Novel Finding of the Effect of Triple Bond on the Photochemical *cis–trans* Isomerization of C=C Double Bond

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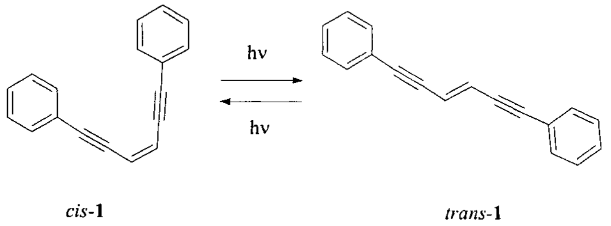
Both *cis*- and *trans*-1,2-bis(phenylethynyl)ethenes (**1**) gave fluorescence emission with considerably high quantum yield and intersystem crossing to the triplet state which underwent *cis–trans* isomerization. On the basis of the results, a novel potential energy surface of isomerization of **1** was proposed.

(Phenylethynyl)ethenes have already been prepared and donor acceptor complexes between (phenylethynyl)ethenes and electron acceptors have extensively been studied to construct a new materials with useful optical and electronic properties.[1–6] In addition, enediynes can produce a highly reactive 1,4-biradical intermediate either thermally or photochemically which expresses the biological activity.[7] However, the photochemical *cis–trans* isomerization of enediynes has scarcely been studied. In this respect, we have prepared 1,2-bis(phenylethynyl)ethenes (**1**). We wish to report here the novel effect of triple bond on the photochemical as well as photophysical properties of ethenes. In brief, on direct irradiation both *cis*- and *trans*-**1** gave fluorescence emission with considerably high quantum efficiency in addition to the efficient intersystem crossing to the triplet state undergoing *cis–trans* isomerization. Furthermore, not only the planar *trans* triplet state ($^3t^*$) and perpendicular triplet state ($^3p^*$), but also the *cis* triplet state ($^3c^*$) is equilibrated in the triplet state and one can induce the deactivation from all of the three conformations by choosing appropriate experimental conditions.

Both *cis*- and *trans*-**1** gave the fluorescence emission with maxima at 364 and 387 nm and at 362 and 382 nm, respectively in benzene (Figure 1). The quantum yield of fluorescence emission was determined to be 0.31 and 0.42 for *cis*- and *trans*-**1**, respectively. On direct irradiation with 328 nm light, **1** underwent mutual isomerization between *cis*- and *trans*-isomers giving the *trans*-to-*cis* isomer ratio at the photostationary state of $([t]/[c])_{pss} = 44/56$ in benzene. The quantum yields of *cis–trans* and *trans–cis* isomerization were determined to be 0.27 and 0.17, respectively. Contrary to the results reported by Turro for 1,2-bis(phenylethynyl)benzene,[7] photochemical Bergman cyclization was not observed in **1**.

On 308 nm laser excitation, *cis*- and *trans*-**1** gave the similar transient absorption spectrum with the absorption maximum at 450 nm and the lifetime of 370 ns (Figure 2). The observed transient was quenched by oxygen with the rate constant of 5.6×10^9 M^{-1} s^{-1} indicating that the observed transient is assigned to the triplet state. Furthermore, the transient was quenched by the triplet quenchers such as azulene with the rate constant of 7.0×10^9 M^{-1} s^{-1}. These results suggest that **1** undergoes intersystem crossing to the triplet state where $^3t^*$, $^3p^*$, and $^3c^*$ could be equilibrated. Since both *cis*- and *trans*-isomers of **1** seem to have no considerable steric effect, they seem to be nearly the same in energy and in population in the triplet state as well as in the ground state. If this is the case, we can depict a novel potential energy surface of *cis–trans* isomerization with $^3c^*$, $^3t^*$ and $^3p^*$ equilibrated with each other. The equilibration in the excited triplet state is usually accomplished much faster than the decay to the ground state.[9]

In order to shed light on the above possibility, we have studied the effect of azulene (Az) concentration on the photostationary state isomer ratios on triplet sensitization.[8,9] The



cis-**1** *trans*-**1**

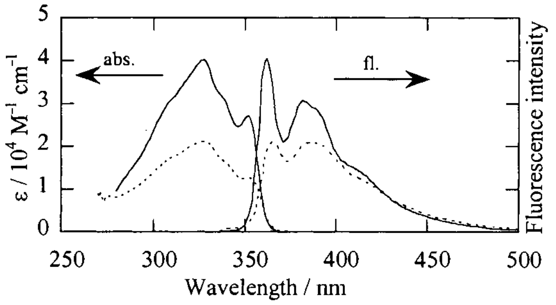


Figure 1. Absorption and fluorescence spactra of *trans*-**1** (solid line) and *cis*-**1** (dotted line) in benzene.

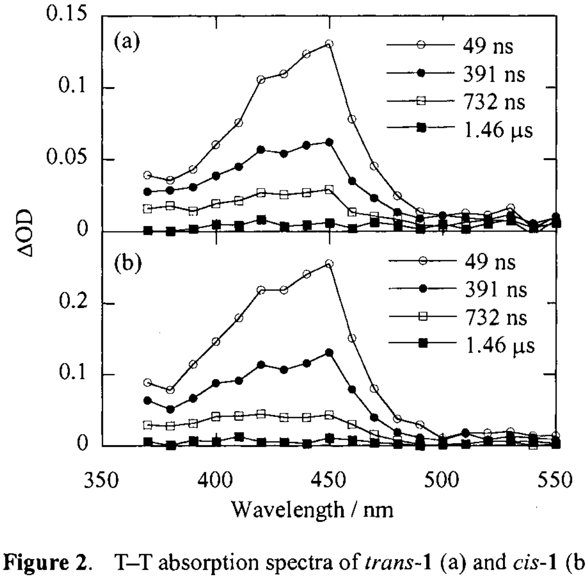


Figure 2. T–T absorption spectra of *trans*-**1** (a) and *cis*-**1** (b) in benzene observed on direct excitation with 308 nm laser pulse.

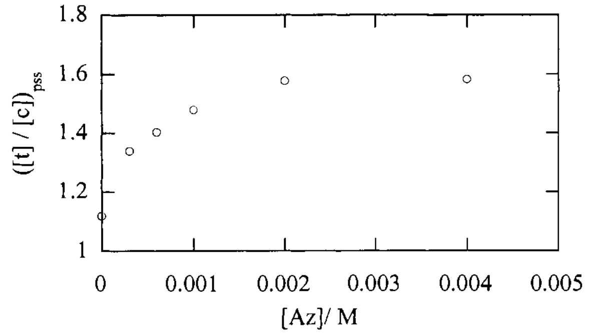


Figure 3. The effect of Az concentration on $([t]/[c])_{pss}$ on camphorquinone sensitization in benzene.

$([t]/[c])_{pss}$ value observed on camphorquinone (E_T = 51.5 kcal mol^{-1}) sensitization at 435 nm was 53/47 in the absence of Az, but increased with increasing Az concentration as shown in Figure 2. At first sight the Az effect seems to indicate the equilibration between $^3t^*$ and $^3p^*$. If this is the case, the $([t]/[c])_{pss}$ value must linearly increase with increasing Az concentration.[8,9] However, the $([t]/[c])_{pss}$ value became almost constant to give the value of 61/39 at Az concentration of 4.0×10^{-3} M. Since Az quenched the triplet state exclusively by energy transfer mechanism with k_{az} as the diffusion controlled rate constant, the above results indicate that Az interacts not only with $^3t^*$, but also with $^3c^*$ to result in energy transfer to give triplet Az and *trans*- and *cis*-**1**. In this case, most of the deactivation takes place by energy transfer from both $^3t^*$ and $^3c^*$ to Az to give *trans*- and *cis*-**1** resulting in the isomer ratio of $([t]/[c])_{pss}$ = 61/39 in the presence of Az with the concentration higher than 2×10^{-3} M, while the deactivation takes place exclusively from $^3p^*$ to give *trans*- and *cis*-**1** with the isomer ratio of $([t]/[c])_{pss}$ 53/47 in the absence of Az. Thus, we can estimate the equilibrium constant between $^3t^*$ and $^3c^*$ from the above value to be 61/39.

The triplet lifetime of **1** (370 ns) is much longer than that of stilbene (60 ns), which indicates the existence of equilibration between the planar triplet states ($^3c^*$ and $^3t^*$) and $^3p^*$. Since the deactivation rate constant from $^3t^*$ to *trans*-**1** is reasonably estimated to be the same with that from $^3c^*$ to *cis*-**1**, the equilibrium constant between the planar triplet state ($^3t^*$ and $^3c^*$) and the perpendicular triplet state ($^3p^*$) can be estimated by observed triplet lifetime. Thus, the triplet lifetime (τ_T) can be expressed by eq 1, where k_d and k_d' are the rate constants for the decativation from the planar triplet state ($^3t^*$ and $^3c^*$) and $^3p^*$, respectively, and K is the equilibrium constant between the planar triplet state ($^3t^*$ and $^3c^*$) and $^3p^*$. The values k_d and k_d' were previously estimated to be 2×10^4 s^{-1} and 2×10^7 s^{-1}, respectively.[9]

$$\tau_T = (1 + K)/(K\, k_d + k_d') \qquad (1)$$

Thus, $K = 0.12 = \{[^3p^*]/([^3t^*]+[^3c^*])\}$ can be obtained. By using this value, one can roughly estimate the proportion of the three conformations to be $^3t^* : {}^3p^* : {}^3c^*$ = 54 : 11 : 35.

On the basis of these arguments, the potential energy surface of *cis–trans* isomerization of **1** in the triplet state was depicted as shown in Figure 4.

The potential energy surfaces of *cis–trans* isomerization depended on the substituents on the ethylenic double bond.[8,9] On triplet sensitization stilbene underwent two-way isomerization. In the triplet state $^3c^*$ is unstable and undergoes isomerization to give $^3p^*$, where $^3t^*$ and $^3p^*$ are equilibrated. The unimolecular deactivation takes place at $^3p^*$, since the decay rate constant from $^3p^*$ is much faster than the decay rate constant from the planar $^3t^*$ as already described. On the other hand, introdcution of anthryl group on the ethylenic carbon resulted in one-way *cis–trans* isomerization, where $^3t^*$ is much more stable than $^3c^*$ and $^3p^*$ and therefore deactivation takes place exclusively from $^3t^*$.

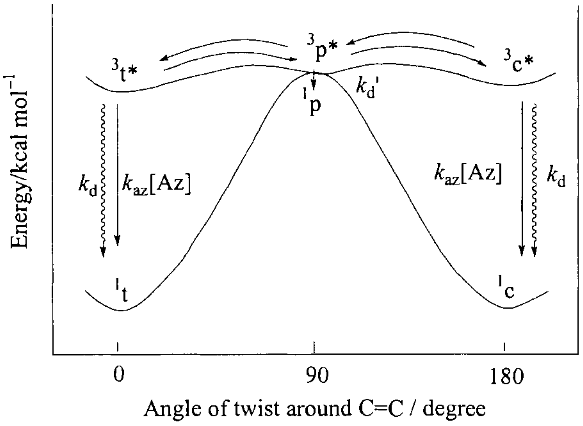


Figure 4. Potential energy surfaces of *cis–trans* isomerization of **1**.

The present findings open a new type of potential energy surafces of *cis–trans* isomerization, where three conformers, $^3t^*$, $^3p^*$, and $^3c^*$ are equilibrated and the deactivation may take place from these conformations by addition of appropriate quenchers. Actually, Az quenched $^3c^*$ and $^3t^*$ giving exclusively ^1c and ^1t, respectively, while unimolecular deactivation took place solely from $^3p^*$ giving ^1c and ^1t with nearly the same ratio.

In summary, the phenylethynyl group instead of phenyl group changed the behavior of stilbene in the excited singlet state to undergo efficient fluorescence emission and intersystem crossing in addition to the *cis–trans* isomerization. Furthermore, three energy minima exist in the triplet state potential surface of **1**, where $^3c^*$ has a considerable population and equilibrated with $^3t^*$ and $^3p^*$.

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References

1 F. Diederich, D. Philp, and P. Seiler, *J. Chem. Soc., Chem. Commun.*, **1994**, 205
2 D. Philp, V. Gramlich, P. Seiler, and F. Diederich, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 875.
3 A. Hilger, J.-P. Gisselbrecht, R. R. Tywinski, C. Boudon, M. Schreiber, R. E. Martin, H. P. Luthi, M. Gross, and F. Diederich, *J. Am. Chem. Soc.*, **119**, 2069 (1997).
4 K. P. C. Vollhardt and L. S. Winn, *Tetrahedron Lett.*, **26**, 709 (1985).
5 H. Taniguchi, K. Hayashi, K. Nishioka, Y. Hori, M. Shiro, and T. Kitamura, *Chem. Lett.*, **1994**, 1921.
6 K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **1975**, 4467.
7 A. Evenzahav and N. J. Turro, *J. Am. Chem. Soc.*, **120**, 1835 (1998).
8 J. Saltiel and M. L. Charlton “Rearrangement in Ground and Excited State,” ed. by P. de Mayo, Academic Press New York (1980), Vol. 3, p 25.
9 T. Arai and K. Tokumaru, *Chem. Rev.*, **93**, 23 (1993).