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Photochemical behavior of 2-[2-(2-pyridyl)ethenyl]indole on triplet sensitization. Spin multiplicity dependence of the isomerization modes of an intramolecularly hydrogen-bonded compound

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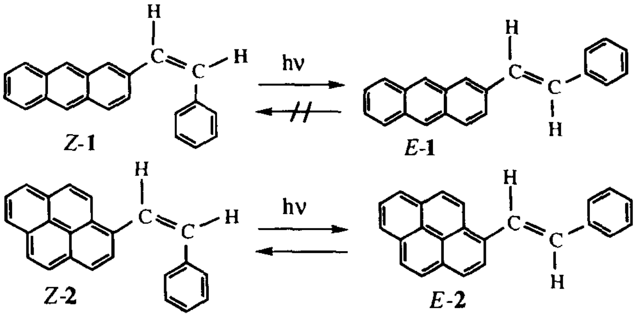
Abstract

Although 2-[2-(2-pyridyl)ethenyl]indole undergoes one-way $E \rightarrow Z$ isomerization in the excited singlet state, it isomerizes between the E and Z isomers in the excited triplet state. On the basis of the determination of the quantum yields of isomerization and the photostationary state isomer ratios, as well as transient spectroscopic measurements, the potential energy surfaces for E–Z isomerization in the triplet state have been proposed. Specific rotamers of the E and Z isomers are found to be responsible for the triplet state isomerization reactions.

Keywords: Isomerization; Intramolecular hydrogen bond; T–T absorption

1. Introduction

The effect of substituents on the mode of Z–E isomerization of double bonds in the excited state has been studied extensively [1–3]. For example, the triplet energy of the aromatic nucleus on the ethylenic carbon determines the mode of isomerization, one-way or two-way, as well as the quantum yields [1]. Stilbene undergoes two-way isomerization between the Z and E isomers in the excited singlet and triplet states [4,5]. However, replacement of a phenyl ring by an anthracene ring with a very low triplet energy brings about a dramatic change in the pathway of isomerization, leading to solely one-way $Z \rightarrow E$ isomerization of 2-styrylanthracene (**1**) in the excited triplet state. Furthermore, the quantum yield of $Z \rightarrow E$ isomerization of 2-anthrylethylenes far exceeds unity. In the potential energy surface of one-way isomerization, the initially produced Z triplet state ($^3Z^*$) isomerizes to the E triplet state ($^3E^*$) by passing through the perpendicular triplet state ($^3p^*$); the deactivation to the ground state takes place only from $^3E^*$ by a unimolecular or bimolecular energy transfer process to the ground state Z isomer, regenerating $^3Z^*$.



1-Styrylpyrene (**2**) exhibits dual character [6]. It undergoes two-way isomerization, but the $Z \rightarrow E$ isomerization proceeds by a quantum chain process as in 2-anthrylethylenes. In the triplet energy surface, **2** exists mostly as $^3E^*$, but is equilibrated with $^3p^*$ by the equilibrium constant K_{tp} ($[^3p^*]/[^3E^*]$) of 10^{-3}. Therefore deactivation can take place both from $^3p^*$ and $^3E^*$ by diabatic and adiabatic processes respectively.

Intramolecular hydrogen bonds may play a role in controlling the mode of isomerization [7–11]. Eenkhoorn et al. [7] and ourselves [9] have previously reported that 2-[2-(2-pyridyl)ethenyl]indole (**3**) undergoes one-way $E \rightarrow Z$ isomerization on direct excitation in benzene. The molecular

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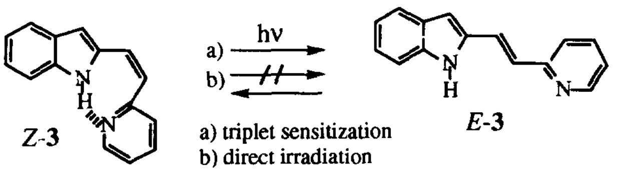
structure and photochemical behavior of **3** were established by NMR spectroscopy and molecular mechanics, as well as quantum yield determination, in various solvents [10].

This one-way isomerization is different from the $Z \rightarrow E$ one-way adiabatic isomerization of anthrylethylenes in the triplet manifold. Thus the isomerization of **3** occurs by a one-way process, but takes place in the singlet manifold and the direction is only $E \rightarrow Z$. The intramolecular hydrogen bond in *Z*-**3** suppresses $Z \rightarrow E$ isomerization by accelerating the deactivation of the *Z* singlet excited state ($^1Z^*$), therefore resulting in one-way $E \rightarrow Z$ isomerization. The one-way isomerization of **3** in the singlet excited state could take place by an adiabatic or diabatic process. The former proceeds by isomerization from the *E* singlet excited state ($^1E^*$) to $^1Z^*$ by passing through the perpendicular singlet state ($^1p^*$) ($^1E^* \rightarrow {}^1p^* \rightarrow {}^1Z^*$), followed by deactivation from $^1Z^*$ to give ^1Z, and the latter by $^1E^* \rightarrow {}^1p^*$, followed by deactivation from $^1p^*$ to give ^1Z and ^1E. Due to the absence of fluorescence emission from $^1Z^*$, definite information on whether the isomerization takes place by the adiabatic process or not is unavailable.



Z-**3** *E*-**3**

In this paper, we report the photochemical behavior of **3** in the triplet state from the viewpoint of the effect of the spin multiplicity on the mode of isomerization and in association with our recent finding of one-way $Z \rightarrow E$ isomerization of aromatic olefins (such as **1**) in the triplet state. Briefly, **3** undergoes two-way isomerization between *Z* and *E* isomers, but with a quantum chain process for the $Z \rightarrow E$ direction on triplet sensitization.

2. Experimental details

The quantum yields of *Z*–*E* isomerization and photostationary state isomer compositions were determined in benzene at ambient temperature in the presence of biacetyl as a triplet sensitizer using 436 nm light from a 400 W high-pressure mercury lamp which was passed through a solution filter (4.4 g dm^{-3} $CuSO_4 5H_2SO_4$ + 2.7 M NH_3 + 75 g dm^{-3} $NaNO_2$ in water) and a Toshiba Y-43 glass filter.

The isomer concentrations were determined by high-performance liquid chromatography (HPLC, Waters 600 multisolvent delivery system and 490 programable multiwavelength detector with a 740 data module) using an Si-60-5 column (4.6 mm × 250 mm) and eluting with hexane–ethyl acetate (85 : 15). The light intensity was measured using potassium tris(oxalato)ferrate(III) actinometry.

Laser flash photolysis was performed using a 425 nm pulsed laser (Lambda Physik FL-3002 dye laser; stilbene 3) pumped by an excimer laser (Lambda Physik LPX105E), with a pulsed xenon arc (Wacom KXL-151, 150 W) as monitoring light source. The detailed set-up is essentially the same as described previously [12].

3. Results and discussion

3.1. Isomerization quantum yields and photostationary state isomer ratios

On biacetyl sensitization with 436 nm irradiation, **3** undergoes two-way isomerization in benzene solution. The quantum yields of $Z \rightarrow E$ isomerization ($\Phi_{Z \rightarrow E}$) on biacetyl (1.17 M) sensitization increase with *Z*-**3** concentration and exceed unity as shown in Fig. 1. The values of the intercept and slope are 0.19 and 5.1×10^2 M^{-1} respectively. However, the quantum yield of $E \rightarrow Z$ isomerization ($\Phi_{E \rightarrow Z}$) is almost constant (0.16), irrespective of the trans isomer concentration. The photostationary state isomer ratio ($([E]/[Z])_{pss}$) increases linearly with the total concentration of **3** on biacetyl (0.08 M) sensitization as shown in Fig. 2, with an intercept and slope of 0.88 and 1.29×10^3 M^{-1} respectively.

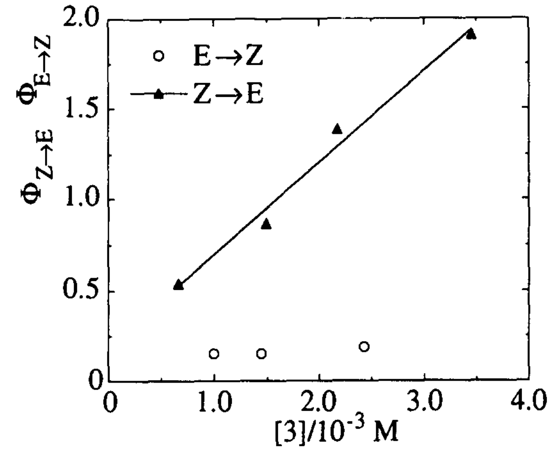


Fig. 1. Quantum yields of $Z \rightarrow E$ ($\Phi_{Z \rightarrow E}$) and $E \rightarrow Z$ ($\Phi_{E \rightarrow Z}$) isomerization of **3** on biacetyl sensitization in benzene.

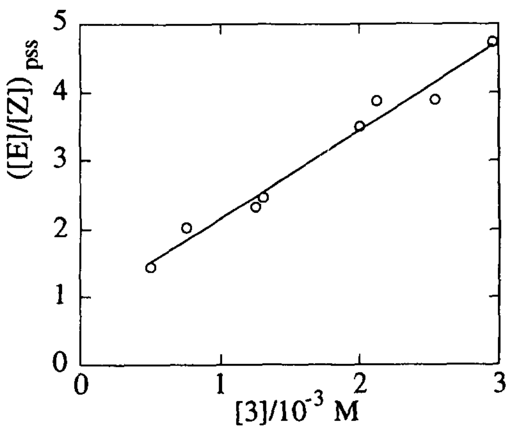


Fig. 2. Effect of total concentration of **3** on the photostationary state isomer ratio ($([E]/[Z])_{pss}$) on biacetyl sensitization in benzene.

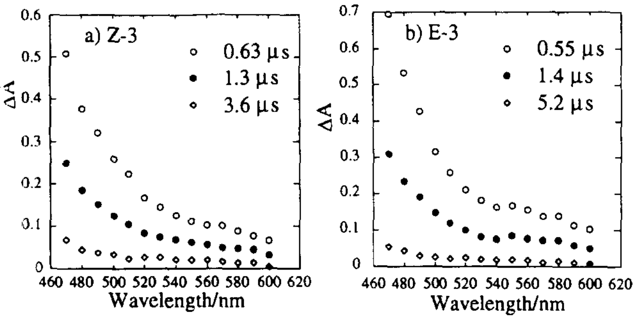


Fig. 3. T–T absorption spectra observed on biacetyl-sensitized laser excitation of Z- and E-3 in benzene.

The quantum yields of isomerization correlate with the photostationary state isomer ratio according to Eq. (1)

$$([E]/[Z])_{\mathrm{pss}}{}^0=(\Phi_{Z\to E}{}^0/\Phi_{E\to Z}{}^0) \qquad (1)$$

On biacetyl sensitization, the observed value of $\Phi_{Z\to E}{}^0/\Phi_{E\to Z}{}^0$ is 1.2 and the observed value of $([E]/[Z])_{\mathrm{pss}}{}^0$ (0.88) is close to unity.

3.2. Triplet–triplet (T–T) absorption spectra

The T–T absorption spectra observed for Z-**3** (1.49×10^{-3} M) and E-**3** (1.57×10^{-3} M) on biacetyl sensitization (0.51 M) in benzene using 425 nm laser pulses are shown in Fig. 3. At approximately 0.6 µs after the laser pulse, Z- and E-**3** exhibit the same absorption spectra with $\lambda_{\max}<460$ nm. The triplet lifetime is 2 µs under an argon atmosphere in benzene starting from both Z- and E-**3**. Oxygen quenches the transient with rate constants of 3.3×10^9 and 3.2×10^9 M^{-1} s^{-1} for Z- and E-**3** respectively in benzene, which are similar to the rate constant usually observed for the quenching of a planar triplet state by oxygen via an energy transfer mechanism, i.e. one-ninth of the diffusion-controlled rate constant for the quenching of a triplet state by oxygen (approximately 3×10^9 M^{-1} s^{-1}) [13]. Therefore the observed T–T absorption spectra are assigned to $^3E^*$.

The T–T absorption of biacetyl ($E_T=56.3$ kcal mol^{-1}) [14] observed on 425 nm laser excitation in benzene is quenched by Z- and E-**3** with rate constants of 5.3×10^9 M^{-1} s^{-1} ($k_q{}^Z$) and 5.4×10^9 M^{-1} s^{-1} ($k_q{}^E$) respectively, which are close to the diffusion-controlled rate constant (k_{dif}). However, the T–T absorption of benzil ($E_T=53.4$ kcal mol^{-1}) [14] is quenched by Z- and E-**3** with lower rate constants of $(3.87\pm0.10)\times10^9$ and $(1.85\pm0.10)\times10^9$ M^{-1} s^{-1} respectively. Using the Sandros equation (Eq. (2)) [15] for slightly endothermic energy transfer processes

$$k_q=k_{\mathrm{dif}}\exp(-\Delta E_a/RT)/[1+\exp(-\Delta E_a/RT)] \qquad (2)$$

where k_q is the quenching rate constant and E_a is the activation energy for energy transfer (roughly equal to the difference between the triplet energies of the quencher and sensitizer), and assuming that $k_{\mathrm{dif}}=5.5\times10^9$ M^{-1} s^{-1}, the triplet energies of Z- and E-**3** (E_T) are estimated to be 52.9 and 53.8 kcal mol^{-1} over their respective ground states.

3.3. Mechanism of Z–E isomerization in the triplet state

The increase in $\Phi_{Z\to E}$ and $([E]/[Z])_{\mathrm{pss}}$ with the concentration of Z-**3** and the total concentration of **3** respectively indicates that the deactivation of **3** takes place not only from ^{3}p*, but also from $^3E^*$ (Scheme 1), as in the triplet-sensitized isomerization of **2** [6]. In Scheme 1, unimolecular deactivation of ^{3}p* gives Z- and E-**3**, with a decay ratio of α from ^{3}p* to the E isomer assumed to be 0.5. $^3E^*$ deactivates via either a unimolecular process or a bimolecular process, undergoing energy transfer from $^3E^*$ to ground state Z-**3** to regenerate $^3Z^*$. The rate constants for unimolecular deactivation from $^3E^*$ and ^{3}p* (k_{Ed} and k_{pd} respectively) can be estimated as 2×10^4 and 2×10^7 s^{-1} [1] respectively at room temperature in fluid deoxygenated solution. According to Scheme 1, $\Phi_{Z\to E}$, $\Phi_{E\to Z}$ and $([E]/[Z])_{\mathrm{pss}}$ are expressed by Eqs. (3)–(5) respectively

$$\Phi_{Z\to E}=\Phi_T(\alpha K_{Ep}k_{pd}+k_{Ed}+k_{EZ}[Z-3])/(K_{Ep}k_{pd}+k_{Ed}) \qquad (3)$$

$$\Phi_{E\to Z}=\Phi_T(1-\alpha)K_{Ep}k_{pd}/(K_{Ep}k_{pd}+k_{Ed}) \qquad (4)$$

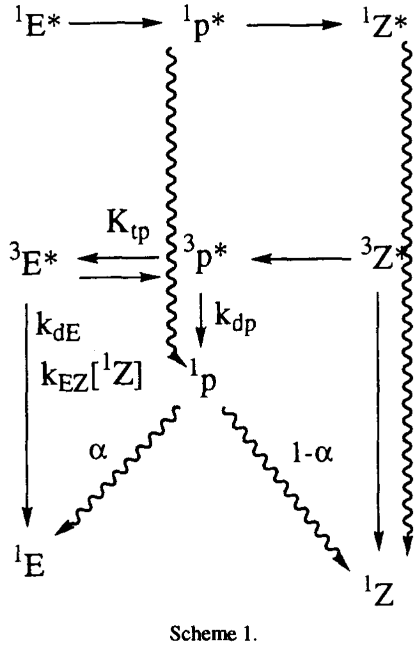
$$([E]/[Z])_{\mathrm{pss}}=(\alpha K_{Ep}k_{pd}+k_{Ed}+k_{EZ}[3])/(1-\alpha)K_{Ep}k_{pd} \qquad (5)$$

As in the isomerization of **2**, it is assumed that the equilibrium between $^3E^*$ and ^{3}p* is established with an equilibrium constant $K_{Ep}=[^3\mathrm{p}^*]/[^3E^*]$ and $k_q{}^Z=k_q{}^E$. Φ_T (equal to unity) [14] is the quantum yield of intersystem crossing from the singlet excited state to the triplet state of the sensitizer.

The K_{Ep} value can be estimated from the observed triplet lifetime ($\tau_T=2$ µs) using Eq. (6)

$$\tau_T=(1+K_{Ep})/(k_{dE}+K_{Ep}k_{dp}) \qquad (6)$$

Thus, using the values of k_{dE} and k_{dp} estimated above, K_{Ep} is determined to be approximately 2×10^{-2}; this value means that $^3E^*$ is 50 times more populated than ^{3}p*, and unimolecular deactivation can take place from both conformations at



Scheme 1.

a ratio of roughly $2\times10^7\times2\times10^{-2}$ to $2\times10^4\times1$, i.e. 20 : 1, for ^{3}p* and ^3E* respectively.

Since the slopes of Fig. 1 ($510\ M^{-1}$) and Fig. 2 ($1290\ M^{-1}$) are described as $\Phi_T k_{EZ}/(K_{Ep}k_{pd}+k_{Ed})$ and $k_{EZ}/(1-\alpha)K_{Ep}k_{pd}$ respectively, we can estimate the k_{EZ} value to be approximately $2.5\times10^8\ M^{-1}\ s^{-1}$ assuming $K_{Ep}=2\times10^{-2}$. The estimated k_{EZ} value indicates that energy transfer from ^3E* to Z-3 is a slightly endothermic process, with an activation energy estimated to be approximately 2 kcal mol^{-1} from Eq. (2).

The $([E]/[Z])_{pss}$ value extrapolated to infinite dilution $(([E]/[Z])_{pss}{}^0=(\alpha K_{Ep}k_{pd}+k_{Ed})/(1-\alpha)K_{Ep}k_{pd}=47/53)$ corresponds to the decay ratio from the triplet state of **3** giving *E*- and *Z*-**3** not accompanied by a quantum chain process. The observed value is similar to that of stilbene (40/60) [5] and β-methylstyrene (45/55) [16,17].

The quantum yields of isomerization at infinite dilution, $\Phi_{Z\to E}{}^0$ and $\Phi_{E\to Z}{}^0$, obtained as the intercepts of the plots of $\Phi_{Z\to E}$ vs. [*Z*-**3**] and $\Phi_{E\to Z}$ vs. [*E*-**3**] are 0.19 and 0.16 respectively. Their sum is only 0.35, which is much smaller than the value of approximately unity in typical triplet-sensitized isomerization reactions of unsaturated compounds [4,5]. Therefore the low value suggests the intervention of deactivation from either the *Z* or *E* triplet states prior to isomerization to ^{3}p*.

3.4. Potential energy surfaces of Z–E isomerization in the triplet state

We have already reported the potential energy surfaces in the ground state and excited singlet state of **3**; the *E* isomer in the solid state is approximately 7 kcal mol^{-1} higher in enthalpy than the *Z* isomer in the ground state as measured by DSC experiments [9]. The free energy change for $^1Z\to{}^1E$ isomerization in the ground state in benzene solution has recently been estimated as 0.2 kcal mol^{-1} from the free-radical-initiated isomerization on irradiation of diphenyl diselenide in benzene solution [10].

Fig. 4 depicts the potential energy surfaces of *Z*–*E* isomerization in the excited triplet state of **3** based solely on the free energy difference in benzene solution between ^{1}Z and ^1E (0.2 kcal mol^{-1}) and the triplet excitation energies estimated from the quenching of the triplet state of benzil. The estimated triplet energies of ^3Z* ($E_T=52.9$ kcal mol^{-1}) and ^3E* ($E_T=53.8$ kcal mol^{-1}) by quenching studies and the energy difference between ^1Z and ^1E (approximately 0.2 kcal mol^{-1}) place ^3Z* and ^3E* at nearly the same energy (^3E* slightly higher than ^3Z*) as shown in Fig. 4. This potential energy surface conflicts with the difference between the triplet excitation energies of the *E* and *Z* isomers estimated from $\Phi_{Z\to E}$. Moreover, in this potential energy surface, if $Z\to E$ isomerization takes place by a quantum chain process, we can also expect quantum chain isomerization for the $E\to Z$ direction. Therefore this potential energy surface is incompatible with the experimental findings of the photoisomerization behavior of **3**.

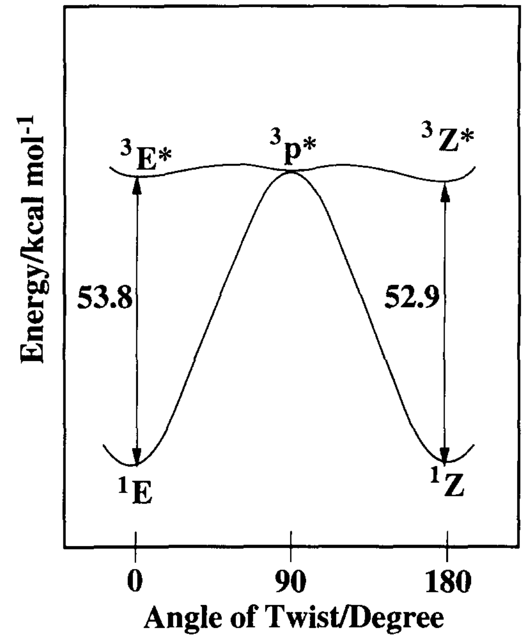
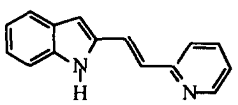
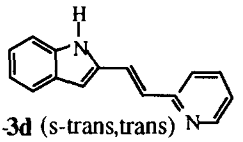
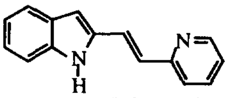


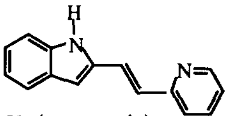
Fig. 4. Potential energy surfaces drawn on the basis of the triplet energies estimated from the rate constants of quenching of the triplet state of benzil.

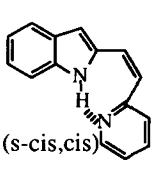
The above discrepancies can be attributed to the fact that the presence of rotamers was ignored. As reported previously, *Z*- and *E*-**3** can exist as mixtures of rotational isomers around the single bond [10]. These rotational isomers can play an important role in the energy transfer process from the triplet sensitizers to **3**, as well as the energy transfer from ^3E* to *Z*-**3** to accomplish the quantum chain process.


E-**3c** (s-cis,trans)


E-**3d** (s-trans,trans)


E-**3a** (s-cis,cis)


E-**3b** (s-trans,cis)


Z-**3a** (s-cis,cis)

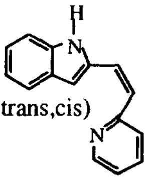

Z-**3b** (s-trans,cis)

Fig. 5 depicts the revised potential energy surfaces taking into account the energetics of the rotamers. Among the rotamers, the s-cis,trans and s-trans,trans conformers are higher in energy because of the non-bonded repulsion between the vinyl-H and the pyridyl-H, which is absent in the lower energy conformers [10]. Thus only s-cis,cis and s-trans,cis isomers (*E*-**3a**, *E*-**3b**, *Z*-**3a** and *Z*-**3b**) are considered as shown in Fig. 5. In the ground state of *Z*-**3**, the s-cis,cis rotamer (*Z*-**3a**) forms an intramolecular hydrogen bond and is more stable than the s-trans,cis rotamer (*Z*-**3b**). Usually,

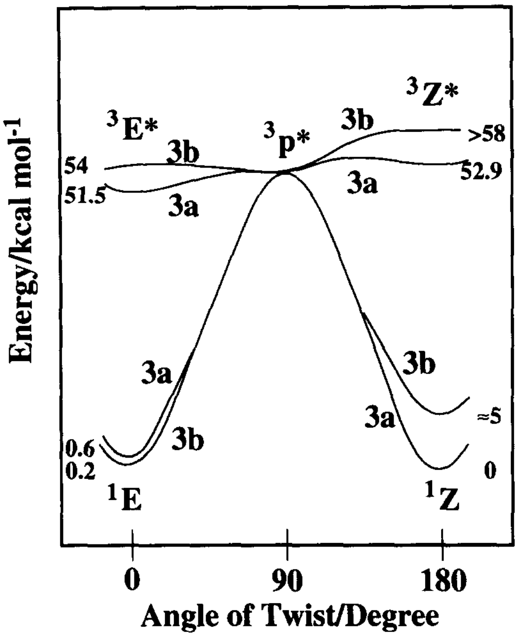


Fig. 5. Potential energy surfaces of Z–E photoisomerization in the triplet excited state including the role of rotamers.

the Z isomers of 1,2-diarylethylenes without intramolecular hydrogen bonds are about 5 kcal mol^{-1} less stable than the E isomers due to steric hindrance. Therefore Z-**3b**, which does not form an intramolecular hydrogen bond, is reasonably assumed to be less stable than Z-**3a** and any of the rotamers of E-**3** (E-**3a** and E-**3b**). Previously, E-**3b** was estimated to be more stable than E-**3a** by 0.4 kcal mol^{-1} from the results of fluorescence spectroscopy [10]. Thus the Z and E isomers of **3** adopt the s-cis,cis (Z-**3a**) and s-trans,cis (E-**3b**) conformations respectively as the most stable conformers in the ground state; Z-**3a** is more stable than E-**3b** by 0.2 kcal mol^{-1}.

Since triplet energy transfer from the triplet sensitizers to Z-**3** mostly takes place to give the s-cis,cis triplet (^{3}Z-**3a***) due to its higher population in the ground state, and internal rotation around the single bonds will not take place in the excited state prior to isomerization around the unsaturated bond, ^{3}Z-**3a*** should exclusively isomerize to ^{3}E-**3a***. Thus the difference between the triplet excitation energies of Z- and E-**3** (approximately 2 kcal mol^{-1} higher for Z than for E), estimated from the concentration dependence of $\Phi_{Z\rightarrow E}$, corresponds to the triplet excitation energy difference between E-**3a** and Z-**3a**. This will place ^{3}E-**3a*** approximately 2 kcal mol^{-1} lower in energy than ^{3}Z-**3a***.

The triplet energies estimated by the quenching of the benzil triplet state by the Z and E isomers correspond to those for s-cis,cis (Z-**3a**) ($E_T = 52.9$ kcal mol^{-1}) and s-trans,cis (E-**3b**) ($E_T = 53.8$ kcal mol^{-1}) respectively.

The above two results obtained from $\Phi_{Z\rightarrow E}$ and the quenching of the triplet state of benzil show that, in the E isomer, ^{3}E-**3a*** (s-cis,cis) is more stable than ^{3}E-**3b*** in the triplet state, whereas E-**3b** (s-trans,cis) is the most stable conformer in the ground state; on the other hand, in the Z isomer, Z-**3a** is the most stable conformer in both the ground and triplet states.

With regard to E–Z isomerization, sensitizers can transfer most of their energy to E-**3b** due to its higher population in the ground state. ^{3}E-**3b*** thus produced undergoes isomerization to ^{3}p*; ^{3}p* deactivates to the ground state to give E and Z isomers. Fig. 5 includes all of the ground and excited state energies necessary to explain the experimental findings.

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