization indicates that a singlet excited state is responsible for the *ttt* → *ctt* isomerization of *ttt*-**1**. In contrast, combination of the enhanced $\phi_{ttt\text{-}tct}$ and T-T absorption intensities in EtI-containing solvent suggests that the *ttt* → *tct* isomerization occurs from a triplet excited state.

The above assignment of the excited states for the isomerizations was confirmed by triplet sensitized experiments. On irradiation of *ttt*-**1** in acetonitrile with light of wavelengths 655 ± 7 nm using Methylene Blue (triplet energy E_T = 138 kJ/mol) as a sensitizer, *tct*-**1** was formed exclusively. The isomer ratio at a photostationary state was *ttt*-**1** : *tct*-**1** = 92 : 8, which was in markedly contrast to the ratio *ttt*-**1** : *ctt*-**1** = 51 : 49 for a photostationary mixture obtained after direct irradiation of *ttt*-**1** with 359[15] ± 7 nm light in the same solvent.

Twisted singlet excited states of polyenes are described as charge-separated, zwitterionic structures in the VB theory (sudden polarization effect), which is in contrast to the fundamental biradicaloid character of twisted triplet states.[16,17] It has been proposed that the charge-separations may bring about very polar excited states if the symmetry is perturbed. Therefore the efficient *ttt* → *ctt* isomerization of *ttt*-**1** from singlet excited state $^1ttt^*$ indicates that the asymmetric, more ionic twisted intermediate $^1ptt^*$ rather than the symmetric, less ionic $^1tpt^*$ is preferentially formed from $^1ttt^*$. On the other hand, the *ttt* → *tct* isomerization from triplet excited state $^3ttt^*$ shows that twisting from $^3ttt^*$ favors the symmetric $^3tpt^*$ rather than the asymmetric $^3ptt^*$. The highly polarized, ionic character of $^1ptt^*$ is also suggested from our previous results that the *ttt* → *ctt* isomerization occurs more efficiently in polar solvents.[8]

From the quenching of fluorescence and the enhancement of T-T absorption intensities, the quantum yield of S → T intersystem crossing, ϕ_{isc}, of *ttt*-**1** in THF were evaluated to be 0.17 by Wilkinson method.[18] In spite of the moderate value of ϕ_{isc}, *tct*-**1** was not detected in the reaction mixture in THF, suggesting the low efficiency of isomerization from $^3ttt^*$. This is consistent with the fact that the photostationary state reached by the sensitized irradiation is considerably rich in the *ttt* isomer. The low efficiency of isomerization from $^3ttt^*$ is tentatively explained in terms of the equilibrium $^3ttt^* \rightleftharpoons {}^3tpt^*$. It is probable, by analogy with 1,4-diphenyl-1,3-butadiene,[19] that the minimum in the triplet potential energy surface of compound **1** occurs at a twisting angle of $^3tpt^*$ less than 90°.

Irradiation of *ttt*-**1** in heavy-atom solvent EtI produced *tct*-**1**, which was not detected in the photostationary mixture obtained after irradiation in common organic solvents. Based on the measurements of $\phi_{ttt\text{-}ctt}$, $\phi_{ttt\text{-}tct}$, ϕ_f and the T-T transient absorption spectra, we conclude that the *ttt* → *ctt* and *ttt* → *tct* isomerizations predominantly occur from singlet and triplet excited states of *ttt*-**1**, respectively. The stereoselectivity in the triplet isomerization was shown to be entirely different from that in the singlet isomerization.

References and Notes

1 D. C. Rodenberger, J. R. Heflin, and A. F. Garito, *Nature*, **359**, 309 (1992).
2 Y. Sonoda, Y. Suzuki, E. Van Keuren, and H. Matsuda, *Macromolecules*, **29**, 288 (1996).
3 M. T. Allen and D. G. Whitten, *Chem. Rev.*, **89**, 1691 (1989).
4 J. Saltiel, D. -H. Ko, and S. A. Fleming, *J. Am. Chem. Soc.*, **116**, 4099 (1994).
5 J. Saltiel, S. Wang, D. -H. Ko, and D. A. Gormin, *J. Phys. Chem. A.*, **102**, 5383 (1998).
6 Y. Sonoda and K. Kaeriyama, *Polymer*, **33**, 2437 (1992).
7 Y. Sonoda and Y. Suzuki, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 401.
8 Y. Sonoda and Y. Suzuki, *Chem. Lett.*, **1996**, 659.
9 Y. Sonoda, H. Morii, M. Sakuragi, and Y. Suzuki, *Chem. Lett.*, **1998**, 349.
10 Concentration of *ttt*-**1** was kept high enough to minimize the fraction of light absorbed by the solvent, as EtI absorbs to a small extent at 420 nm (< 0.01 OD for [EtI] = 3.13 M in THF solution). Optical density of *ttt*-**1** in THF-EtI mixed solvent was approximately 2.0 at 420 nm.
11 Since the *cis* isomers were thermally unstable to return to *ttt*-**1** on heating in the presence of EtI, the THF - EtI solvent was quickly evaporated from the irradiated sample solution at 0-10 °C. The resulting residue in acetonitrile was subjected to HPLC analysis.
12 *tct*-**1**: ^{1}H NMR (270 MHz, CDCl$_3$) δ 10.00 (s, 2H), 7.88 (d, J = 8.1, 4H), 7.64 (d, J = 8.1, 4H), 7.50-7.60 (m, 2H), 6.71 (d, J = 15.1, 2H), 6.34- 6.40 (m, 2H); UV-vis / nm (CH$_3$CN) λ_{max} (ε / dm^{3}mol^{-1}cm^{-1}) 388 (5.5 x 10^4), 300 (2.4 x 10^4).
13 Triplet lifetimes, τ_T, were evaluated from the decay of T-T transient absorption to be 5.5 and 1.3 μs for [EtI] = 0.0 and 3.13 M, respectively. The decrease in τ_T with increasing [EtI] shows that not only S → T but also T → S intersystem crossing rates were enhanced by the heavy-atom effect of EtI.
14 S. K. Chattopadhyay, P. K. Das, and G. L. Hug, *J. Am. Chem. Soc.*, **104**, 4507 (1982).
15 Wavelength of the isosbestic point of *ttt*-**1** and *ctt*-**1** in acetonitrile.[8]
16 L. Salem, *Acc. Chem. Res.*, **12**, 87 (1979).
17 M. Klessinger and J. Michl, "Excited States and Photochemistry of Organic Molecules," VCH Publishers Inc., New York (1995), pp. 361-378.
18 A. R. Horrocks, A. Kearvell, K. Tickle, and F. Wilkinson, *Trans. Faraday Soc.*, **62**, 3393 (1966).
19 S. K. Chattopadhyay, C. V. Kumar, and P. K. Das, *J. Photochemistry*, **26**, 39 (1984).