Isomerization of *cis,trans*- and *trans,trans*-1,4-diphenylbuta-1,3-dienes by photoinduced electron transfer

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Photosensitization of *cis,trans*- or *trans,trans*-1,4-diphenylbuta-1,3-diene using a light-absorbing acceptor such as 9,10-dicyanoanthracene results in their geometric isomerization and leads to a photostationary mixture rich in *trans,trans*-1,4-diphenylbuta-1,3-diene (> 94%) in benzene or acetonitrile. Spectroscopic studies in conjunction with quantum yield measurements suggest that a mechanism involving the triplet excited butadienes is feasible in benzene whereas a cation radical chain mechanism is operative in acetonitrile.

Cation radicals of alkenes and polyenes can be generated by electron transfer and there has been considerable interest in their reactivity.[1,2] Geometric isomerization is one of the most fundamental reactions of their cation radicals.[2–4] Photoinduced electron transfer (PET)[3] is a powerful means to investigate the isomerization of alkene and polyene cation radicals. For example, *cis–trans* isomerization of stilbenes by PET[5,6] has attracted considerable attention in recent years. Various techniques have been utilized to investigate the behaviour of stilbene cation radicals. It has been shown that stilbene cation radicals undergo one-way isomerization from *cis* to *trans* in not only the ground state[5,6] but also the excited state.[7a–c] As for the vinylene analogues of stilbene, all-*trans*-1,6-diphenylhexa-1,3,5-triene cation radical is also found to undergo photochemical geometric isomerization to a *cis* derivative.[7d] 1,4-Diphenylbuta-1,3-diene, **1**, is also an interesting system. Hug *et al.*[8a] have observed cation radicals of the three isomers (*cc*-**1**, *ct*-**1** and *tt*-**1**) by laser flash photolysis and found that cation radical cc-$\mathbf{1}^{\cdot+}$ undergoes relatively slow isomerization to tt-$\mathbf{1}^{\cdot+}$ with an estimated lifetime of *ca.* 25 µs. However, little is known about the reactivity of the other isomers, *ct*-**1** and *tt*-**1**, particularly under steady-state photolysis conditions. It was not clear whether or not the isomerizations of *ct*-**1** and *tt*-**1** can be promoted by PET. We have investigated the sensitized photoreactions of *ct*-**1** and *tt*-**1** by using electron-accepting sensitizers such as 9,10-dicyanoanthracene (DCA), and observed that the isomerization of *ct*-**1** to *tt*-**1** occurs predominantly.[9]

Results

Fluorescence quenching experiment

Dienes *ct*-**1** and *tt*-**1** are good electron donors and their oxidation potentials (E_{ox}), +1.26 and +1.21 V *vs.* SCE in acetonitrile, respectively, are low enough for ET from the dienes to the singlet excited DCA (^{1}DCA*).§ Calculations by using the Weller equation[10] show that the free energy changes (ΔG) for the ET processes in acetonitrile are exothermic for both *ct*-**1** and *tt*-**1**, −0.68 and −0.73 eV, respectively (Table 1). In accord with this, fluorescence of DCA is efficiently quenched by **1** with diffusion-controlled rate constants. As summarized in Table 1, quenching experiments with other singlet sensitizers§ such as 2,6,9,10-tetracyanoanthracene (TeCA), and *N*-methylacridinium tetrafluoroborate (NMA) show that their fluorescence is also quenched efficiently by *ct*-**1** and *tt*-**1**.

In a nonpolar solvent, benzene, fluorescence of the sensitizers is also quenched by **1**. In the case of DCA, the k_q values are lower compared to those in acetonitrile. Upon quenching of DCA fluorescence by either *ct*-**1** or *tt*-**1**, weak, structureless exciplex emission is observed in the longer wavelength region than DCA fluorescence itself. In the case of other sensitizers no exciplex emissions can be observed. The emission maxima for the *ct*-**1**–DCA and *tt*-**1**–DCA exciplex are 561 nm and 572 nm, respectively. The excitation spectrum coincided with the absorption spectrum of DCA. The apparent lifetime monitored at their maxima are 34.5 and 27.3 ns under nitrogen saturated conditions, which are longer than that of ^{1}DCA* in benzene (12.5 ns). Oxygen seems to quench the exciplexes since the lifetimes are shorter under oxygen saturated conditions, 17.0 and 15.9 ns for the *ct*-**1**–DCA and *tt*-**1**–DCA exciplex, respectively. The rate constants for oxygen quenching are evaluated to be 3.3×10^9 and 2.9×10^9 dm^3 mol^{-1} s^{-1} for the *ct*-**1**– and *tt*-**1**–DCA exciplex, respectively.

Steady-state photoreaction of 1

Steady-state photolyses were carried out by using a 500 W xenon-mercury lamp equipped with a glass filter (λ > 410 nm). Both *ct*-**1** and *tt*-**1** are transparent in the wavelength region. Irradiation of 2 cm^3 acetonitrile solutions of *ct*-**1** and DCA for 15 min afforded a 2.5:97.5 steady-state mixture of *ct*-**1** and *tt*-**1**. In a similar manner the photoreaction with *tt*-**1** afforded a photostationary mixture with essentially the same ratio (2.1:97.9) as that from *ct*-**1**. In benzene the isomerization from *ct*-**1** to *tt*-**1** is also prevalent. From *ct*-**1** a mixture consisting of 5.2% *ct*-**1** and 94.8% *tt*-**1** was obtained and from *tt*-**1** a mixture of 4.1% *ct*-**1** and 95.9% *tt*-**1**. Similar results were obtained with TeCA or NMA. No isomerization was observed in the absence of a sensitizer. The ratios indicate that the isomerization of *ct*-**1** to *tt*-**1** is predominant.

(1)

Under the steady-state photolysis conditions the isomeriz-

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§ The singlet excitation energies of DCA, TeCA and NMA are 2.89, 2.89 and 2.75 eV, respectively and their reduction potentials are −0.95, −0.45 and −0.48 V *vs.* SCE in acetonitrile, respectively.[11]

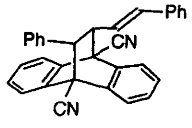
Table 1 Calculated free energy change (ΔG)[a] for electron-transfer fluorescence quenching in acetonitrile, quenching rate constants (k_q), and photostationary ratio (ct-**1** : tt-**1**)[b] of the sensitized isomerization of **1**

			$k_q/10^{10}$ dm^3 mol^{-1} s^{-1}		ct-**1** : tt-**1**	
Sensitizer	Diene	ΔG/eV	Acetonitrile	Benzene	Acetonitrile	Benzene
DCA	ct-**1**	−0.68	2.2	1.3	2.5:97.5	5.2:94.8
DCA	tt-**1**	−0.73	2.5	1.7	2.1:97.9	4.1:95.9
TeCA	ct-**1**	−1.18	2.5	2.6	3.9:96.1	3.8:96.2
TeCA	tt-**1**	−1.23	2.7	2.7	3.2:96.8	4.2:95.8
NMA	ct-**1**	−1.01	2.5	—	6.1:93.9	—
NMA	tt-**1**	−1.06	2.6	—	4.3:95.7	—

[a] Calculated according to the Weller equation.[9] [b] Typically a 2 cm^3 solution of **1** (1.5×10^{-3} mol dm^{-3}) and DCA (5×10^{-4} mol dm^{-3}) was irradiated ($\lambda > 410$ nm) using a 500 W Xe-Hg lamp.

ation reaction is generally efficient and the quantum yield (Φ) for the isomerization of ct-**1** exceeds unity in acetonitrile (Table 2, Run 1–4). Photolysis with lower light intensity results in higher Φ (Run 4 *vs.* 2). In the presence of oxygen or 1.5×10^{-4} mol dm^{-3} of tetramethoxybenzene (TMB, $E_{ox} = 0.75$ V *vs.* SCE), Φ decreases significantly (Run 5–7 *vs.* 1, 2). The quantum yields for the isomerization of ct-**1** in benzene are five to nine times lower than those in acetonitrile.

The photoisomerization proceeded with excellent material balance, 95% or higher. When the DCA-sensitized photoisomerization reaction was carefully monitored by HPLC or UV–VIS, we noticed that after the photostationary state was attained DCA was gradually consumed over a prolonged period of irradiation. HPLC analysis of the photolysate showed a new peak ascribable to a new product. We found that consumption of DCA was due to slow formation of a [4 + 2] cycloaddition product **2**. Adduct **2** was obtained by an independent experiment using a relatively larger amount of DCA and tt-**1** under prolonged irradiation conditions. With TeCA or NMA no formation of addition products was observed and only the isomerization proceeded.



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Laser flash photolysis study

In our previous study on the photooxygenation of tt-**1** sensitized by DCA,[12] we were able to observe ^{3}DCA* by the flash photolysis of the tt-**1**–DCA system in carbon tetrachloride or benzene. This time we found that ^{3}DCA* was also generated from the ct-**1**–DCA system in benzene though the intensity is low. The spectral shape, the position of the maxima (λ_{max}/nm 660, 730 and 810), and its oxygen sensitive nature are in agreement with our previous observations. No absorption due to ion radicals such as ct-**1**$^{\bullet+}$ or DCA$^{\bullet-}$ was observed in benzene.

Fig. 1(*a*) shows the transient absorption spectra at 200 ns after the pulsed laser excitation of the ct-**1**–DCA and tt-**1**–DCA systems in acetonitrile. These transients are readily assigned as being due to the corresponding cation radicals, ct-**1**$^{\bullet+}$ and tt-**1**$^{\bullet+}$. Indeed, their shape and maxima (543 and 530 nm for ct-**1**$^{\bullet+}$ and tt-**1**$^{\bullet+}$, respectively) well compare with those reported previously.[8a,12–14] Similar transient spectra with much better signal-to-noise ratio were obtained by using 0.1 mol dm^{-3} of biphenyl as a co-sensitizer[5b,c] [Fig. 1(*b*)]. Under the conditions, much more efficient formation of ct-**1**$^{\bullet+}$ and tt-**1**$^{\bullet+}$ was ensured by high-yield formation of biphenyl cation radical and by the following exothermic ET from ct-**1** or tt-**1** to biphenyl (E_{ox} = 1.85 V *vs.* SCE) cation radical. Weak absorptions due to DCA$^{\bullet-}$ (707 and 640 nm) could also be seen in this case. In the presence of biphenyl the ratio of the intensities of the transient absorption maxima of ct-**1**$^{\bullet+}$ and tt-**1**$^{\bullet+}$ at zero time corresponds to the ratio of their extinction coefficients (ε). By using ε of tt-**1**$^{\bullet+}$ (6.8×10^4 dm^3 mol^{-1} cm^{-1} at 530 nm),[13a] ε of ct-**1**$^{\bullet+}$ was determined to be 2.6×10^4 dm^3 mol^{-1} cm^{-1} at 543 nm. Either with or without biphenyl, both transients due to ct-**1**$^{\bullet+}$ and tt-**1**$^{\bullet+}$ decayed with second-order kinetics and the rate constants, k_t and $k_{t'}$, in Scheme 1, were determined to be near diffusion-controlled values, 2–3 × 10^{10} dm^3 mol^{-1} s^{-1}.

Table 2 Effects of light intensity (I) and additives on the quantum yield (Φ) of the DCA-sensitized photoisomerization of ct-**1**[a]

Run	Solvent	[ct-**1**]/10^{-3} mol dm^{-3}	$I/10^9$ einstein s^{-1}	Additive	Φ
1	MeCN	4.52	3.75	None	1.4
2	MeCN	17.7	3.75	None	3.1
3	MeCN	47.7	3.21	None	6.6
4	MeCN	17.7	0.328	None	8.6
5	MeCN	4.52	3.75	O_2, 1 atm	0.53
6	MeCN	17.7	3.75	O_2, 1 atm	1.7
7	MeCN	4.52	3.75	TMB, 0.3 mmol	0.36
8	MeCN	4.52	3.75	None	0.16
9	Benzene	14.6	2.71	None	0.65
10	Benzene	4.52	3.75	O_2, 1 atm	(0.20)[b]

[a] 2 cm^3 solutions of ct-**1** and DCA (3×10^{-4} mol dm^{-3}) were photolysed using a 150-W Xe lamp equipped with a monochrometor (λ = 420 nm). Photolysates were analysed using HPLC. [b] Disappearance of ct-**1** due to the oxygenation.

Discussion

It is known that isomerization of 1,4-diphenylbuta-1,3-dienes occurs upon direct photolysis[8b,15,16] or triplet sensitized photolysis.[8b,17] The present study shows that the isomerization can also be induced by ET through fluorescence quenching. It is interesting that the isomerization from ct-**1** to tt-**1** is dominant regardless of the solvent polarity. Photostationary state rich in tt-**1** was observed in both acetonitrile and benzene. However, the mechanism varies according to the solvent polarity.

In a nonpolar solvent, benzene, the DCA-sensitized photolyses of ct-**1** and tt-**1** result in their isomerization and afford photostationary mixtures consisting of 4–5% of ct-**1** and 96–95% of tt-**1**. The quantum yields for the isomerization of ct-**1** to tt-**1** are lower than those in acetonitrile but still moderately high. Observation of exciplex emission upon quenching of ^{1}DCA* by **1** may suggest a possibility of fast ct-**1** $\longrightarrow$ tt-**1** isomerization within the exciplex manifold, namely adiabatic exciplex isomerization.[18] However, this is unlikely since the emission maxima of the exciplexes of ct-**1** (561 nm, 2.21 eV) and tt-**1** (572 nm, 2.17 eV) are different. A mechanism involving triplet state isomerization seems to be feasible in benzene, considering the fact that the formation of ^{3}DCA* is observed by laser flash photolyses of the ct-**1**–DCA and tt-**1**–DCA systems.

Since the quantum yield of the intersystem crossing of

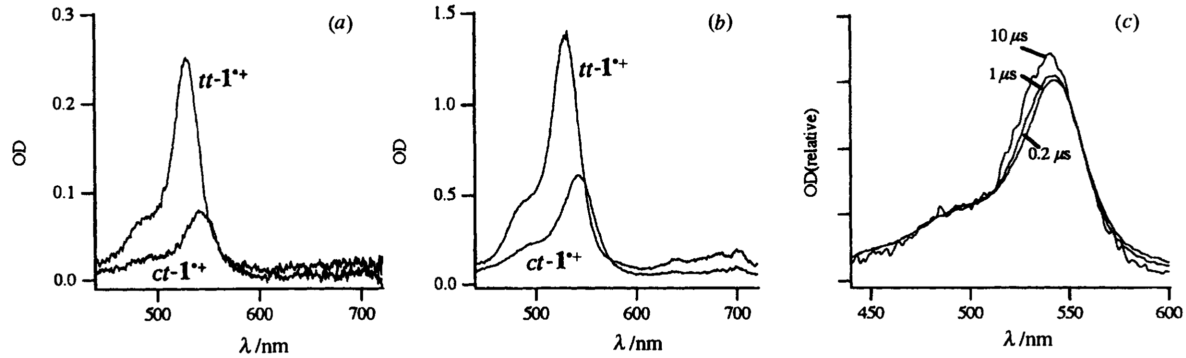


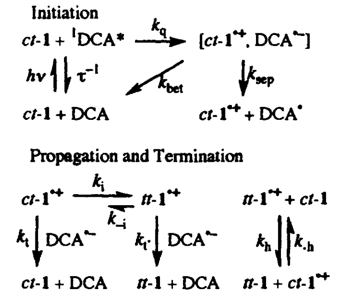
Fig. 1 Transient absorption spectra of ct-$\mathbf{1}^{\bullet+}$ and tt-$\mathbf{1}^{\bullet+}$ in N_2-saturated acetonitrile obtained by laser flash photolyses: (*a*) from *ct*-**1** and *tt*-**1** (1.0×10^{-2} mol dm^{-3} each) with DCA (3×10^{-4} mol dm^{-3}), and (*b*) from *ct*-**1** (8.2×10^{-4} mol dm^{-3}) and *tt*-**1** (8.6×10^{-4} mol dm^{-3}) with DCA (3×10^{-4} mol dm^{-3}) and biphenyl (0.1 mol dm^{-3}) at 200 ns after excitation. (*c*) Transient spectra of ct-$\mathbf{1}^{\bullet+}$ normalized at 550 nm.

^{1}DCA* itself is as low as 0.003,[19] this process would have no or little contribution to the formation of ^{3}DCA*. It is most likely that the exciplexes play an important role as a precursor to ^{3}DCA*. The energy levels of the exciplexes can be evaluated to be 2.61 and 2.53 eV, respectively, from their emission maxima and calculated internal reorganization energies, 0.37 and 0.39 eV for the *ct*-**1**–DCA and *tt*-**1**–DCA exciplex, respectively.¶ They are energetically higher than those of ^{3}*tt*-**1*** (1.82 eV), ^{3}*ct*-**1*** (*ca.* 1.7 eV),[8b] or ^{3}DCA* (1.65 eV).[21] It is possible that intersystem crossing of the exciplexes results in either of the triplet states.

It has been suggested that ^{3}*tt*-**1*** is in fast equilibrium with an intermediate (^{3}*tp*-**1***) which has perpendicular geometry at one end of the diene and *trans* at the other end.[17] According to Yee *et al.*,[8b] conversion of ^{3}*ct*-**1*** to ^{3}*tp*-**1*** is very rapid and ^{3}*tp*-**1*** may undergo unimolecular decay to afford *ct*-**1** and *tt*-**1**. In the presence of an added quencher, ^{3}*tt*-**1*** can be quenched to give *tt*-**1**. At high concentration of *ct*-**1**, bimolecular decay through quenching of ^{3}*tt*-**1*** by *ct*-**1** is possible, affording *tt*-**1** and ^{3}*ct*-**1***. The resulting ^{3}*ct*-**1*** gives *tt*-**1** through ^{3}*tt*-**1***, thus leading to prevalent formation of *tt*-**1**.

Under the DCA sensitized conditions, the concentration of DCA is high enough to act as a quencher. In addition, the bimolecular quenching of ^{3}*tt*-**1*** by *ct*-**1** is also possible. Although the unimolecular decay of ^{3}*tp*-**1*** is reported to result in *ct*-**1** and *tt*-**1** in a ratio of 45 : 55,[8b] photostationary state rich in *tt*-**1** can be achieved under the present conditions owing to the bimolecular processes.

In acetonitrile the photoisomerization of *ct*-**1** to *tt*-**1** under the steady-state photolysis conditions is generally efficient. The observation of higher quantum yields than unity in conjunction with the results of quencher effects suggest a chain mechanism as shown in Scheme 1. Basically the same mechanisms have been proposed for ET induced cycloreversion of hexamethyl(Dewarbenzene),[22a] isomerization of stilbenes,[5a] [2 + 2] cycloadditions and cycloreversions.[22b] The mechanism involves: (*i*) the formation of free ct-$\mathbf{1}^{\bullet+}$ (and DCA$^{\bullet-}$) as an initiation step, (*ii*) the unimolecular isomerization of ct-$\mathbf{1}^{\bullet+}$ to tt-$\mathbf{1}^{\bullet+}$ prevalently, and (*iii*) the regeneration of ct-$\mathbf{1}^{\bullet+}$ by hole transfer from tt-$\mathbf{1}^{\bullet+}$ to *ct*-**1**. The latter two processes compete with charge recombination processes (k_t and $k_{t'}$) and can be inhibited by the addition of a quencher such as TMB. It is likely that slow formation of [4 + 2] adduct is due to inefficient reaction of ion pairs [tt-$\mathbf{1}^{\bullet+}$, DCA$^{\bullet-}$], which can be generated either through ET quenching of ^{1}DCA* by the resulting *tt*-**1** or through charge recombination between tt-$\mathbf{1}^{\bullet+}$ and DCA$^{\bullet-}$.



Scheme 1

Recently, Tokumaru *et al.*[6b] determined the rate constant for the isomerization of the *cis*-stilbene cation radical to be 3.0×10^5 s^{-1} in acetonitrile at 19 °C. As mentioned in the introduction, cc-$\mathbf{1}^{\bullet+}$ undergoes isomerization to tt-$\mathbf{1}^{\bullet+}$ with an estimated lifetime of *ca.* 25 μs,[8b] which suggests that the isomerization rate constant is about 4×10^5 s^{-1}. In the present case, spectral change of ct-$\mathbf{1}^{\bullet+}$ can be visualized when the time-resolved spectra obtained by using biphenyl are normalized at the isosbestic point, 550 nm [Fig. 1(*c*)]. Slight blue-shifting and increase in the intensity of the spectra at 1 and 10 μs are most likely due to the conversion of ct-$\mathbf{1}^{\bullet+}$ to tt-$\mathbf{1}^{\bullet+}$ since tt-$\mathbf{1}^{\bullet+}$ has shorter absorption maximum and higher ε than ct-$\mathbf{1}^{\bullet+}$. Based on ε of tt-$\mathbf{1}^{\bullet+}$ we estimate that 6% of ct-$\mathbf{1}^{\bullet+}$ isomerizes to tt-$\mathbf{1}^{\bullet+}$ in 10 μs, which corresponds to a rate constant (k_i) of *ca.* 6×10^3 s^{-1}.

Spectral change of ct-$\mathbf{1}^{\bullet+}$ without biphenyl is obscure because of the lower signal-to-noise ratio of the spectra, which is due to the fact that the efficiency for separation (f_{sep}) [eqn. (2)] of the

$$f_{sep} = \frac{k_{sep}}{k_{sep} + k_{bet}} \qquad (2)$$

photogenerated ion pair [ct-$\mathbf{1}^{\bullet+}$, DCA$^{\bullet-}$] is low. Previously, we have determined f_{sep} of the photogenerated ion pair [tt-$\mathbf{1}^{\bullet+}$, DCA$^{\bullet-}$] to be 0.11.[13b] By using ε values and the ratio of the extrapolated intensities of ct-$\mathbf{1}^{\bullet+}$ and tt-$\mathbf{1}^{\bullet+}$ at zero time, f_{sep} for [ct-$\mathbf{1}^{\bullet+}$, DCA$^{\bullet-}$] can be evaluated to be 0.08.

Since both the efficiency of the initiation step and the k_i value are lower, chain length must be long. Chain length n at an early stage of the reaction can be evaluated by using eqn. (3), where f_{et}

$$n = \frac{\Phi}{f_{et} \times f_{sep}} \qquad (3)$$

is the efficiency of the ET quenching and τ being the lifetime of DCA [eqn. (4)]. For example, Φ of 3.1 at 17.7 mmol dm^{-3} of *ct*-**1** (Table 1, run 2) results in a calculated n of 44. The calculated

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¶ The internal reorganization energies were evaluated from the difference in the heat of formation between **1**–DCA in the equilibrium nuclear geometry of $\mathbf{1}^{\bullet+}$–DCA$^{\bullet-}$ and **1**–DCA in its equilibrium nuclear geometry. Heats of formation and geometries of **1**, $\mathbf{1}^{\bullet+}$, DCA and DCA$^{\bullet-}$ were calculated by PM3/RHF using DOUBLET for the ions. Analogous calculations for other exciplexes have been reported elsewhere.[20]

$$f_{et} = \frac{k_q[ct\text{-}\mathbf{1}]}{\tau^{-1} + k_q[ct\text{-}\mathbf{1}]} \quad (4)$$

result suggests that the hole-transfer process, $k_h[ct\text{-}\mathbf{1}]$, is also more efficient than the termination steps under the steady-state photolysis conditions.

It appears a little confusing that the stady-state photosensitized isomerization of *ct*-**1** to *tt*-**1** is so efficient despite the fact that the rate constant (k_i) for the unimolecular isomerization of *ct*-$\mathbf{1}^{\bullet+}$ to *tt*-$\mathbf{1}^{\bullet+}$ is much smaller compared to those of the cation radicals of *cis*-stilbene and *cc*-**1** and that the termination steps (k_t and $k_{t'}$) proceed with diffusion-controlled rates. However, it is important to note that the rate of termination steps are dependent on the concentration of $DCA^{\bullet-}$. Both k_i and $k_h[ct\text{-}\mathbf{1}]$ can be larger than $k_t[DCA^{\bullet-}]$ and $k_{t'}[DCA^{\bullet-}]$ if $[DCA^{\bullet-}]$ is very low.

Under the laser flash photolysis conditions, where $[DCA^{\bullet-}]$ can be of the order of 10^{-5} mol dm^{-3} or higher, $k_t[DCA^{\bullet-}]$ and $k_{t'}[DCA^{\bullet-}]$ are expected to be as large as 2–3 $\times$ 10^5 s^{-1}. In fact only 6% of *ct*- to *tt*-**1** conversion is observed in the 10 μs time scale. On the other hand, $k_t[DCA^{\bullet-}]$ and $k_{t'}[DCA^{\bullet-}]$ should become as low as 2–3 s^{-1} because $[DCA^{\bullet-}]$ would be as low as *ca.* 10^{-10} mol dm^{-3} under steady-state photolysis conditions. Under the circumstances k_i of *ca.* 6 $\times$ 10^3 s^{-1} is indeed high enough to exceed the termination steps. Hole transfer from *tt*-$\mathbf{1}^{\bullet+}$ to *ct*-**1** may efficiently proceed particularly when the concentration of *ct*-**1** is high, since the oxidation potential of *ct*-**1** is higher than that of *tt*-**1** by only 0.05 V in acetonitrile. There exist a number of experimental precedents and theoretical support for such an endothermic ET reaction to proceed with considerable efficiency.[23] It is reasonable that the ET reaction with endothermicity of 0.05 eV may proceed with rate constant of 10^8–10^9 dm^3 mol^{-1} s^{-1}.[23a]

Recently, Lewis *et al.*[5c] proposed a mechanism for the ET induced isomerization of *cis*-stilbene involving the formation of acyclic dimer cation radicals (σ-type 1,4-cation radicals) as a key process. The dimer cation radicals may revert with loss of stereochemistry to give *trans*-stilbene (*t*-S) and its cation radical. There has been considerable interest in the role of dimeric cation radical species of stilbenes in relation to the isomerization of *cis*-stilbene.[24] In less polar solvents such as halogenated solvents, *cis*-stilbene is suggested to form σ-type dimer cation radical[24b,c] while *trans*-stilbene affords π-type dimer cation radical.[24a,25] On the other hand, the experimental evidence for the formation of σ-type dimer cation radical in acetonitrile seems to remain inconclusive.

A mechanism involving similar dimer cation radical $(\mathbf{1})_2^{\bullet+}$ is considered for the present case. Even if this is the case, the mechanism would be kinetically indistinguishable from Scheme 1. At this stage, we have not been able to observe the dimer formation in the flash photolysis experiments with **1**. Moreover, no indication for the formation of dimer cation radical has been obtained in a pulse radiolysis study with *tt*-**1**.[26] Thus, the mechanism shown in Scheme 1 is most likely in the present case.

Conclusions

The present study shows that the isomerization of *ct*- and *tt*-**1** can be induced by ET through fluorescence quenching. Photostationary mixtures rich in *tt*-**1** are obtained in both acetonitrile and benzene. The mechanism varies according to the solvent polarity. A mechanism involving triplet state isomerization seems to be feasible in benzene. In acetonitrile, the steady-state photosensitized isomerization of *ct*-**1** to *tt*-**1** proceeds efficiently with quantum yields higher than unity. Although the unimolecular isomerization of *ct*-$\mathbf{1}^{\bullet+}$ to *tt*-$\mathbf{1}^{\bullet+}$ proceeds apparently slowly with an estimated rate constant of *ca.* 6 $\times$ 10^3 s^{-1}, the steady-state photosensitized isomerization of *ct*-**1** to *tt*-**1** proceeds efficiently. It is shown that the termination steps are effectively too slow to compete with the unimolecular isomerization of *ct*-$\mathbf{1}^{\bullet+}$ to *tt*-$\mathbf{1}^{\bullet+}$ or the propagation steps under the steady-state photolysis conditions. Accordingly, the cation radical chain mechanism is most likely in acetonitrile.

Experimental

Materials

Butadiene *tt*-**1** was purchased from Aldrich and recrystallized from methylcyclohexane. Butadiene *ct*-**1** was synthesized by photoisomerization of *tt*-**1** as reported elsewhere[15] and purified by silica gel column chromatography. 9,10-Dicyanoanthracene (DCA) was purchased from Tokyo Kasei. 2,6,9,10-Tetracyanoanthracene (TeCA),[27] *N*-methylacridinium tetrafluoroborate (MA)[11] and 1,2,4,5-tetramethoxybenzene (TMB)[28] were synthesized according to the reported procedures. Spectroscopic grade acetonitrile and benzene were distilled over calcium hydride prior to use.

Instrumentation

Electronic spectra were measured on a Hewlett-Packard HP8452A diode-array spectrophotometer. Fluorescence spectra were recorded on a Hitachi F4010 or MPF-4 fluorescence spectrometer. Fluorescence lifetimes were measured by a single-photon-counting method on a Horiba NAES-110 fluorescence spectrometer. Cyclic voltammetric measurements were carried out in acetonitrile solution with 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte and a saturated calomel electrode (SCE) as the reference electrode by using a Yanagimoto P-1000 voltammetric analyser equipped with a function generator. HPLC analyses were performed with a Waters HPLC system. Time-resolved differential absorption spectra were obtained by using a Lumonics dye-laser (Stilbene 420 in methanol, 5 ns pulse) pumped by a Lumonics excimer laser (XeCl, 308 nm). The probe assembly consists of a 150 W xenon lamp, a polychromator equipped with an image intensifier (Hamamatsu C2925) coupled with an image sensor (Hamamatsu C2327), and a microcomputer. The monitoring beam was collimated and was perpendicular to the excitation pulse. A combination of a monochromator, a photomultiplier tube (Hamamatsu R2949), and a digitizing oscilloscope (Hewlett-Packard 54510A) was used for measurement of the decay kinetics. An analogous flash photolysis system has been described elsewhere.[29]

Fluorescence quenching experiments

Sample solutions containing 5 $\times$ 10^{-5} mol dm^{-3} of a sensitizer and a given amount of **1** were prepared and the fluorescence spectra were recorded at 20 °C. The relative fluorescence intensities at the emission maxima were measured under aerated conditions. The quenching rate constants were evaluated by using the Stern–Volmer relation, $I_0/I = 1 + k_q\tau[Q]$, where I and I_0 being fluorescence intensities with and without **1**, respectively, and τ being the fluorescence lifetime of a sensitizer in aerated solvent. Slopes of the Stern–Volmer plots were determined by a linear least-squares method and quenching rate constants were calculated from τ values, 12.7, 15.1 and 32.9 ns for DCA, TeCA and NMA, respectively.

Steady-state photosensitization of 1

Typically, a 2 cm^3 sample solution containing **1** and a sensitizer in a cuvette was saturated with nitrogen and irradiated at 20 °C using a 500 W xenon-mercury lamp equipped with an aqueous IR filter ($CuSO_4$) and Toshiba Y-43 glass filter ($\lambda > 410$ nm). The isomer ratio was followed by HPLC analyses in the course of the photolysis.

Determination of the quantum yields for the isomerization of *ct*-1 to *tt*-1

Quantum yields for the isomerization of *ct*-**1** were determined for nitrogen- or oxygen-purged solutions of *ct*-**1** and 5×10^{-4} mol dm^{-3} of DCA irradiated at 420 nm using a 150 W xenon lamp equipped with a grating monochromator (a 10 nm bandpass). Light intensities at 420 nm were determined by fluorescence spectrometry with Rhodamine B in conjunction with Aberchrome 540 actinometry[30] at 365 nm. The conversions (< 10%) of *ct*-**1** to *tt*-**1** were determined by HPLC analyses using a reverse-phase column (Merck Superspher RP-18) with a mixture of acetonitrile and water (70:30 v/v).

Formation of adduct 2

A mixture of *tt*-**1** (62 mg, 0.30 mmol) and DCA (8.5 mg) in 15 cm^3 benzene was saturated with nitrogen and irradiated for 2 h by using a 2 kW xenon lamp with a Toshiba Y-43 glass filter ($\lambda > 410$ nm). Then 8 mg of DCA was added to the mixture and was irradiated for additional 28 h. Removal of the solvent afforded 86 mg of yellow solid, which was subjected to preparative silica gel TLC. Development with a 1:1 mixture of hexane and methylene chloride gave 7 mg of practically pure adduct **2**, 9,10-dicyano-11-phenyl-12-styryl-9,10-dihydro-9,10-ethanoanthracene. Recrystallization from a mixture of hexane and methylene chloride afforded pure **1** as colourless plates, mp 175 °C (decomp.). Anal. found: C, 88.3; H, 5.3; N, 6.6%. Calc. for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10; N, 6.45%. δ_H(200 MHz, [$^2H_6$]acetone) (*J* values in Hz) 3.32 (1 H, dd, *J* 9.1, 5.3, 8-H), 3.46 (1 H, d, *J* 5.3, 7-H), 5.68 (1 H, dd, *J* 15.6, 9.1, styryl α-H), 6.55 (1 H, d, *J* 15.6, styryl β-H), 6.64–6.71 (2 H, m, 11-phenyl *o*-H), 7.16–7.33 (8 H, m, phenyl), 7.38–7.92 (8 H, m, benzo). δ_C(50 MHz, [$^2H_6$]acetone) 52.50 (C-9 or C-10), 52.99 (C-10 or C-9), 56.57 (C-12), 56.72 (C-11), 116.89 (CN), 117.28 (CN), 123.21, 123.28, 125.02, 125.85, 127.29 (styryl C-α), 127.39 (2C), 128.86, 129.08, 129.15 (3C), 129.32, 129.40, 129.59, 129.64, 130.01 (2C), 134.69 (11-phenyl, C-1), 135.97 (styryl C-β), 137.15 (phenyl, C-1), 138.40, 138.44, 138.49 (2C). ν_{max}/cm^{-1} (KBr) 3010, 2230, 1597, 1486, 1454, 1297, 1068, 1033, 967, 766, 750, 702, 641, 596, 557, 485. *m*/*z* (70 eV) 229 ($C_{16}H_8N_2^+ + 1$, 14%), 228 ($C_{16}H_8N_2^+$, 80), 207 (17), 206 ($C_{16}H_{14}^+$, 100), 205 (23), 191 (15), 129 (13), 128 (21), 115 (11), 91 (38).

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