Substituent Effect on the *cis-trans* Photoisomerization of *trans,trans,trans*-1,6-Diphenyl-1,3,5-hexatrienes

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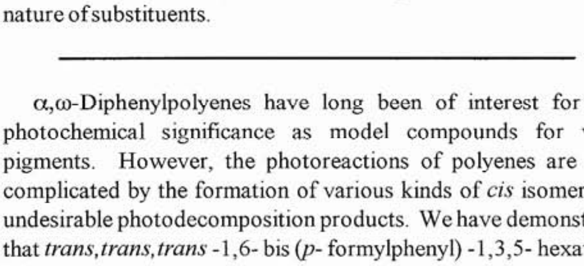
Quantum yield of *trans,trans,trans* → *cis,trans,trans* photoisomerization of *p,p'*-disubstituted 1,6-diphenyl-1,3,5-hexatriene increased as the polarity of substituents increased, regardless of their electron-withdrawing or donating nature. On the contrary, quantum yield of *trans,trans,trans* → *trans,cis,trans* isomerization increased with increasing the electron-donating nature of substituents.

α,ω-Diphenylpolyenes have long been of interest for their photochemical significance as model compounds for visual pigments. However, the photoreactions of polyenes are often complicated by the formation of various kinds of *cis* isomers and undesirable photodecomposition products. We have demonstrated that *trans,trans,trans*-1,6-bis(*p*-formylphenyl)-1,3,5-hexatriene (*ttt*-**1**, R = CHO) isomerized to give the *cis,trans,trans* (*ctt*) isomer stereoselectively without formation of any sizable amounts of other isomers or other photoproducts.[1] The stereoselectivity was not affected by the solvent polarity.[2] The photochemical behavior is exceptionally simple and clear compared to complex one of other polyenes including unsubstituted 1,6-diphenyl-1,3,5-hexatriene (DPH).[3,4] We now report that *p,p'*-disubstituted DPH derivatives having electron-withdrawing groups on the phenyl rings undergo stereoselective *ttt* → *ctt* isomerization like the formyl derivative, whereas derivatives with electron-donating or less polar groups exhibit non-stereoselective *ttt* → *ctt* + *trans,cis,trans* (*tct*) isomerization, resulting from differential substituent effects on the *ttt* → *ctt* and *ttt* → *tct* isomerizations.



On irradiation[5] of an argon-saturated solution of the *ttt* isomers of *p,p'*-dicyano, di(methoxycarbonyl), diformyl, dichloro, dimethyl and dimethoxy derivatives[6] (*ttt*-**1**, R = CN, $COOCH_3$, CHO, Cl, CH_3, and OCH_3, respectively) in acetonitrile ($1\text{-}2 \times 10^{-5}$ mol dm^{-3}), the UV-vis spectrum changed rapidly to reach a photostationary state. The photostationary mixture contained only *cis-trans* isomers as monitored by HPLC with a multichannel photodetector. The derivatives with electron-withdrawing substituents such as cyano and methoxycarbonyl groups, underwent stereoselective isomerization to give mixtures of *ttt* and *ctt* isomers, similarly to the formyl derivative (Table 1). On the contrary, the derivatives with electron-donating methoxy, or less polar substituents such as methyl and chloro groups, isomerized non-stereoselectively to give photostationary mixtures containing *ttt*, *ctt*, *tct* and occasionally trace amounts of *cis,cis,trans* (*cct*) isomers (Table 1).[10]

The stereoselective *ttt* → *ctt* isomerization observed for the derivatives with the electron-withdrawing groups reflects large difference between the quantum yields[12] of the *ttt* → *ctt*, $\phi_{ttt\text{-}ctt}$, and *ttt* → *tct* isomerization, $\phi_{ttt\text{-}tct}$. The non-stereoselective isomerization for the derivatives with the electron-donating or less polar groups, on the other hand, corresponds to relatively small difference between $\phi_{ttt\text{-}ctt}$ and $\phi_{ttt\text{-}tct}$ (Table 1). These are attributed to differential substituent effects on the *ttt* → *ctt* and *ttt* → *tct* isomerizations; $\phi_{ttt\text{-}ctt}$ increased as the polarity of substituents increased regardless of their electron-withdrawing or donating nature, whereas $\phi_{ttt\text{-}tct}$ gradually but clearly increased with increasing the electron-donating nature of substituents. It is obvious that substituent effect on $\phi_{ttt\text{-}tct}$ is entirely different from that on $\phi_{ttt\text{-}ctt}$.

By analogy of 1,4-diphenyl-1,3-butadiene,[13] it can be assumed that *ttt* → *ctt* and *ttt* → *tct* isomerizations take place from perpendicular transient states, *ptt** and *tpt**. The observed differential substituent effects on $\phi_{ttt\text{-}ctt}$ and $\phi_{ttt\text{-}tct}$ are due mainly to the substituent-dependence of efficiencies of *ttt** → *ptt** and *ttt** → *tpt** conversions on the excited state surface. The increase in $\phi_{ttt\text{-}ctt}$ with increasing the polarity of substituents is understandable in terms of a greater stabilization of *ptt** by the substituents presumably because of its highly polarized structure. The gradual increase in $\phi_{ttt\text{-}tct}$ suggests that *tpt** is stabilized by electron-donating groups.

Another possible mechanism is that the isomerizations proceed through a common transient state *p**. This *p** state, generated from *ttt**, decays to *p* on the ground state surface, and from there, the *ctt*, *tct*, and *ttt* isomers are produced with probabilities α, β, and 1-α-β, respectively. On this assumption, the substituent effects on $\phi_{ttt\text{-}ctt}$ and $\phi_{ttt\text{-}tct}$ can be attributed to the substituent-dependence of α and β; for the derivatives with the electron-withdrawing groups, *p* gives the *ctt* isomer favorably, while for the derivatives with the electron-donating groups, not only *ctt* but also *tct* isomers are efficiently formed from *p*. For all of the diphenylhexatrienes under study, the isomerization behavior in air was not significantly different from that in argon. Values of $\phi_{ttt\text{-}ctt}$ and $\phi_{ttt\text{-}tct}$ in air for the methoxy derivative, for example, were 0.27 and 0.10 respectively. This suggests that the direct isomerization of diphenylhexatrienes occurs, at least mainly, from singlet excited states. Direct internal conversion, *ttt** → *ttt*, for the derivatives with polar substituents appears inefficient since $\phi_{ttt\text{-}ctt} + \phi_{ttt\text{-}tct}$ is relatively large. If very small quantum yields of intersystem crossing and internal conversion are assumed, then the values of α and β, and rate constant for *ttt** → *p** process, k_p, can be estimated as α = 0.48, β

Table 1. UV-vis absorption maxima, isomerization and fluorescence quantum yields, singlet lifetimes of *ttt*-**1** and isomer ratios at photostationary states in acetonitrile

Derivative R for *ttt*-**1**	Hammett parameter σ_p[a]	λ_{max}[b] / nm (ε[c])	$\phi_{ttt\text{-}ctt}$[d]	$\phi_{ttt\text{-}tct}$[d]	ϕ_f[e]	τ_s[f] / ns	Isomer ratio[g]			
							ttt	*ctt*	*tct*	*cct*
CN	0.66	374 (6.60×10^4)	0.46	0.00[h]	0.032	0.17	37	63	0	0
$COOCH_3$	0.45	376 (7.86×10^4)	0.36	0.00[h]	0.060	0.20	41	59	0	0
CHO	0.42	390 (8.24×10^4)	0.33	0.00[h]	0.073	0.13	38	62	0	0
Cl	0.23	359 (8.86×10^4)	0.14	0.082	0.22[j]	3.5	54	38	8	trace
H	0.00	352 (8.44×10^4)	0.075[i]	0.049[i]	0.23	3.2	59[i]	29[i]	10[i]	2[i]
CH_3	- 0.17	357 (7.72×10^4)	0.12	0.096	0.32[j]	4.6	62	24	14	trace
OCH_3	- 0.27	365 (8.05×10^4)	0.29	0.13	0.07[j]	0.55	43	50	7	trace

[a] Reference 8. [b] Absorption maxima in acetonitrile. [c] Molar absorption coefficient ($dm^3\ mol^{-1}\ cm^{-1}$). [d] Irradiation wavelength $\lambda_{irr} = \lambda_{max} \pm 7$ nm; for the formyl derivative, 365 ± 7 nm. [e] $\lambda_{irr} = 360$ nm. [f] $\lambda_{irr} = 337$ nm. [g] $\lambda_{irr} = \lambda_{max} \pm 0.7$ nm. [h] No *tct* isomer was detected by HPLC. [i] Reference.4; $\lambda_{irr} = 366$ nm. [j] Reference 9.

$=0.00$ and $k_p = 5.6 \times 10^9\ s^{-1}$ for the cyano derivative, and $\alpha = 0.31$, $\beta = 0.14$ and $k_p = 1.7 \times 10^9\ s^{-1}$ for the methoxy derivative, from measured $\phi_{ttt\text{-}ctt}$, $\phi_{ttt\text{-}tct}$, fluorescence quantum yield, ϕ_f, and singlet lifetime, τ_s (Table 1).[12]

Our present results clearly demonstrate the differential substituent effects on *ttt* → *ctt* and *ttt* → *tct* isomerizations.[14] The values of $\phi_{ttt\text{-}ctt}$ increased with increasing the polarity of substituents, whereas $\phi_{ttt\text{-}tct}$ increased as the electron-donating nature of substituent increased. It is suggested that an electron-withdrawing group conjugating with conjugated double bonds plays a key role in exhibiting stereoselective isomerization of polyenes. This may closely be related to the well-known stereoselective *cis-trans* isomerization of rhodopsin, which is the crucial molecule for vision.

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References and Notes

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10 Geometries of *ttt*, *ctt* and *tct* isomers were confirmed by comparison of ^1H NMR and UV-vis absorption spectra with those of authentic samples of the corresponding isomers of DPH prepared by Wittig reaction.[11] *cct* Isomers were identified from the UV-vis spectra by comparing with that of *cct*-DPH.[3]

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12 Quantum yields of isomerization were measured using the formyl derivative ($\phi_{ttt\text{-}ctt} = 0.33$ in acetonitrile)[2] as a reference. Concentrations of the *ctt* and *tct* isomers were determined from the combination of initial concentration of the *ttt* isomer and an isomer ratio at the stage of 5 - 10 % conversion. Fluorescence quantum yields were measured as previously described.[2] Singlet lifetime was evaluated from fluorescence lifetime, which was measured by the single photon counting method. A gated pico-second nitrogen laser provided excitation with half-band width of 1.0125 ns. Sample solution in acetonitrile was degassed with argon. Concentrations were 0.03 - 0.04 OD at the excitation wavelength.

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14 The presence of a ground-state s-*cis* conformer, which is ignored in the present study, may be important in quantum yield measurement of *cis-trans* isomerization of polyenes, because the double bond isomerization of s-*cis* conformer is considered to be sterically hindered. The fluorescence spectrum of s-*cis* conformer(s) of *ttt*-DPH is red-shifted compared to that of all-s-*trans* conformer.[15] Therefore, to understand the role of s-*cis* conformer(s) in the isomerization of the diphenylhexatrienes, it is necessary to investigate the product distribution after extreme red edge excitation of the absorption spectrum of the *ttt* isomer.

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