

Adiabatic Two-way Isomerization of an Arylethene: an Observation of Extremely High Energy Barrier for Excited State Z-E Isomerization

Tatsuo Arai* and Osamu Takahashi

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

A peryleneethene **1** undergoes two-way isomerization through an adiabatic process in the triplet state on direct irradiation as well as on Michler's ketone sensitization.

The photoisomerization of arylethenes in the excited triplet state have been extensively investigated.¹⁻⁵ Stilbene undergoes two-way isomerization between *Z* and *E* isomers as a diabatic process decaying at the perpendicular triplet state (³p*).^{1,2} However, 2-anthrylethenes exhibit one-way *Z* → *E* isomerization by an adiabatic process through a direct conversion from the *Z* triplet (³Z*) to the *E* triplet states (³E*).⁵

We now report that the adiabatic photoisomerization does not necessarily bring about only one-way isomerization but two-way isomerization can take place as an adiabatic process in the excited triplet state. Thus, 3-(prop-1-enyl)perylene **1** underwent two-way isomerization in the triplet state on direct as well as Michler's ketone sensitization.

A mixture of *Z*- and *E*-**1** was prepared from the Wittig reaction of ethyltriphenylphosphonium bromide with 3-perylenecarbaldehyde. The *Z*- and *E*-**1** were separated by column chromatography and were purified by recrystallization with hexane and hexane-benzene, respectively.[†]

Irradiation of pure *Z*- or *E*-**1** in benzene in the presence of Michler's ketone as a sensitizer under degassed conditions with

366 nm light from a 400 W high-pressure mercury lamp afforded a photostationary mixture of *Z*- and *E*-**1** in a ratio of 19:81. On direct irradiation **1** gave a photostationary mixture of *Z* and *E* isomers in a ratio of 15.5:84.5 at 436 nm light irradiation. Therefore, **1** underwent two-way isomerization on direct irradiation as well as on triplet sensitization.

The quantum yields of *Z* → *E* isomerization ($\Phi_{Z \rightarrow E}$) on direct irradiation at 436 nm were determined as low as 2.5×10^{-3} at 34.7 °C and increased with temperature up to 2.3×10^{-2} at 63.7 °C. The quantum yields of *E* → *Z* isomerization ($\Phi_{E \rightarrow Z}$) are even lower, increasing from 6.7×10^{-4} to 1.8×10^{-3} upon increasing the temperature from 49 to 64.8 °C. The low quantum yields for both *Z* → *E* and *E* → *Z* isomerization indicate that the activation barrier of the isomerization is considerable and therefore, deactivation to the ground state precedes the isomerization at room temperature.

Fig. 1 shows *T*-*T* absorption spectra of *Z*- and *E*-**1** in benzene under an argon atmosphere in the presence of Michler's ketone at room temperature. Similar *T*-*T* absorption spectra were observed on direct irradiation using a 425 nm laser. *Z*- and *E*-**1** exhibited different *T*-*T* absorption spectra with λ_{\max} at 520 and 540 nm, respectively, and decayed without changing the spectral profile, indicating that the conversion between ³Z* and ³E* is inefficient even in the 10 μs time range. These results are in accordance with the observed very low values of $\Phi_{Z \rightarrow E}$ and $\Phi_{E \rightarrow Z}$. The quantum yields of intersystem crossing from the singlet excited state to the triplet state of *Z*- (Φ_{isc}^Z) and *E*-**1** (Φ_{isc}^E) were determined as 0.23 and 0.28, respectively, using Zn(tpp) (tpp = 5,10,15,20-tetraphenylporphyrinate) ($\Phi_{isc} = 0.83$)⁶ as a standard. The triplet lifetimes of *Z*- and *E*-**1** were determined as ca. 50 μs under degassed conditions.

The observation of the *T*-*T* absorption spectra on direct irradiation indicates that even on direct irradiation the *Z*-*E* isomerization would take place in the excited triplet state. To confirm this proposition, we have examined the effect of

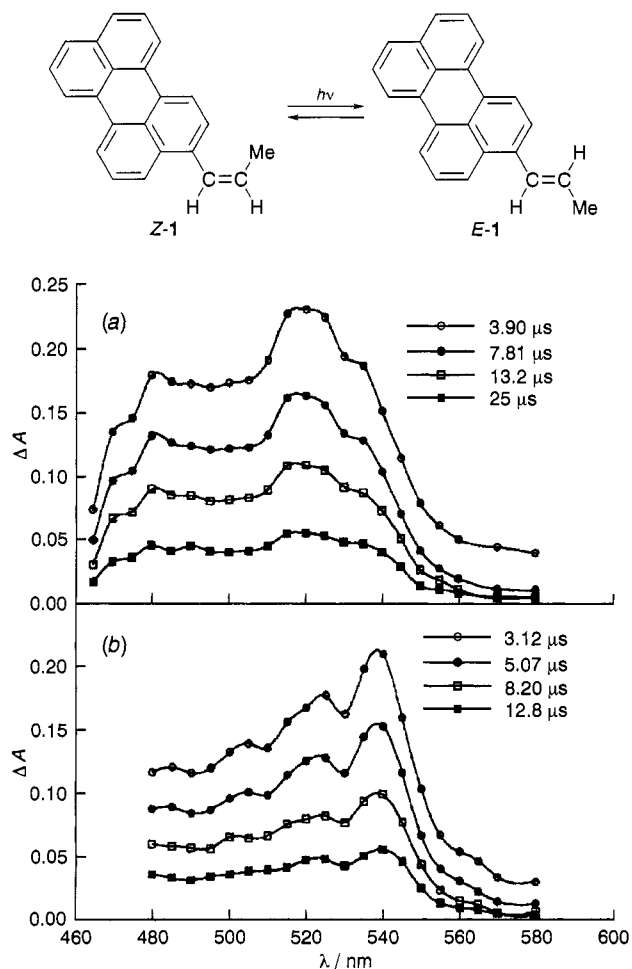


Fig. 1 *T*-*T* absorption spectra of *Z*- (a) and *E*-**1** (b) in benzene under an argon atmosphere

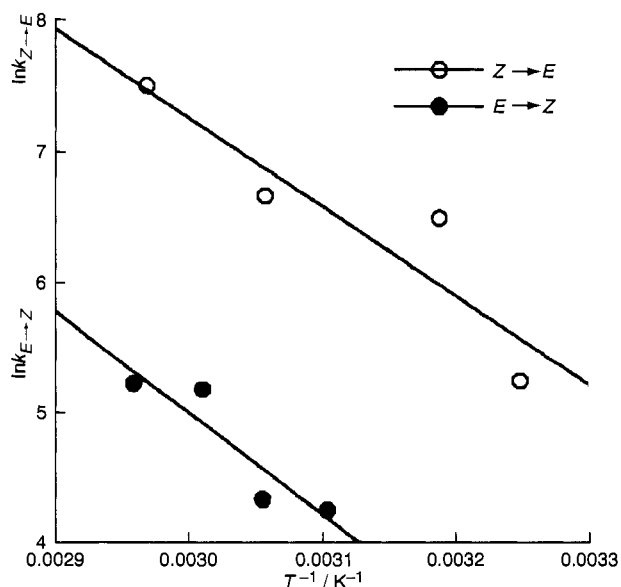


Fig. 2 Arrhenius plots of the temperature dependence of $k_{Z \rightarrow E}$ and $k_{E \rightarrow Z}$ values

oxygen on the quantum yield of isomerization; if the isomerization takes place in the excited triplet state the quantum yields of isomerization should be appreciably reduced. We thus determined the $\Phi_{Z \rightarrow E}$ and $\Phi_{E \rightarrow Z}$ values in air, and practically no isomerization took place: $\Phi_{Z \rightarrow E} < 10^{-5}$ and $\Phi_{E \rightarrow Z} < 10^{-5}$. Thus, the experimental findings clearly show that **1** undergoes mutual photoisomerization between *Z* and *E* isomers exclusively in the triplet state on direct irradiation as well as on triplet sensitization.[‡]

The *Z*-*E* isomerization on direct irradiation can be rationalized by Scheme 1. In the present system, k_d^Z , k_d^E , $k_{Z \rightarrow E}$ and $k_{E \rightarrow Z}$ are almost two orders of magnitude smaller than $k_q^Z[Z]$ and $k_q^E[E]$ and therefore, $k_{Z \rightarrow E}$ and $k_{E \rightarrow Z}$ can be described by eqns. (1) and (2) and were calculated from the measured

$$k_{Z \rightarrow E} \approx \frac{\Phi_{Z \rightarrow E} k_d^Z}{\Phi_{isc}^Z} \quad (1)$$

$$k_{E \rightarrow Z} \approx \frac{\Phi_{E \rightarrow Z} k_d^E}{\Phi_{isc}^E} \quad (2)$$

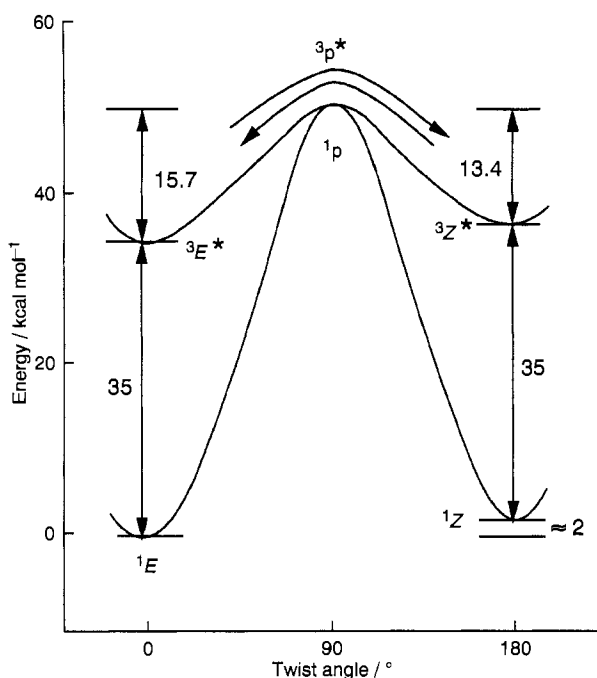
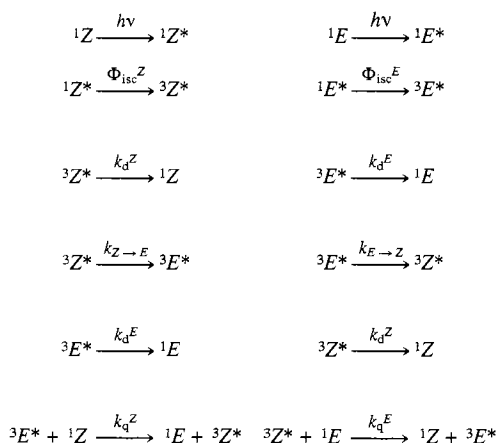


Fig. 3 Potential energy surfaces of *Z*-*E* isomerization of **1**



Scheme 1

$\Phi_{Z \rightarrow E}$ and $\Phi_{E \rightarrow Z}$ values at varying temperatures. The Arrhenius plots of the $k_{Z \rightarrow E}$ and $k_{E \rightarrow Z}$ values vs. $1/T$ (Fig. 2) gave the activation energies and the frequency factors of *Z* \rightarrow *E* and *E* \rightarrow *Z* isomerization in the triplet state as 13.4 and 15.7 kcal mol⁻¹ (1 cal = 4.184 J) and 9.1×10^{11} and 2.8×10^{12} s⁻¹, respectively.

Usually the two-way *Z*-*E* isomerization takes place with the potential energy surface descending toward ³p* as proposed for stilbene. However, **1** undergoes two-way photoisomerization having to overcome a activation barrier of more than 13 kcal mol⁻¹. Activation barriers for isomerization in the triplet state have only been successfully determined for a few compounds; and is in the range of 6–7 kcal mol⁻¹ for 2-(3,3-dimethylbut-1-enyl)anthracene⁵ and 3-styrylperylene.⁷

The triplet energy of *Z*- and *E*-**1** should be similar to or slightly lower than the parent hydrocarbon perylene ($E_T = 35.1$ kcal mol⁻¹), since normally, the triplet energies of *Z* and *E* isomers of polycyclic arylenes are similar to the parent hydrocarbon as observed for anthracene ($E_T = 42.5$ kcal mol⁻¹)⁸ and (3,3-dimethylbut-1-enyl)anthracene ($E_T = 42.5$ kcal mol⁻¹).⁵ Thus, we assume the E_T values for *Z*- and *E*-**1** as ca. 35 kcal mol⁻¹. The difference of activation energy for *Z* \rightarrow *E* and *E* \rightarrow *Z* isomerization in the triplet state corresponds to the energy difference between ³Z* and ³E* and also ¹Z and ¹E. Therefore, the potential energy surface of *Z*-*E* isomerization of **1** can be depicted as shown in Fig. 3.

To the best of our knowledge, the present energy barrier for isomerization is the highest observed for *Z*-*E* isomerization in the excited state. Furthermore, the present findings clearly show that two-way isomerization takes place through adiabatic conversion in the excited state in both directions.

The authors thank Professor Katsumi Tokumaru for discussions and encouragement. This work was partially supported by the Ministry of Education, Science and Culture, Grant-in-Aid for Specially Promoted Research No. 03101004.

Received, 8th June 1995; Com. 5/03685B

Footnotes

[†] Selected spectroscopic data: *Z*-**1**: ¹H NMR (270 MHz, CDCl₃) δ 1.81 (dd, *J* 2.0, 6.9 Hz, 3 H, methyl H), 6.05 (qd, 6.9 11.5 Hz, 1 H, CH=CH), 6.84 (qd, *J* 2.0, 11.5 Hz, 1 H, CH=CH), 7.35–8.25 (m, 11 H, perylene H). *E*-**1**: ¹H NMR (270 MHz, CDCl₃) δ 2.02 (dd, *J* 1.7, 6.6 Hz, 3 H, methyl H), 6.30 (qd, 6.6, 15.8 Hz, 1 H, CH=CH), 7.06 (qd, *J* 1.7, 15.8 Hz, 1 H, CH=CH), 7.40–8.25 (m, 11 H, perylene H).

[‡] The singlet lifetimes of *Z*- and *E*-**1** were measured as 3.5 and 2.9 ns, respectively in benzene. Taking into account the lifetimes of the excited states and the quenching rate constants by oxygen, in air only 10% of the S₁ state would be quenched by oxygen, while more than 99% of the T₁ state would be quenched by oxygen. Thus, if the isomerization takes place exclusively in the triplet excited state, the efficiency of isomerization should be considerably reduced in the presence of air, while if the isomerization takes place partially or totally in the excited singlet state, oxygen may only partly or scarcely reduce the efficiency of isomerization.

References

- G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, *J. Am. Chem. Soc.*, 1964, **86**, 3197.
- J. Saltiel and Y.-P. Sun, *Photochromism. Molecules and Systems*, ed. H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, p. 64.
- H. Goerner and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1981, **85**, 1835.
- H.-D. Becker, *Chem. Rev.*, 1993, **93**, 145.
- T. Arai and K. Tokumaru, *Chem. Rev.*, 1993, **93**, 23.
- J. K. Hurley, N. Sinai and H. Linschitz, *Photochem. Photobiol.*, 1983, **38**, 9.
- T. Arai, O. Takahashi, T. Asano and K. Tokumaru, *Chem. Lett.*, 1994, 205.
- S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973, p. 1.