Photochemistry of 1,2-Bis(heteroaryl)ethylenes: Photoisomerization of 1-Pyrazinyl-2-(4-quinolinyl)ethylene

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The direct and sensitized photoisomerization of 1-pyrazinyl-2-(4-quinolyl)ethylene (4-PyQE) has been investigated under various conditions. Azulene quenches the direct and triplet-sensitized *E*→*Z* photoisomerization very efficiently. Azulene quenching and direct and sensitized *E*→*Z* photoisomerization studies indicate an efficient intersystem crossing on direct excitation of (*E*)-4-PyQE and direct *E*→*Z* photoisomerization proceeds through a triplet excited state.

The photophysical and photochemical behaviour of stilbene-like compounds has been a subject of great interest for a long time.[1] A singlet mechanism for direct photoisomerization of stilbene has been well established by quenching experiments,[1a] theoretical calculations,[2] and photophysical measurements.[3] The photochemical reactions and spectroscopy of nitrogen containing heterocyclic compounds have also received much attention.[4] The (n,π^*) states introduced by the heteroatoms markedly affect the photophysical and photochemical behaviour of the compounds. For many azastilbenes and diazastilbenes, the vibronic perturbation (proximity effect) of the lowest (n,π^*) or (π,π^*) singlet states leads to efficient internal conversion or intersystem crossing.[5]

The direct photoisomerization of 1,2-bis(pyrizinyl)ethylene (BPyE) proceeds through the triplet manifold in contrast with stilbene.[6] Gennari *et al.*[7] reported the same mechanism for photoisomerization of 3-styrylquinoline (3-StQ). They, however, showed in the subsequent paper on the compound[8] that the potential-energy surfaces of the two electronically excited conformers of 3-StQ have rather different properties so that one of the excited conformers is deactivated mainly through fluorescence emission and the other mainly through a photochemical channel, the *E*→*Z* geometrical isomerization. No information on the multiplicity for the latter process was available.

We therefore studied the photophysical and photochemical properties of 1-pyrazinyl-2-(4-quinolyl)ethylene (4-PyQE), a triaza-analogue of 1-styrylnaphthalene (1-StN), to obtain insight into the mechanism of *E*→*Z* photoisomerization. The replacement of the naphthyl and phenyl groups of 1-StN by quinoline ($\Phi_{fl} < 10^{-4}$)[9] and pyrazine ring ($\Phi_{fl} = 0$, $\Phi_{isc} = 1.0$, $\Phi_{ph} = 1.0$),[5] makes the lowest $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states very close. The results are compared with those of the stilbenes, azastilbenes, diazastilbenes, 3-StQ, StNs, and BPyE.

Experimental

Materials.—Extra pure solvents were used as received or after distillation. (*E*)-4-PyQE was prepared by the condensation of 4-methylquinoline with pyrazinecarbaldehyde in acetic anhydride at *ca.* 170 °C[10] and recrystallized from hexane. (*Z*)-4-PyQE was prepared from (*E*)-4-PyQE by photoisomerization. (*E*)-4-PyQE was dissolved in methanol, degassed by bubbling with nitrogen gas for 1 h, and irradiated with UV light (350 nm) in a Rayonet photochemical reactor for 30 min. (*Z*)-4-PyQE was isolated by low-pressure preparative liquid chromatography (column, Lichro-prep RP-8 Lobar prepacked column; detector, Bio-Rad Model 1300 UV monitor at 280 nm; eluting solvents, water–methanol–tetrahydrofuran; 20:20:3, v/v). The purity of the *E* and *Z* isomers was checked by high performance liquid chromatography. Biacetyl and azulene (Aldrich) were used after fractional distillation and vacuum sublimation, respectively.

Spectra and Quantum Yield Measurements.—The apparatus and quantum-yield measurement techniques have been described previously.[6b] UV absorption spectra were recorded on a Cary 17 spectrophotometer or a Hitachi 330 spectrophotometer. The fluorescence spectra were measured on an Aminco-Bowman spectrofluorometer or a Hitachi 4 spectrofluorimeter. In order to obtain the corrected spectra, a JASCO FP 770 spectrofluorimeter with rhodamine B as a quantum counter was used. High performance liquid chromatography was performed on a Waters Associate Model 244 liquid chromatograph equipped with a Model 6000 A solvent-delivery system, a Model 440 absorbance detector fixed at 254 nm, and a Model U6K universal injector. The fluorescence quantum yields at room temperature and 77 K were determined by three or four independent experiments using quinine sulphate [Φ_{fl} (298 K) = 0.55 in H_2SO_4 (0.1 mol dm^{-3})] and/or 9,10-diphenylanthracene [Φ_{fl} (298 K) = 1.0 in cyclohexane, Φ_{fl} (77 K) = 1.0 in ethanol] as standards.[11] The maximum optical density of the solution used for determination of the fluorescence quantum yields was less than 0.1 in a cell 1 cm thick and all the quantum yields were corrected for the differences between refractive indices of solvents. Quantitative analyses were carried out by HPLC [column, μ-Bondapak C_{18} (3.9 mm i.d. × 30 cm); eluting solvent, water–methanol–tetrahydrofuran; 14:20:3, v/v]. Irradiations were carried out within low conversions (1–5%) to prevent back-reaction.

Results and Discussion

Direct Photoisomerization.—Quantum yields for direct photoisomerization of (*E*)-4-PyQE at 366 nm in several solvents are summarized in Table 1. The data in Table 1 indicate that deactivation of the singlet excited states of (*E*)-4-PyQE must include radiationless decay processes which proceed by a path not involving *E*→*Z* isomerization. An obvious possibility for explaining the rapid radiationless decay in (*E*)-4-PyQE is the involvement of an (n,π^*) state. There is increasing evidence that aza-aromatics with the lowest-lying (n,π^*) state undergo rapid internal conversion or intersystem crossing.[5] From studies of several aza-aromatics,[13] the compounds that have either the lowest (n,π^*) state or (π,π^*) state where (n,π^*)–(π,π^*)

Table 1. Quantum yields on direct and biacetyl-sensitized isomerization of (*E*)-4-PyQE.

	λ = 320 nm	λ = 366 nm			at 435.8 nm[a]			
Solvent	Φ_{fl}	$\Phi_{E\rightarrow Z}$	$\Phi_{Z\rightarrow E}$	$([t]/[c])_{pss}$	$\Phi_{E\rightarrow Z}$	$([t]/[c])_{pss}$	Φ_{isc}[b]	Φ_{isc}[c]
Benzene	0.03	0.19 0.07[j]	0.10	0.06	0.60	0.67	0.32	0.32
Hexane	0.02	0.22	0.08	0.04	0.61	0.69	0.36	—
THF	0.01	0.17	0.07	0.05	0.60	0.67	0.28	—
Ethanol	0.04	0.29 0.16[j]	0.13	0.05	0.60	0.67	0.48	0.48 0.78[d]
Methanol	0.05	0.39	0.09	0.03	0.60	0.67	0.65	—
MeOH–H_2O[e]	0.09	0.39	—	—	0.60	0.67	0.65	—
MeOH–H_2O[f]	0.23	—	—	—	—	—	—	—
MeOH–H_2O[g]	0.30	—	—	—	—	—	—	—
MeOH–H_2O[h]	0.35	—	—	—	—	—	—	—
MeOH–H_2O[i]	0.35	—	—	—	—	—	—	—

[a] Biacetyl-sensitized photoisomerization quantum yields (concentration of biacetyl is 0.1 mol dm^{-3}). [b] Quantum yields of intersystem crossing calculated by equation (1). [c] Obtained by laser flash photolysis (ref. 22). [d] At 77 K. [e] 10% H_2O by volume. [f] 30% H_2O by volume. [g] 50% H_2O by volume. [h] 70% H_2O by volume. [i] 98% H_2O by volume. [j] In deaerated solutions.

mixing occurs, show enhanced radiationless transitions. Contrary to stilbene and some aza- and diaza-analogues in which Φ_{fl} tends to unity[14] at low temperature and the isomerization is completely inhibited, Φ_{fl} remains far less than unity even at 77 K in (*E*)-4-PyQE. Radiationless decay processes seem to be the predominant deactivation pathways under these experimental conditions. It appears from Table 1 that the internal conversion is probably a negligible process while efficient intersystem crossing is operative in polar solvents and/or at low temperature.

The direct *E*→*Z* photoisomerization quantum yields of (*E*)-4-PyQE are markedly influenced by solvent polarity in contrast to stilbene[15] and 4,4′-dinitrostilbene[16] which are affected by solvent viscosity but not by solvent polarity. On variation of solvents from non-polar (hexane) to polar (methanol–water), these at first decrease reaching the minimum 0.17 then increase in the same way as the fluorescence quantum yields. In non-polar solvents (hexane to tetrahydrofuran), the $^1S \rightsquigarrow S_0$ internal conversion is enhanced and Φ_{fl} decreases because the proximity effect of the lowest $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states is enhanced as the energy of the lowest $^1(n,\pi^*)$ is elevated and the energy of $^1(\pi,\pi^*)$ is lowered as the solvent polarity increases. In polar solvents (tetrahydrofuran to methanol–water), however, intersystem crossing is enhanced and Φ_{fl} increases as the solvent polarity increases. This is probably due to the change in the electronic configuration of the lowest excited singlet state from $^1(n,\pi^*)$ to $^1(\pi,\pi^*)$ and also due to the enhanced intersystem crossing in polar solvents because the energy level of the $^1(\pi,\pi^*)$ state is lowered as the solvent polarity increases leading to the extensive spin–orbit coupling of the lowest $^1(\pi,\pi^*)$ and $^1(n,\pi^*)$ states. Such a solvent effect was also observed in the direct *E*→*Z* photoisomerization of (*E*)-BPyE,[6b] (*E*)-3-StQ,[17] and 1-(1-naphthyl)-2-(4-nitrophenyl)ethylene.[18]

The direct *Z*→*E* photoisomerization of (*Z*)-4-PyQE, however, is not affected by solvent polarity or viscosity. The quantum yields of direct *Z*→*E* isomerization are smaller than those of *E*→*Z* isomerization as observed in simple stilbenes[19] and BPyE.[6b] No fluorescence or phosphorescence from (*Z*)-4-PyQE was observed at room temperature and 77 K.

Sensitized Photoisomerization.—Under sensitized excitation using various triplet donors where only the donors absorb the exciting radiation, stilbene photoisomerization has been proposed to occur *via* a common twisted triplet intermediate which lies lower in energy than *cisoid* triplets but is nearly isoenergetic with *transoid* triplets.[1,20] It was found that the StPs and DPEs undergo reasonably efficient photosensitized isomerization.[21] Quantum yields for biacetyl-sensitized isomerization of (*E*)-4-PyQE at 435.8 nm in several solvents are summarized in Table 1. As shown in the table, the sensitized photoisomerization is not affected by the solvent polarity in contrast with direct photoisomerization. The quantum yields of benzophenone sensitized isomerization of azastilbenes are also reported to be relatively unaffected by solvents.[21]

The quantum yields of intersystem crossing ($^1S \rightsquigarrow {}^3T$) were calculated by use of equation (1) assuming that photoisomerization occurs *via* the triplet manifold only.

$$\Phi^{E}_{isc} = \Phi^{dir}_{E\rightarrow Z}\text{ (at 366 nm)}/\Phi^{sens}_{E\rightarrow Z}\text{ (at 435.8 nm)} \qquad (1)$$

The higher *E*→*Z* quantum yields in biacetyl sensitized photoisomerization than those for direct photoisomerization in polar solvents indicate that the excited singlet state does not exclusively decay to the triplet state on direct irradiation or that isomerization occurs on the singlet surface less efficiently than on the triplet surface. The intersystem crossing quantum yields of (*E*)-4-PyQE calculated by equation (1) were about the same as those determined by laser flash photolysis at room temperature,[22] substantiating the assumption that the direct *E*→*Z* photoisomerization of (*E*)-4-PyQE proceeds *via* a triplet excited state only. The solvent effect on the intersystem crossing quantum yields of (*E*)-4-PyQE is the same as that of direct *E*→*Z* isomerization quantum yields as shown in Table 1.

Photophysical and Photochemical Properties.—The fluorescence quantum yields indicate that the process is not the main deactivation path for the excited singlet state of 4-PyQE. This leads to the working hypothesis that the non-activated intersystem crossing, followed by rotation to $^3p^*$, becomes the preferred channel for photoisomerization. Laser flash photolysis in a solution at room temperature and in a matrix at 77 K indicates that the triplet state is easily populated under these conditions.[22]

The reported quantum yields of the direct photoisomerization of StNs[4a,19,23] and BPyE[6b] are far less than those of the sensitized processes. The intersystem-crossing efficiencies of stilbene and their aza-analogues are much smaller than the values calculated by equation (1).[21] The intersystem crossing of these compounds (stilbene and its aza-analogues) is reported to be almost negligible in solution at room temperature.[24] Furthermore, triplet–triplet absorptions have been observed by laser flash photolysis of 2-StN[25] and BPyE[6a] at room temperature. Therefore, the higher quantum yields of photoisomerization,

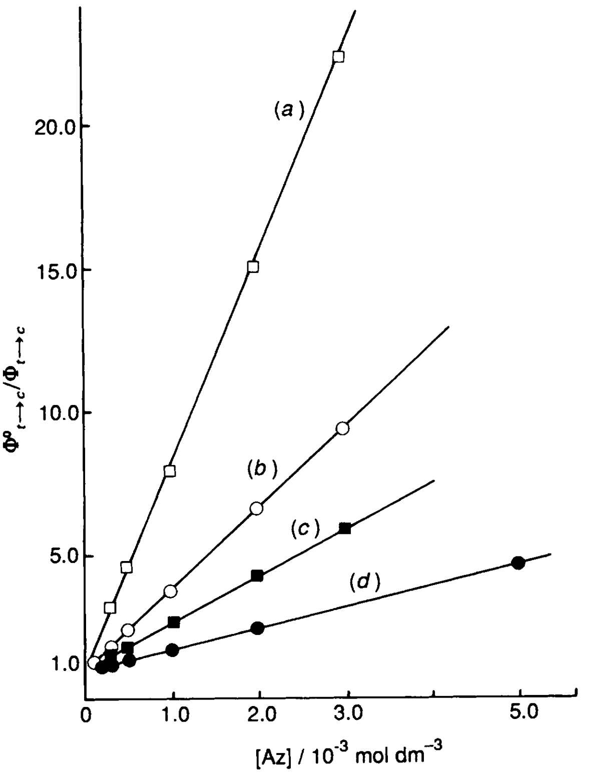

Figure 1. Stern–Volmer plots for direct $E\to Z$ photoisomerization of (*E*)-4-PyQE: (*a*) and (*b*), in benzene; (*c*) and (*d*), in ethanol; ○, deoxygenated solutions; ●, non-deoxygenated solutions.

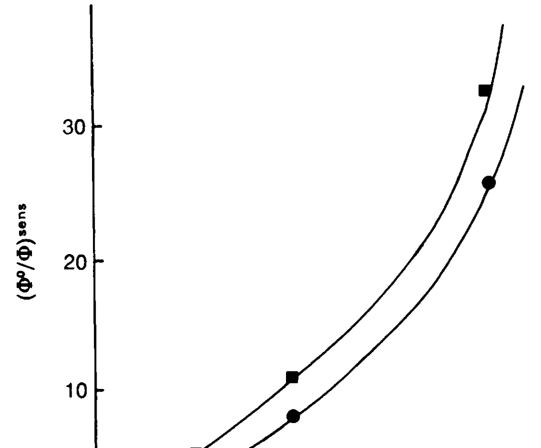

Figure 2. Stern–Volmer plots for sensitized $E\to Z$ photoisomerization of (*E*)-4-PyQE: ■, in benzene; ●, in ethanol.

always found in the sensitized reactions, indicate that the excited singlet state does not exclusively decay to the triplet state. The lower quantum yields of the direct $E\to Z$ photoisomerization compared with those of the sensitized photoisomerization for StNs, 3-StQ, and BPyE are largely explained as resulting from a low population of the triplet state by intersystem crossing and not from the radiationless decay ($^1t^*\to{}^1p^*$ rotation process) of the excited singlet states. The major fraction of the excited singlet states in aza- and diaza-analogues of stilbene, however, is deactivated by net internal conversion and intersystem crossing is almost negligible in fluid solution. The quantum yields of the $E\to Z$ isomerization of (*E*)-4-PyQE on direct irradiation are similar to those of BPyE,[6b] and the sensitized photoisomerization quantum yields are larger than those of stilbene[1] and BPyE.[6b] These results are attributed to the efficient intersystem crossing in (*E*)-4-PyQE and suggest that the $E\to Z$ photoisomerization of (*E*)-4-PyQE proceeds *via* a triplet state as observed in BPyE.[6b]

Azulene Quenching Studies.—Azulene, which is a suitable quencher of singlet and triplet states of stilbene and its aza- and diaza-analogues,[1b,26] was used in order to obtain more information on the excited state responsible for the $E\to Z$ photoisomerization. Although direct energy transfer from $^3p^*$ of stilbene to azulene is energetically forbidden,[27] Saltiel *et al.*[28] have suggested that azulene quenches $^3p^*$, the excited phantom triplet state of stilbene which has a finite lifetime but does not affect the short-lived *cisoid* triplet state in the triplet sensitized photoisomerization. Assuming the selective quenching of the *transoid* excited state by azulene and using the steady-state approximation on the excited species, the Stern–Volmer relationship [equation (2)] can be derived where, k_q is the

$$\Phi^0_{E\to Z}/\Phi_{E\to Z} = 1 + k_q\tau[\mathrm{Az}] \qquad (2)$$

quenching rate constant of the triplet state of (*E*)-4-PyQE by azulene, τ is the lifetime of quenched species of (*E*)-4-PyQE which is assumed to be the same as the triplet lifetime obtained by laser flash photolysis,[22] and $\Phi^0_{E\to Z}$ is the quantum yield of $E\to Z$ isomerization in the absence of azulene.

Azulene quenching of the direct and sensitized $E\to Z$ isomerization of 4-PyQE can be conveniently assessed by measuring initial isomerization efficiencies. The data on the azulene effect on direct isomerization in deaerated solutions yields good linear Stern–Volmer plots (Figure 1). In the triplet sensitized photoisomerization, however, the plots of $(\Phi^0/\Phi)^{sens}$ *vs.* [Az] are not linear but the plot of $(\Phi^0/\Phi)^{sens}$ *vs.* $[\mathrm{Az}]^2$ is linear as shown in Figure 2. This is because azulene also quenches the triplet state of the sensitizer (biacetyl). The plot of $(\Phi^0/\Phi)^{sens}/(\Phi^0/\Phi)^{dir}$ *vs.* [Az] is linear (Figure 3).

Since the concentration of azulene (1–5 mmol dm^{-3}) was kept low and the molar extinction coefficients of (*E*)-4-PyQE (ε *ca.* 7.7×10^3, 1.0 mmol dm^{-3} at 366 nm) and sensitizer, biacetyl, (ε *ca.* 20, 0.25 mol dm^{-3} at 435.8 nm) are much larger than that of azulene (ε *ca.* 10, at 366 nm and ε *ca.* 0 at 435.8 nm), the absorption of light by azulene itself is negligible. The excited singlet state of (*E*)-4-PyQE can also be quenched by azulene during direct irradiation. The singlet quenching, however, is negligible under our experimental conditions because the singlet lifetime (τ_S *ca.* 0.47 ns) is much smaller than the triplet lifetime (τ_T *ca.* 1.0 μs) in (*E*)-4-PyQE.

Examination of all the kinetic possibilities for photoisomerization of stilbene[29] indicates that the linear plots of equation (2) for the direct photoisomerization have a smaller slope value than that obtained for the singlet path only. Contrary to these results of stilbene and their aza- and diaza-analogues, azulene quenching studies by Gennari *et al.*[7] and Schulte-Frohlinde *et al.*[26b] indicated that the $E\to Z$ photoisomerization of 3-StQ and 4-nitrostilbene on direct excitation proceeds *via* the triplet manifold.

As shown in Figures 1 and 2, and Table 2, azulene quenches the direct and triplet sensitized $E\to Z$ photoisomerization very efficiently and the slope is dependent on the triplet lifetime of (*E*)-4-PyQE (τ_T = 1.0 μs in ethanol and 1.86 μs in benzene) which was obtained by laser flash photolysis[22] and on the viscosity of the solvents. The slope in the Stern–Volmer plots are 7.10×10^3 dm^3 mol^{-1} in deaerated benzene, 2.80×10^3

Table 2. Azulene quenching of direct and sensitized photoisomerization of (*E*)-4-PyQE.

Compounds	Direct		Sensitized	
	Intercept	Slope/intercept/dm^3 mol^{-1}	Intercept	Slope/intercept/dm^3 mol^{-1}
Stilbene[a]	0.17	14.0, 22	0.69	53
3,3′-DPE[b]	—	90	—	250
4,4′-DPE[b]	—	70	—	280
β-StN[c]	0.61	190	1.00	165
3-StQ[c]	0.75	165	0.90	150
(*E*)-BPyE[d]	0.01_5	1.4×10^3	1.19	1.4×10^3
(*E*)-4-PyQE[e]	—	2.8×10^3[e]	—	2.8×10^3[e]
	—	7.1×10^3[f]	—	7.1×10^3[f]

[a] From ref. 29(*b*). [b] From ref. 31. [c] From ref. 7. [d] From ref. 6(*b*). [e] From our experimental results in ethanol. [f] In benzene.

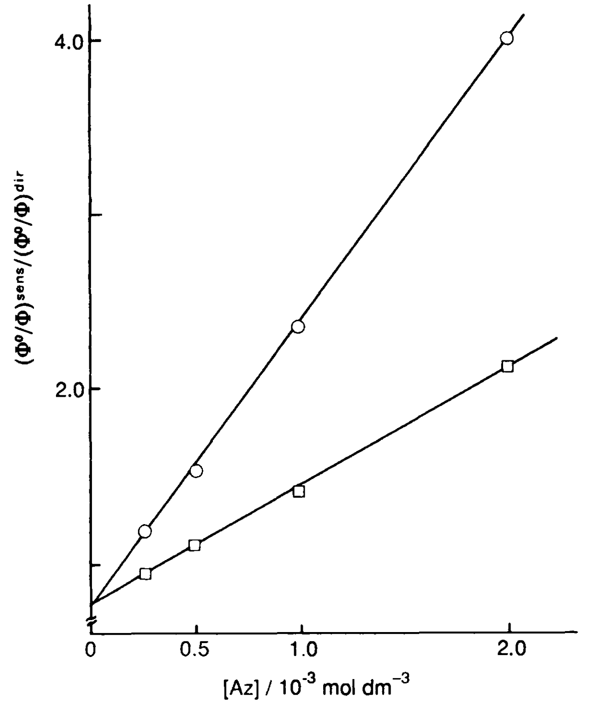

Figure 3. A plot of $(\Phi^0/\Phi)^{sens}/(\Phi^0/\Phi)^{dir}$ *vs.* [Az]: ○, in ethanol; □, in benzene.

dm^3 mol^{-1} in deaerated ethanol, 1.7×10^3 dm^3 mol^{-1} in air-saturated benzene, and 7.0×10^2 dm^3 mol^{-1} in air-saturated ethanol ($\tau_T = 0.25$ μs), respectively. In triplet-sensitized photoisomerization, azulene competes with (*E*)-4-PyQE for the sensitizer (biacetyl) triplets, *i.e.*, azulene can quench both sensitizer and (*E*)-4-PyQE triplets. If the intersystem-crossing efficiency is small in direct excitation, different slopes are expected in the Stern–Volmer plots for direct and triplet sensitized photoisomerization. In our previous paper,[6b] however, we reported that the same slope is obtained in the Stern–Volmer plots for direct and sensitized photoisomerization of (*E*)-BPyE because of the very efficient triplet formation on direct excitation [for (*E*)-BPyE, $\Phi_{isc} = 0.56$ in benzene and $\Phi_{isc} = 0.98$ in methanol]. These results indicate that the efficiency of intersystem crossing to the triplet state of (*E*)-4-PyQE is smaller than that of (*E*)-BPyE.

The effect of oxygen on the photoisomerization and photostationary states is rather puzzling in some aspects. Gorman and Rodgers[12] reported that the quenching of stilbene triplets by oxygen in benzene produces singlet oxygen with an efficiency of 18 ± 5%. They have also shown that the singlet oxygen produced cannot be the consequence of exclusive oxygen quenching of a low concentration of the planar *transoid* triplet which is in rapid equilibrium with the perpendicular form and the percentage of stilbene triplets scavenged by oxygen in oxygenated benzene is 77%. The photostationary states in the triplet-sensitized isomerization for 2-StN and 3-StQ[7] are nearly the same in the presence and absence of oxygen. Gennari *et al.*[7] reported that oxygen quenches the phantom triplet state without affecting the decay ratio for deactivation to either ground-state isomers, as found for stilbene.[30] However, the slopes in the Stern–Volmer plots for (*E*)-4-PyQE are different in deaerated and in air-saturated solutions (Figure 1) and the quantum yields of *E*→*Z* isomerization in deaerated solutions are larger than those in air-saturated solutions (Table 1); these results imply that oxygen, a well-known triplet quencher, exerts non-negligible quenching on the triplet alkene compared with azulene in contrast with the case of 2-StN and 3-StQ.[7] These results are supported by the fact that the triplet lifetime of (*E*)-4-PyQE in air-saturated solutions is much smaller than that in deaerated solutions.[22] Like stilbene triplets,[1a] almost all (*E*)-4-PyQE triplets are probably in a twisted configuration, ^{3}p*, which is deactivated to either ground state isomers. The ^{3}p* state of (*E*)-4-PyQE may be quenched by oxygen if its energy is higher than that of $^1O_2$ ($^1\Delta_g$, 22 kcal mol^{-1} *). If a triplet mechanism is involved in direct photoisomerization, this will enhance both the $^3\mathrm{p}^* + \mathrm{O}_2 \xrightarrow{k_{\mathrm{O}_2}[\mathrm{O}_2]} \alpha \mathrm{c}_0 + (1 - \alpha)\, \mathrm{t}_0$ isomerization process and the $^3\mathrm{p}^* + \mathrm{O}_2 \xrightarrow{k'_q[\mathrm{O}_2]} \mathrm{t}_0$ quenching process in (*E*)-PyQE, where k'_q is the quenching rate constant by oxygen.

The simplest mechanism that accounts for these observations is shown in Scheme 1. More recent studies[20c,28] have shown that $^3\mathrm{t}^* \rightleftarrows {}^3\mathrm{p}^*$ equilibration and quenching of ^{3}t* only is not a unique mechanism for the temperature dependence of the azulene effect on stilbene triplet decay. An alternative mechanism involving the quenching of ^{3}p* to t_0 was proposed, and the mechanism is strongly supported by the observation that both stilbene isomers are non-vertical acceptors of triplet energy.

The mechanism in the Scheme leads to equations (3)–(7).

$$\Phi^0_{E\rightarrow Z} = \Phi_{isc}\alpha \tag{3}$$

$$(\Phi^0_{E\rightarrow Z}/\Phi_{E\rightarrow Z})^{dir} = 1 + k_q[\mathrm{Az}]/k_d \tag{4}$$

$$(\Phi^0_{E\rightarrow Z}/\Phi_{E\rightarrow Z})^{sens} = (1 + k_q[\mathrm{Az}]/k_d)(1 + k''_q[\mathrm{Az}]/k_{et}[\mathrm{t}]) \tag{5}$$

$$\Phi^{\mathrm{O}_2}_{E\rightarrow Z} = \Phi_{isc}\alpha(k_d + k_{\mathrm{O}_2}[\mathrm{O}_2])/\{k_d + (k'_q + k_{\mathrm{O}_2})[\mathrm{O}_2]\} \tag{6}$$

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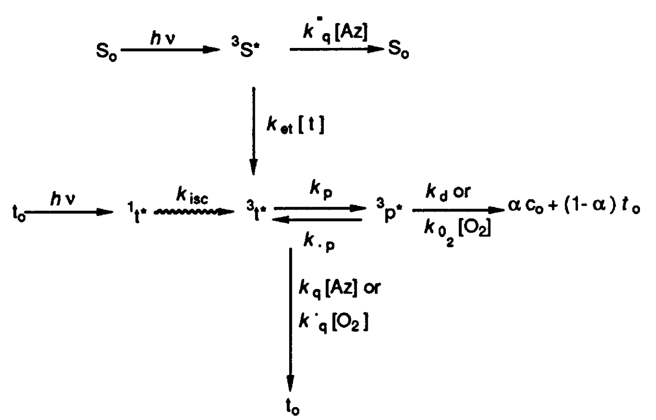
* 1 cal = 4.184 J.



Scheme 1. Mechanism of the $E \rightarrow Z$ photoisomerization of (*E*)-4-PyQE and interaction with quenchers.

$$(\Phi^0_{E\to Z}/\Phi_{E\to Z})^{\text{dir}}_{O_2} = 1 + k_q[\text{Az}]/\{k_d + (k'_q + k_{O_2})[O_2]\} \quad (7)$$

When the steady-state approximation is applied to the excited species, equations for $E \rightarrow Z$ photoisomerization quantum yields and Stern–Volmer relationships can be derived: when the deoxygenated solution is directly irradiated [equations (3) and (4)]; and in the triplet sensitized photoisomerization [equation (5)]; and when the air-saturated solution is directly irradiated [equations (6) and (7)], where α is the fraction of decay ${}^3p^*$ to c_0 (which was found to be 0.6), Φ_{isc} is the intersystem crossing quantum yield, $\Phi^0_{E\to Z}$ is the $E \rightarrow Z$ photoisomerization quantum yield in the absence of azulene, k''_q is the quenching rate constant of the triplet state of sensitizer (biacetyl) by azulene, k_{et} is the rate constant for energy transfer from sensitizer to (*E*)-4-PyQE, k'_q is the quenching rate constant of the phantom triplet state to ground state of (*E*)-4-PyQE by oxygen, and k_d and k_{O_2} are the decay rate constants of the phantom triplet state to either ground-state isomer in the absence and presence of oxygen, respectively.

From equations (3) and (6), and triplet lifetimes, we calculate that $k'_q = 0.9 \times 10^9$ dm^3 mol^{-1} s^{-1} and $k_{O_2} = 0.6 \times 10^9$ dm^3 mol^{-1} s^{-1} in ethanol, respectively. This indicates that the percentage of (*E*)-4-PyQE triplets scavenged by oxygen, $k'_q/(k'_q + k_{O_2})$, is 60%.

Equations (2), (4), and (7) clearly indicate that the slope for the direct photoisomerization should be equal to $k_q\tau = k_q/k_d$ in the deoxygenated solution and $k_q\tau = k_q/\{k_d + (k'_q + k_{O_2})[O_2]\}$ in the air-saturated solution, respectively. The quenching rate constant can be calculated from the lifetime obtained by laser flash photolysis.[22] The quenching rate constant calculated, k_q, is 3.80×10^9 dm^3 mol^{-1} s^{-1} in benzene ($\tau_T = 1.86$ μs) and $k_q = 2.80 \times 10^9$ dm^3 mol^{-1} s^{-1} in ethanol ($\tau_T = 1.0$ μs), respectively. We therefore conclude that azulene quenches the excited phantom triplet state at a rate slower than the diffusion-controlled rate. From these results, it is concluded that direct photoisomerization of (*E*)-4-PyQE occurs on the triplet surface.

Conclusions

The quantum yields of the direct $E \rightarrow Z$ photoisomerization and intersystem crossing of (*E*)-4-PyQE are changed by varying the solvent polarity, while the quantum yields of the direct $Z \rightarrow E$ and biacetyl sensitized $E \rightarrow Z$ photoisomerization are not affected by the solvent polarity. Azulene quenches the direct and triplet sensitized $E \rightarrow Z$ photoisomerization very efficiently. Azulene quenching and direct and triplet-sensitized $E \rightarrow Z$ photoisomerization indicate an efficient intersystem crossing on direct excitation of (*E*)-4-PyQE and direct $E \rightarrow Z$ photoisomerization proceeds through a triplet excited state in contrast with stilbene.

Acknowledgements

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