

THERMOCHROMISM AND PHOTOCHROMISM OF ARYL-SUBSTITUTED ACYCLIC AZINES III: INVESTIGATIONS ON THE MECHANISM OF PHOTOCHEMICAL ISOMERIZATION

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Summary

We studied the reaction mechanism of the unsensitized as well as the sensitized photochemical *E-Z* and *Z-E* isomerizations of benzophenone-9-anthraldehyde azine. The photochemistry of this compound follows a unitary $E \rightleftharpoons Z$ reaction. For qualitative investigations we used benzophenone-9-acridinealdehyde azine, 9-anthranil-2-pyridinealdehyde azine, 9-anthranil-3-quinolinealdehyde azine, 9-anthranil-9-acridinealdehyde azine and 9-acridinealdehyde azine. The experimental results are consistent with the following mechanism for the photoisomerization of azines. In the photochemical *E-Z* isomerization the S_1 state of the *E* isomer is reactive; sensitization of the triplet state does not induce the reaction. A singlet mechanism is also very probable for the *Z-E* isomerization. The most effective photochemical processes competing with isomerization are intersystem crossing in the *E* isomer and radiationless internal conversion in the *Z* isomer.

1. Introduction

By investigating variously substituted 2,3-diazabutadienes (azines) (Fig. 1) we have shown [1, 2] that photochromism is a general property of this class of compounds and that it is based on an *E-Z* isomerization about the C=N bond. However, no results on the mechanism of the photoisomerization

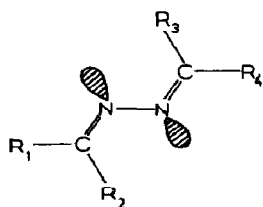


Fig. 1. The general structure of the 2,3-diazabutadienes (azines).

have been reported. There is a particular interest in investigating the mechanism of the photochemical *E-Z* isomerization because, in contrast with the various and detailed studies on the photoisomerization about the C=C bond in stilbenes, butadienes and indigoid compounds, little is known about the photoisomerization of the C=N bond. The reports are usually restricted basically to oxime ethers [3], azomethine dyes [4] and phenylhydrazones [5].

It follows then that the mechanism of the photochemical *E-Z* isomerization is heterogeneous. With benzylidene aniline [6, 7], aryl-substituted phenylhydrazones [5] and benzylidene oxime [8] a triplet mechanism is proposed whereas a singlet pathway is assumed for the unsensitized photo-reaction of oxime ethers [3] and azomethines [4]. How far these reactions may also originate from a triplet state, if properly sensitized, is still an open question.

We studied the reaction mechanism of the unsensitized as well as that of the sensitized photochemical *E-Z* and *Z-E* isomerizations, and we essentially restricted ourselves to benzophenone-9-anthraldehyde azine (BPhAA) with $R_1 \equiv R_2 \equiv \text{phenyl}$, $R_3 \equiv \text{H}$ and $R_4 \equiv 9\text{-anthranyl}$ (see Fig. 1) in the quantitative investigations. The photochemistry of this compound follows a unitary $A \rightleftharpoons B$ (*E* \rightleftharpoons *Z*) reaction. For more qualitative investigations we used benzophenone-9-acridinealdehyde azine (BPhAcA) ($R_1 \equiv R_2 \equiv \text{phenyl}$, $R_3 \equiv \text{H}$, $R_4 \equiv 9\text{-acridinyl}$), 9-anthranyl-2-pyridinealdehyde azine (APA) ($R_1 \equiv 9\text{-anthranyl}$, $R_2 \equiv R_3 \equiv \text{H}$, $R_4 \equiv 2\text{-pyridyl}$), 9-anthranyl-3-quinolinealdehyde azine (ACA) ($R_1 \equiv 9\text{-anthranyl}$, $R_2 \equiv R_3 \equiv \text{H}$, $R_4 \equiv 3\text{-quinolyl}$), 9-anthranyl-9-acridinealdehyde azine (AAA) ($R_1 \equiv 9\text{-anthranyl}$, $R_2 \equiv R_3 \equiv \text{H}$, $R_4 \equiv 9\text{-acridinyl}$), 9-acridinealdehyde azine (AA) ($R_1 \equiv R_4 \equiv 9\text{-acridinyl}$, $R_2 \equiv R_3 \equiv \text{H}$) and 9-anthraldehyde azine (A) ($R_1 \equiv R_4 \equiv 9\text{-anthranyl}$, $R_2 \equiv R_3 \equiv \text{H}$).

2. Experimental

The procedures for preparation of the compounds, purification of the solvents, recording the absorption spectra and the determination of the quantum yields have been given elsewhere [2]. Sensitizers and quenchers were purchased from Merck, Schuchardt and Fluka; they were used without further purification. The conditions of sensitization were chosen so that all radiation near the irradiation wavelength was absorbed by the sensitizer and that side reactions of the dye with itself or by photobleaching did not occur [9]. The sensitizer concentration was between 2.5×10^{-5} and 3.5×10^{-5} M and the concentration of *E*-BPhAA was between 2×10^{-5} and 9×10^{-5} M. The photochemical *Z-E* isomerization was studied by starting with the photostationary equilibrium established with radiation of wavelength $\lambda' = 436$ nm which contained a high proportion of the *Z* isomer. The concentration of *Z*-BPhAA after photochemical enrichment varied from 1.5×10^{-5} to 7×10^{-5} M.

The concentration of triplet quenchers was varied from 10^{-3} to 10^{-2} M (10- to 100-fold excess). Solutions were degassed either by the freeze-thaw technique, using a final pressure of 10^{-4} Torr and sealing off the cells, or by purging with nitrogen or oxygen-free argon. Measurements under an excess pressure of oxygen were performed in toluene using a Varian pressure cell. Fluorescence measurements were accomplished by means of a spectrofluorimeter Fica 55 (ARL, France).

3. Results

3.1. Quenching experiments

The quenchers listed in Table 1 having triplet energies between 65.7 and 35 kcal mol⁻¹ were selected for the investigation of the influence of triplet quenchers on the quantum yield of the *E-Z* isomerization as well as of the *Z-E* isomerization of BPhAA. In no case was either the quantum yield of the *E-Z* isomerization or that of the *Z-E* isomerization affected. The quantum yields in air-saturated and degassed solutions were also identical.

The azines BPhAcA, APA, ACA, AAA and AA showed the same result. Anthracene and *trans*-stilbene, additionally applied in the concentration range 10^{-1} - 10^{-2} M, also had no influence on the quantum yields of the *E-Z* isomerization of these azines.

3.2. Sensitization

To sensitize the triplet state of BPhAA we preferred to choose those sensitizers with an S₁ state lying below that of the azine and with a longest wavelength absorption band which did not overlap with that of the azine. Table 2 lists the most suitable sensitizers which we used for studying the *E-Z* and *Z-E* isomerizations of BPhAA.

It can be seen from Table 2 that in no case can the photochemical *E-Z* isomerization be sensitized. In the presence of eosin Y, erythrosin, rose bengale or 2'-acetonaphthone, the *Z-E* isomerization can be induced by

TABLE 1

Triplet quenchers for the *E-Z* and *Z-E* isomerizations of BPhAA

Quencher	E_T [10] (kcal mol ⁻¹)	Quencher	E_T [10] (kcal mol ⁻¹)
Biphenyl	65.7	<i>trans</i> -Stilbene	50
Phenanthrene	62	Ferrocene	43
Naphthalene	60.9	Anthracene ^a	42
2'-Acetonaphthone	59.4	3,3,4,4-Tetramethyl-1,2-diazetin-1,2-dioxide	
Chrysene	56.6	(Ullman quencher) ^a [11]	35
Benzil	53.4		
Fluorenone	53		

^aConcentration, 0.1 M.

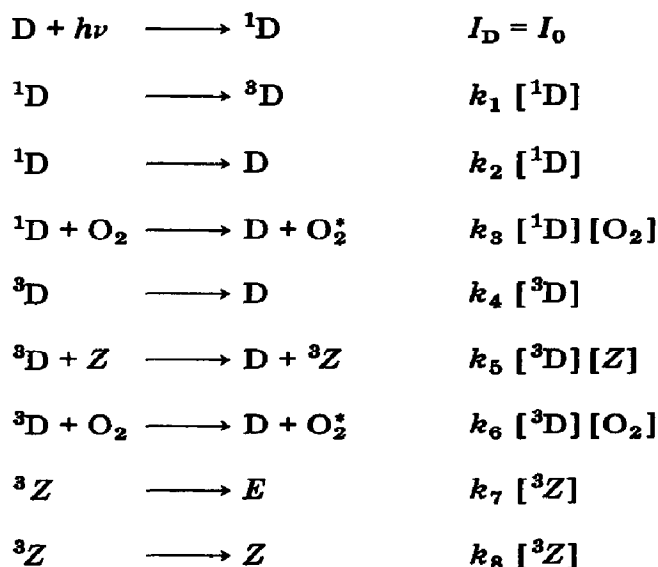
TABLE 2

Qualitative results of the triplet-sensitized photoreaction of BPhAA

Sensitizer	E_T (kcal mol ⁻¹)	ϕ_{ISC}^D	Observed isomerization ^a	
			<i>E-Z</i>	<i>Z-E</i>
2'-Acetonaphthone	59.3 [2]	0.84 [12]	—	+
Eosin Y	42.6 [12]	0.43 [12]	—	+
	43.2 - 46.0 [14]	0.25 [13]		
	45.5 [15]			
Erythrosin	44.0 [12]	1.06 [12]	—	+
	42.0 - 41.7 [13]	0.62 [13]		
	43.1 - 45.8 [14]			
Rose bengale	39.4 [13]	0.76 [13]		
	39.5 - 42.2 [14]	0.80 [14]	—	+
Methylene blue	34.0 [14]	0.52 [9]	—	—
Thionine	36 ^b	0.62 [12]	—	—
Crystal violet	39.2 [16]	?	—	—

^a—, no isomerization observed; +, isomerization observed.^bEvaluated using the singlet-triplet splitting of methylene blue [14].

radiation corresponding to the longest wavelength absorption band of the sensitizer (with eosin Y and erythrosin $\lambda' = 546$ nm; in the case of 2'-acetonaphthone the experimental conditions were chosen in such a manner that the radiation was preferentially absorbed by the sensitizer with $c_{sens} = 10^{-2}$ M, solution degassing using the freeze-thaw technique, $E' \approx 15$, $\lambda' = 333$ nm).



Consequently using the relations

$$\varphi_{ISC}^D = \frac{k_1}{k_1 + k_2 + k_3 [O_2]}$$

and

$$\varphi_{TR} = \frac{k_7}{k_7 + k_8}$$

it follows that

$$\frac{1}{(\varphi_E^Z)_{sens}} = \frac{1}{\varphi_{ISC}^D \varphi_{TR}} \left(1 + \frac{k_4 + k_6 [O_2]}{k_5} \frac{1}{[Z]} \right) \quad (1)$$

for the quantum yield of the sensitized $Z-E$ isomerization.

The Stern-Volmer relation (eqn. (1)) for the sensitizers eosin Y and erythrosin is shown in Fig. 2; the intercepts as well as the slopes of the straight lines are given in Table 3. The Stern-Volmer relation eqn. (1) also holds for BPhAcA using eosin Y and erythrosin as sensitizers.

The triplet reaction quantum yield φ_{TR} and the rate constant k_5 of the energy transfer process were derived from the intercept and the slope of the

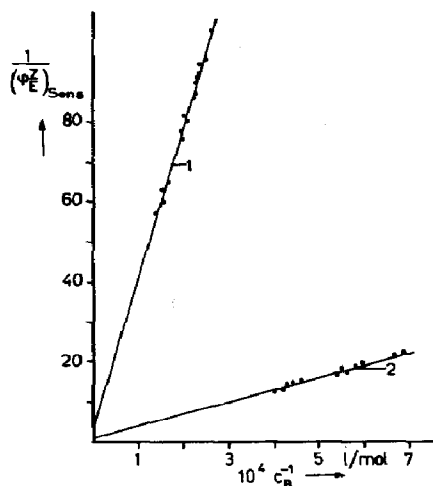


Fig. 2. A Stern-Volmer plot of the sensitized $Z-E$ isomerization of BPhAA: curve 1, eosin Y as sensitizer; curve 2, erythrosin as sensitizer.

TABLE 3

Intercepts and slopes of the Stern-Volmer plot of the sensitized $Z-E$ isomerization of BPhAA

Sensitizer	Intercept	Slope
Eosin Y	2.75 ± 1.15	$(3.41 \pm 0.55) \times 10^{-8}$
Erythrosin	0.97 ± 0.14	$(3.76 \pm 0.09) \times 10^{-4}$

Stern–Volmer plot using the known quantities $\varphi_{\text{ISC}}^{\text{D}}$ [12], k_4 [12] and k_3 [13]. The unknown oxygen concentrations were taken as 0 and 10^{-5} M. The results are given in Table 4.

3.3. Perturbation experiments

The quantum yields of the photochemical E – Z and Z – E isomerizations were evaluated under increased oxygen pressure as well as in heavy atom solvents. The results are shown in Table 5.

The quantum yield φ_Z^E of the E – Z isomerization is unaffected by oxygen or by heavy atom solvents. The quantum yield φ_Z^E depends on the Lewis acidity of the solvents. It has been shown by regression analysis that φ_Z^E increases with increasing acceptor number (according to Gutmann [17]). The slightly enhanced quantum yields in bromobenzene and iodobenzene compared with that in benzene are solely due to the differing Lewis acidity in this series of solvents.

In contrast, the quantum yield φ_E^Z of the Z – E isomerization is increased by both perturbation effects. We obtained the same result with BPhAcA; the quantum yields of the E – Z isomerization for the azines APA, ACA, AAA and AA are also unaffected by perturbation.

3.4. Fluorescence

The thermodynamically stable E isomers of all the aryl- or heteroaryl-substituted azines investigated do not show fluorescence even if low temperatures are applied. Fluorescence of the Z isomer was examined using Z -BPhAA as an example. At room temperature even in highly viscous solvents no fluorescence could be detected with this compound, but it could be observed at 77 K in methylcyclohexane–isopentane and in ether–isopentane–ethanol. The fluorescence spectrum shows a vibrational structure and is

TABLE 4

Triplet reaction quantum yields φ_{TR} of 3Z -BPhAA and rate constants k_5 of the energy transfer

Sensitizer	φ_{TR}	k_5 ($c_{\text{O}_2} = 0$ M)	k_5 ($c_{\text{O}_2} = 10^{-5}$ M)
Eosin Y	0.87 ± 0.37	$(2.42 \pm 1.02) \times 10^6$	$(1.21 \pm 0.51) \times 10^7$
Erythrosin	0.97 ± 0.15	$(1.65 \pm 0.24) \times 10^6$	$(4.76 \pm 0.68) \times 10^7$

TABLE 5

Perturbation effect on the quantum yields of the E – Z and Z – E isomerizations of BPhAA

Solvent	φ_Z^E	φ_E^Z
Toluene–benzene	0.005 ₃	0.2 ₁
Toluene–benzene ($p_{\text{O}_2} = 25$ atm)	0.005 ₃	0.2 ₆
Bromobenzene	0.005 ₈	0.2 ₅
Iodobenzene	0.005 ₉	0.2 ₈

closely similar to that of 9-butylanthracene [18]. The fluorescence quantum yield was evaluated to be about 1×10^{-3} at 77 K.

The different fluorescence behaviour of the *E* and *Z* isomers of the azines corresponds well with the different nature of the lowest energy electronic transitions. Whereas the longest wavelength main absorption band scarcely allows the detection of a solvent influence, its longest wavelength shoulder shows a hypsochromic shift with increasing solvent polarity. Thus, the lowest energy transition of the *E* isomers is an $n-\pi^*$ transition.

However, the longest wavelength absorption band of the *Z* isomers shows the vibrational structure typical of anthracene derivatives without the solvent-dependent shoulder observed with the *E* isomers [1, 2]. Hence the lowest excited state of the *Z* isomers should have a $\pi\pi^*$ configuration.

Consequently the (anthranlyl-substituted) azines exhibit the general fluorescence behaviour of the *meso*-substituted anthracenes [19]. Those anthracene compounds the longest wavelength absorption bands of which no longer show the vibrational structure typical of anthracenes, like the *E* isomers, do not fluoresce.

4. Discussion

4.1. Sensitized photoreaction

With the exception of 2'-acetonaphthone all the sensitizers employed absorb at longer wavelengths than do the azines; thus a singlet-singlet energy transfer can be ruled out. Since the effectiveness of the sensitized photoreaction depends on the intersystem crossing probability of the sensitizers and since it is substantially more consistent with the O_2 dependence of the triplet lifetime of the sensitizers if oxygen is removed, only the triplet state of the sensitizer can be responsible for the sensitization process. It can be seen from Table 2 that sensitizers with triplet energies $E_T > 40 \text{ kcal mol}^{-1}$ are able to sensitize the photochemical *Z-E* isomerization. Since sensitizers with $E_T \leq 36 \text{ kcal mol}^{-1}$ no longer induce the photoreaction, the triplet state of the *Z* isomer is localized. The assumed triplet-triplet energy transfer is confirmed by the quantitative analysis of the sensitized photoreaction.

Thus, the Stern-Volmer equation eqn. (1) exhibits the expected linearity, and the ratio of the intercepts of the Stern-Volmer lines for two different sensitizers is identical with the ratio of the intersystem crossing quantum yields of those sensitizers. The ratio of the intercepts of the sensitizers erythrosin and eosin is 2.8 ± 1.2 , and $\varphi_{ISC}(\text{erythrosin})/\varphi_{ISC}(\text{eosin Y})$ has been evaluated to be 2.5 ± 0.3 [20]. The same close correspondence of these values was found with BPhAcA.

The triplet reaction quantum yield φ_{TR} almost approaches the limiting value of unity (see Table 4). Accordingly the triplet state of the *Z* isomer populated by sensitization decays nearly quantitatively by forming the ground state of the *E* isomer. Consequently radiationless decay generating the S_0 state is not dominant in 3Z .

However, the triplet state of the *E* isomer is quantitatively deactivated by radiationless internal conversion to its S_0 state. These experimental findings are consistent with the assumption of a triplet state common to both isomers.

Therefore the photochemical *Z*-*E* isomerization may proceed via a triplet state if this is populated by sensitization. This is impossible in the case of the *E*-*Z* isomerization.

The experimentally determined rate constants k_5 of the energy transfer (see Table 4) fall far below the values expected for diffusion-controlled processes. Upon sensitization by xanthene dyes deviations of a similar order of magnitude have also been reported by other authors [20]. In this case two reasons have to be considered:

- (1) the energy transfer process to the twisted *Z* isomer is sterically hindered, by analogy with phenylhydrazones [5];
- (2) the triplet energy of the *Z* isomer differs only slightly from those of the sensitizers and thus an energy back transfer may reduce the experimental values of k_5 .

4.2. Unsensitized photoreaction

Since the photochemical *E*-*Z* isomerization cannot be induced by triplet sensitizers and since it cannot be affected by triplet quenchers, the assumption is justified that the unsensitized photoreaction originates from the singlet state. As a preliminary this does not hold for the *Z*-*E* isomerization. Since not only quenchers having lower triplet energies and employed in high concentrations but also oxygen do not have any influence on the quantum yield, a singlet path seems to be probable for the *Z*-*E* isomerization as well.

According to Birks [21], conclusions cannot be drawn from the sign of the perturbation effect for the reaction mechanism without detailed photo-physical knowledge. In the present case the results of the sensitization experiments were taken into consideration. The following relations were obtained:

$$\Phi_Z^E > \varphi^3_Z^E \approx 0$$

$$\varphi^3_E^Z \approx 1 > \Phi_E^Z$$

From Table 5 it follows that oxygen and heavy atom solvents increase only the quantum yield of the *Z*-*E* isomerization whereas that of the *E*-*Z* isomerization remains unaffected. For the time being, because of the missing perturbation effect, no statements about the mechanism can be made concerning the *E*-*Z* isomerization. This also applies to the *Z*-*E* isomerization because, according to the second relation, a perturbation effect can only affect the quantum yields by increasing them, regardless of the mechanism of the *Z*-*E* isomerization in light atom solvents.

To account for a missing or small perturbation effect generally two reasons have to be taken into consideration. Either the intersystem crossing process is already so effective that perturbation affects it very slightly or not at all, or the energy gap between the S_1 state and the nearest lower lying T_n

state or the nearest higher lying T_m state respectively, if the latter is not too high, is very large [22]. From the spectroscopic point of view the Z isomer of BPhAA is comparable with 9-(*n*-butyl)-anthracene owing to the strong torsion of the C=C (anthranyl) bond. It is known [19, 23] that the S_1 state of anthracene is lowered by 9-alkyl substitution and that it drops below the T_2 state, in contrast with unsubstituted anthracene. Because of the large S_1-T_1 energy gap (the lowest excited state of the Z isomer has the $\pi\pi^*$ configuration) intersystem crossing is most probably not realized by an S_1-T_1 but rather by a thermally activated S_1-T_n ($T_2?$) transition. The probability of this, however, is low due to the high energy barrier. The large energy difference between the S_1 state and the nearest lower T_n state (probably T_1 with an S-T splitting of about $11\,000 - 15\,000\text{ cm}^{-1}$) should therefore be responsible for the small perturbation effect in the $Z-E$ isomerization.

The missing perturbation effect in the $E-Z$ isomerization has to be discussed in another manner. Considering the mean S-T splitting evaluated for azomethines [6] it has to be expected for the E isomer that the T_n ($n\pi^*$) state corresponding to the S_1 ($n\pi^*$) state should be placed only slightly below the latter. Therefore the intersystem crossing process is already very effective without perturbation.

In summary, we propose the following picture for the photoisomerization of azines.

In the photochemical $E-Z$ isomerization the S_1 state of the E isomer is reactive; sensitization of the triplet state does not induce the reaction. A singlet mechanism is also highly probable for the $Z-E$ isomerization because quenchers, even with low triplet energies and in high concentrations, do not affect the isomerization quantum yield. While the S_1 state of the Z isomer is preferentially deactivated by internal conversion to the ground state, in the case of the E isomer deactivation proceeds via intersystem crossing, the triplet state being nearly quantitatively deactivated to the ground state. (An influence on the rate constants of radiationless deactivation by *meso* substitution of anthracene is also known with 9-alkyl-substituted anthracene derivatives which are spectroscopically similar to the Z isomer of BPhAA [19].)

The most effective photophysical processes competing with isomerization are intersystem crossing in the E isomer and radiationless internal conversion in the Z isomer.

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