Solvent-Dependent *cis-trans* One-Way Photoisomerization of Bisformyl-Substituted 1,6-Diphenyl-1,3,5-hexatriene

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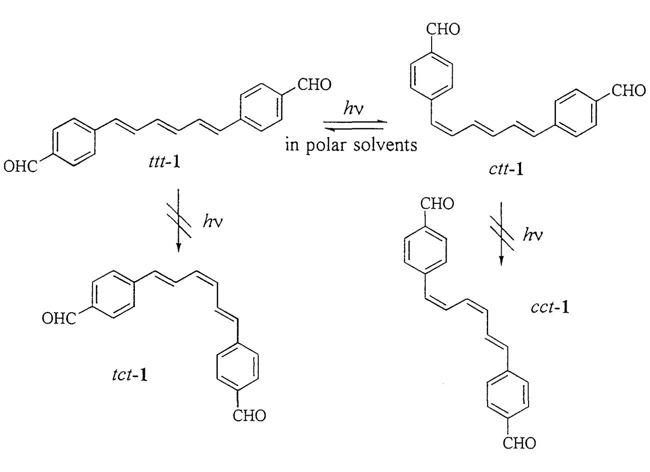
trans,trans,trans-1,6-Bis(*p*-formylphenyl)-1,3,5-hexatriene underwent stereoselective photoisomerization to give its *cis,trans,trans* isomer regardless of the solvent polarity. Quantum yields of *trans,trans,trans*-to-*cis,trans,trans* isomerization decreased dramatically with decreasing solvent polarity, whereas those of the reverse reaction gradually increased. This led to the *cis,trans,trans*-to-*trans,trans,trans* 'one-way' isomerization in nonpolar solvents.

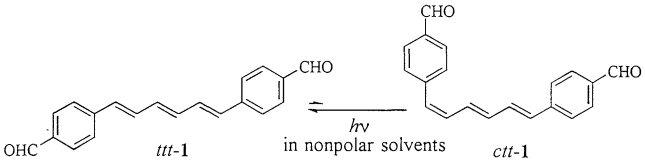
Irradiation of *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH) in solution gives a mixture of *cis,trans,trans* (*ctt*), *trans,cis,trans* (*tct*) and *cis,cis,trans* (*cct*) isomers,[1] from which various kinds of photoproducts are formed.[2] The low stereoselectivity in the isomerization and the irreversibility of the reaction prevent us from full understanding of the *cis-trans* isomerization of DPH.

Recently, we have found[3] that the *ttt* isomer of bisformyl-substituted DPH, 1,6-bis(*p*-formylphenyl)-1,3,5-hexatriene (*ttt*-**1**), showed a very simple, clear photochemical behavior which is quite different from that of the unsubstituted parent compound; it undergoes the terminal bond isomerization to give the *ctt* isomer (*ctt*-**1**) stereoselectively without formation of any sizable amounts of other isomers or other photoproducts. A report of the differential solvent effect on the *ttt*-to-*ctt* and *ttt*-to-*tct* isomerization of *ttt*-DPH[1] prompted us to examine the effect of solvent polarity on the stereoselectivity in the isomerization of **1**. We now report that the solvent polarity does not affect the stereoselectivity but affects the mode, 'mutual' or 'one-way', of the isomerization.

On direct irradiation of a degassed solution of *ttt*-**1**[4a] ($1\text{-}2 \times 10^{-5}$ mol dm^{-3}) in polar solvents such as acetonitrile and methanol with light of wavelengths around the absorption maximum, the UV-vis spectrum changed rapidly with an isosbestic point to reach a photostationary state. HPLC and UV-vis spectrum analyses showed the photostationary mixture to contain only *ttt*-**1** and *ctt*-**1**. Irradiation of *ctt*-**1**[4b] led to the same photostationary state as that obtained from *ttt*-**1**. Neither measurable amounts of other isomers including *tct*- and *cct*-**1**, nor other photoproducts were detected in the photostationary mixture. Also in the solvents with medium polarity such as dichloromethane and chloroform, the stereoselective terminal isomerization was similarly observed. The differences between the quantum yields of *ttt*-to-*ctt* isomerization, $\phi_{ttt\text{-}ctt}$, and those of the reverse reaction, $\phi_{ctt\text{-}ttt}$,[5a] were relatively small in these solvents (Table 1). This led to the 'mutual' isomerization between the two isomers.



Irradiation of *ttt*-**1** in nonpolar solvents, for example toluene and methylcyclohexane, gave a very little change to the UV-vis spectrum before the system reached a photostationary state. The photostationary mixture was shown by HPLC and UV-vis spectra to be extremely rich in *ttt*-**1**, and to contain only a trace amount of the *ctt* isomer. On irradiation of *ctt*-**1**, the spectrum changed rapidly with an isosbestic point to reach the photostationary state. Thus almost 'one-way' isomerization was observed in nonpolar solvents. The photostationary state with a very high composition of *ttt*-**1** results from the much higher $\phi_{ctt\text{-}ttt}$ compared with $\phi_{ttt\text{-}ctt}$; in toluene, $\phi_{ctt\text{-}ttt}$ was more than 200 times larger than $\phi_{ttt\text{-}ctt}$ (Table 1). In contrast to this strong solvent dependence of the isomer ratio at the photostationary state, the stereoselectivity in the isomerization of *ttt*-**1** was not affected by the solvent polarity. Even in nonpolar solvents, only the terminal isomerization was observed.



The solvent-independent stereoselectivity in the isomerization of *ttt*-**1** indicates that the terminal twisted singlet excited state, $^1ptt^*$, is energetically lower than the central twisted state, $^1tpt^*$, at least in any solvents used in our experiments. If we assume that $^1ptt^*$ is more ionic than $^1tpt^*$, then the lower energy of $^1ptt^*$ would be reasonable because $^1ptt^*$ of **1** is expected to be more stabilized than $^1tpt^*$ by the intrinsic polarity of the molecule **1** due to the polarization of C=O groups. Although further experiments are required to confirm this idea, the assumption of the more ionic character of $^1ptt^*$ is in consistent with that postulated for DPH by Saltiel and co-workers.[1] Studies are now in progress to clarify the substituent effect on the stereoselectivity in the isomerization of diphenylhexatrienes.

The mode of isomerization drastically changed from 'mutual' to 'one-way' as the solvent polarity decreased. This can be explained by the changes in the relative energy of $^1ptt^*$ and $^1ttt^*$. We propose that in polar solvents, $^1ptt^*$ is at an energy minimum on the potential energy surface. In this case, both *ttt*-to-*ctt* and the reverse isomerization should occur from $^1ptt^*$. The small differences between $\phi_{ttt\text{-}ctt}$ and $\phi_{ctt\text{-}ttt}$ is reasonable, if we assume an equal partitioning from $^1ptt^*$ to *ttt*-**1** and *ctt*-**1**, by analogy of stilbene.[7] In nonpolar solvents, however, $^1ptt^*$ may no longer be at an energy minimum. We believe the formation of $^1ttt^*$ from $^1ptt^*$ more readily occurs

Table 1. UV-vis spectral characteristics, isomer ratios at the photostationary states, isomerization and fluorescence quantum yields of *ttt*-**1** and *ctt*-**1**

Solvent	dielectric constant [a]	λ_{max} [b] (ε [c] x 10^4) *ttt*-**1**	*ctt*-**1**	λ_{iso} [d]	isomer ratio [e] *ttt*-**1** : *ctt*-**1**	$\phi_{ttt\text{-}ctt}$	$\phi_{ctt\text{-}ttt}$ [e]	$\phi_{F(ttt)}$	$\phi_{F(ctt)}$ [f]
Acetonitrile	35.9	390 (8.2)	382 (5.4)	359	49 : 51	0.33	0.29	0.073	0.042
Methanol	32.7	389 (6.7)	380 (4.9)	365	55 : 45	0.23	0.35	0.061	0.015
Dichloromethane	8.9	395 (8.9)	389 (5.7)	363	54 : 46	0.27	0.23		
Chloroform	4.8	397 (8.7)	391 (5.5)	368	66 : 34	0.13	0.39		
Toluene	2.4	394 (8.0)	391 (5.6)	363	> 99 : < 1	< 0.003	0.68	0.76	0.59 [g]

[a] Ref. 9. [b] Absorption maxima (nm). [c] Molar absorption coefficient (mol^{-1} dm^3 cm^{-1}). [d] Isosbestic points of *ttt*- and *ctt*-**1** (nm). [e] Irradiation wavelength: $\lambda_{iso} \pm$ 7 nm in each solvent. [f] Excitation wavelength: 360 nm. [g] Fluorescence from $^1ttt^*$.

from the unstabilization of $^1ptt^*$. Therefore this will lead to an inefficient conversion from $^1ttt^*$ to $^1ptt^*$, which account for the very small $\phi_{ttt\text{-}ctt}$ observed in toluene.[8] The *ctt*-to-*ttt* isomerization, as opposed to the reverse isomerization from $^1ptt^*$, occurs mainly from $^1ttt^*$ because of the highly efficient conversion from $^1ptt^*$ to $^1ttt^*$. Efficient deactivation from $^1ttt^*$ to *ttt*-**1** resulting from the inefficient conversion from $^1ttt^*$ to $^1ptt^*$ leads to the relatively large $\phi_{ctt\text{-}ttt}$ in toluene.

Fluorescence spectrum data for *ttt*-**1** and *ctt*-**1** strongly support the idea of the efficient formation of $^1ttt^*$ from $^1ptt^*$ in nonpolar solvents. In acetonitrile and methanol, fluorescence spectra of *ttt*-**1** and *ctt*-**1** differed significantly, suggesting that these correspond to the emission from $^1ttt^*$ and $^1ctt^*$, respectively. While in toluene, the fluorescence spectrum of *ctt*-**1** was identical to that of *ttt*-**1**. Moreover, the spectrum of *ctt*-**1** was considered to be the emission from $^1ttt^*$, since it was almost the mirror image of the absorption spectrum of *ttt*-**1**. The fluorescence quantum yields of *ttt*-**1**, $\phi_{F(ttt)}$, and those of *ctt*-**1**, $\phi_{F(ctt)}$,[5b] increased as the solvent polarity decreased. These results correspond to the decrease in $\phi_{ttt\text{-}ctt}$ and the increase in $\phi_{ctt\text{-}ttt}$. The product of $\phi_{ctt\text{-}ttt}$ and $\phi_{F(ttt)}$ in toluene is nearly equal to $\phi_{F(ctt)}$, suggesting that both the isomerization and emitting fluorescence of *ctt*-**1** would occur mainly by deactivation from $^1ttt^*$.

Our present results show that the solvent polarity did not affect the stereoselectivity but affected the manner in the isomerization of *ttt*-**1**. The drastic change in the mode of isomerization with change in the solvent polarity can be explained by the efficient formation of $^1ttt^*$ from $^1ptt^*$ in nonpolar solvents. The fluorescence spectrum data of *ttt*-**1** and *ctt*-**1** are evidence for this postulate.

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4 a) The *ttt* isomer of **1** was prepared by the Wittig reaction of the ylide from *trans*-1,4-dichloro-2-butene and terephthalaldehyde.[3a] It was separated from by-products by recyclable GPC, and further purified by recrystallization from acetonitrile. b) The *ctt* isomer of **1** was isolated by GPC or preparative TLC from an isomeric mixture obtained by irradiation of *ttt*-**1** in chloroform.[3b]

5 a) For measurements of quantum yields of isomerization, the concentrations of each isomer in the reaction mixtures were determined from UV-vis spectra at the stage of 8-10% conversion. Light intensity was determined by potassium tris(oxalato)ferrate(III) actinometry; b) The reported values of $\phi_{F(ttt)}$ and $\phi_{F(ctt)}$ were determined by comparison of the integrated area of the fluorescence spectra with those of *ttt*-DPH in the corresponding solvents. For measurements of the fluorescence quantum yields of *ttt*-DPH in different solvents, *ttt*-DPH in cyclohexane (ϕ_F = 0.65)[6] was used as the reference. The integrated areas of the spectra were multiplied by the square of the refractive index of the solvent used and compared with that obtained for the reference. All the emission spectra were obtained with diluted solutions (OD < 0.05) optically matched at the excitation wavelength (360 nm) using a fully corrected spectrofluorimeter with a rhodamine B photoncounter.

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8 The very small $\phi_{ttt\text{-}ctt}$ in toluene can also be understood by postulating enhancement of activation energy, ΔE_a, for conversion from $^1ttt^*$ to $^1ptt^*$ in nonpolar solvents. However, if we assume an equal partitioning from $^1ptt^*$ to *ttt*-**1** and *ctt*-**1**, this can not explain the large $\phi_{ctt\text{-}ttt}$ in toluene. For the enhancement of ΔE_a in nonpolar solvents for diphenylpolyenes, see: S.L.Bondarev and S.M.Bachilo, *J.Photochem.Photobiol.A*, **59**, 273 (1991).

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