

THERMOCHROMISM AND PHOTOCHROMISM OF ARYL-SUBSTITUTED ACYCLIC AZINES II: PHOTOKINETICS

K. APPENROTH, M. REICHENBÄCHER and R. PAETZOLD
Sektion Chemie der Friedrich-Schiller-Universität, Jena (G.D.R.)
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Summary

Acyclic azines with higher condensed aromatic and heterocyclic substituents are photochromic and show both thermal isomerization and photochemical isomerization. From the point of view of formal kinetics the azines can be divided into four reaction types depending on the substituents R_i . The correspondence of the expected formal kinetic behaviour of the azines with the experimental results is a direct proof of a photochemical $E-Z$ isomerization of these compounds. We investigated acyclic azines which fulfil all criteria of a complicated unitary photoreaction of the type $A \rightleftharpoons B$ as well as those azines showing a reversible consecutive photoreaction $A \rightleftharpoons B \rightleftharpoons C$. All quantum yields were determined using formal kinetics.

1. Introduction

The photochemical $E-Z$ isomerization of the $C=N$ bond has been extensively studied with hydrazones, anils, oxime ethers, azomethine dyes and triazines [1 - 7]. However, little is known about the photochemistry of 2,3-diazabutadienes (azines) (Fig. 1).

With the exception of qualitative investigations of some aryl-substituted azines as mixtures of E and Z isomers on polychromatic irradiation, there have essentially only been reports on the irreversible photolysis of alkyl- and aryl-substituted azines [8 - 13].

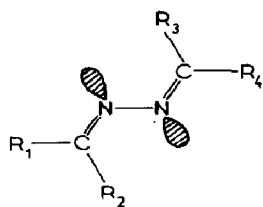


Fig. 1. The general structure of the 2,3-diazabutadienes (azines).

We have found that azines with higher condensed aromatic and heterocyclic substituents show thermal and photochemical isomerizations with large spectral changes, and we have reported [14] on the spectroscopic, thermal and photochemical behaviour of benzophenone-9-anthraldehyde azine.

We have assumed that the photochromism of azines is based on an *E-Z* isomerization about the C=N bond. However, this has not yet been proved experimentally. It is also still unclear whether the photochromism based on photochemical *E-Z* isomerization is a property common to all aryl-substituted azines or whether it is restricted to certain derivatives.

Photokinetics may supply the experimental proof of a photochemical *E-Z* isomerization. Using formal kinetics we selected and investigated 17 differently substituted azines; the results of these studies are reported in this work.

2. Experimental

The azines selected for our study are shown in Table 1. The azines were prepared under exclusion of actinic light according to known procedures, or analogously if synthesized for the first time. We will report elsewhere on the synthesis and the spectroscopic properties of these compounds.

TABLE 1

The azines investigated

Notation	Substituents (according to Fig. 1)			
	R_1	R_2	R_3	R_4
I	Ph	H	H	Ph
II	Ph	Ph	Ph	Ph
III	Ph	Ph	H	Ph
IV	Ph	Ph	H	Mes
V	Ph	Ph	H	NO ₂ -Ph
VI	Ph	Ph	H	Me ₂ N-Ph
VII	Ph	Ph	H	Anth
VIII	Me ₂ N-Ph	Me ₂ N-Ph	H	Anth
IX	Anth	H	H	Anth
X	Mes	H	H	Mes
XI	Ph	Ph	H	Acr
XII	Naph	H	H	Anth
XIII	Quin	H	H	Anth
XIV	Me-Anth	H	H	Me-Anth
XV	MeO-Anth	H	H	MeO-Anth
XVI	Anth	H	H	Acr
XVII	Acr	H	H	Acr

Ph, phenyl; Acr, 9-acridinyl; Mes, Mesityl; NO₂-Ph, *p*-nitrophenyl; Anth, 9-anthranlyl; Me₂N-Ph, *p*-dimethylaminophenyl; Naph, 1-Naphthyl; MeO-Anth, 10-methoxy-9-anthranlyl; Quin, 3-quinolylyl; Me-Anth, 10-methyl-9-anthranlyl.

The solvents used were purified by the usual methods [15]. High pressure mercury lamps (HBO 200, VEB Narva, Berlin) were used as irradiation sources. Certain spectral lines were selected by means of HgMon or metal interference filters (VEB Carl Zeiss, Jena).

Spectra were recorded with a Cary model 17 spectrometer. Partial quantum yields were evaluated according to the methods given previously [16 - 18]. The molar absorptivities of the photoproducts were determined after thin layer chromatography (TLC) separation. It is impossible to separate completely by TLC all isomers in a three-component system. The molar absorptivity ϵ_C of component C of the azine IX was evaluated by extrapolation from the E diagram [16]. Quantum yields were not determined for those few azines which did not allow the separation of the isomers.

3. Results

We have already reported [14] the spectral changes of benzophenone-9-anthraldehyde azine (VII) upon irradiation into the longest wavelength absorption band. The photoreaction can be described by a complicated unitary reaction ("komplizierte, einheitliche Reaktion" according to Mauser's notation [16]):



This is confirmed by the following experimental results.

(1) TLC exhibits only two spots, which can be assigned unequivocally to the A and B isomers.

(2) The Extinktions Differenzen (ED) diagrams [16] of the photochemical forward and back reactions are strictly linear and have the same slope for both reactions. The slope calculated from the ED diagram

$$\frac{\Delta E_1}{\Delta E_2} = \frac{\epsilon_{1B} - \epsilon_{1A}}{\epsilon_{2B} - \epsilon_{2A}}$$

agrees with the experimentally determined slope to within $\pm 2\%$.

(3) The concentration diagram (Fig. 2) shows a ratio ν_A/ν_B of the stoichiometric coefficients of -1 for the photochemical forward and back reactions, as expected for an $A \rightleftharpoons B$ system.

The photochemistry of bis(*p,p'*-dimethylamino)-benzophenone-9-anthraldehyde azine (VIII) and benzophenone-9-acridinealdehyde azine (XI) is essentially identical with that of the photostationary state upon irradiation with $\lambda' = 436$ nm in air-saturated toluene solution (Fig. 3).

The compounds VIII and XI show the same photokinetics as azine VII. Both compounds fulfil all criteria of a complicated unitary photoreaction of type 1, as specified for azine VII.

In Table 2 the quantum yields for VII, VIII and XI in air-saturated toluene are given. In the range 365 - 436 nm the quantum yields are independent of wavelength.

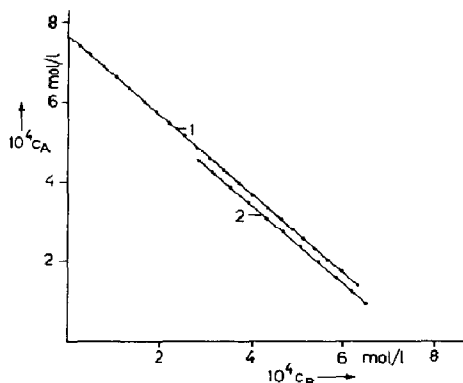


Fig. 2. A concentration diagram of the photoreaction of VII: 1, irradiation with $\lambda' = 436 \text{ nm}$; 2, irradiation of the solution in the photostationary state with $\lambda' = 365 \text{ nm}$.

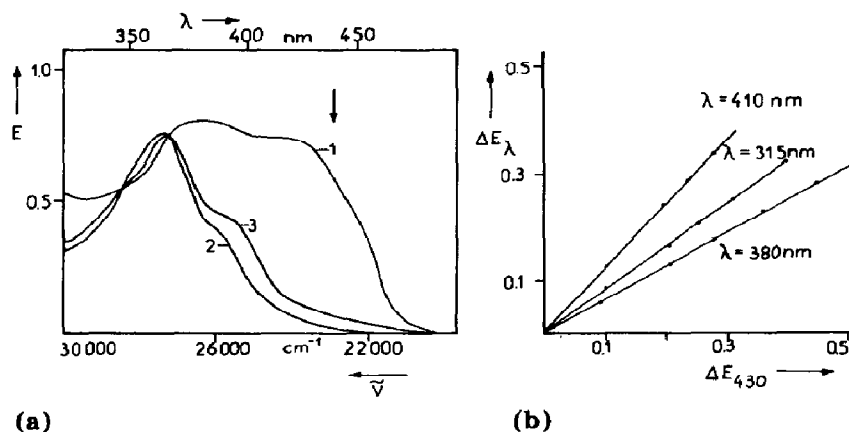


Fig. 3. (a) Absorption spectra of the forms (1) A (*E* isomer) and (2) B (*Z* isomer) of the azine XI and (3) of the photostationary state resulting from irradiation with $\lambda' = 436 \text{ nm}$ in toluene ($C_0 = 6.9 \times 10^{-5} \text{ mol l}^{-1}$); (b) the ED diagram.

TABLE 2

Quantum yields of azines VII, VIII and XI in air-saturated toluene

Compound	ϕ_B^A	ϕ_A^B
VII	0.005 ₃	0.2 ₁
VIII	0.02 ₉	0.1 ₃
XI	0.003 ₃	0.1 ₅

Figure 4 shows the spectral changes upon irradiation into the longest wavelength absorption band of 9-anthraldehyde azine (IX) in cyclohexane as well as the ED and Extinktions Differenzen Quotienten (EDQ) diagrams [16] derived from them. The spectra of the three pure isomers A, B and C of IX are shown in Fig. 5.

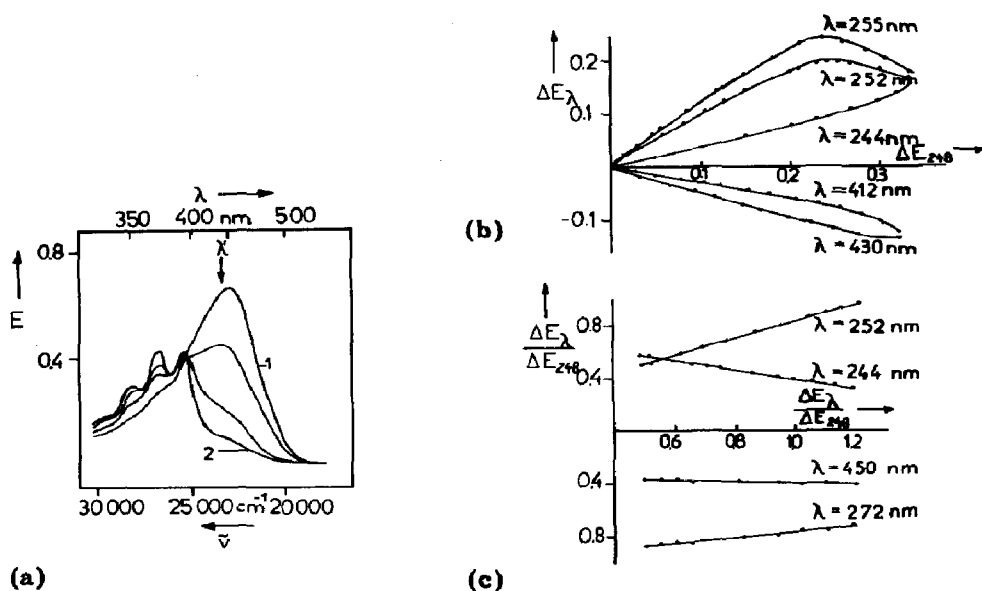


Fig. 4. (a) Spectral changes of the longest wavelength absorption band of IX in cyclohexane ($\lambda' = 436 \text{ nm}$): 1, form A ($C_0 = 3.15 \times 10^{-5} \text{ mol l}^{-1}$); 2, photostationary state. (b) ED diagram; (c) EDQ diagram.

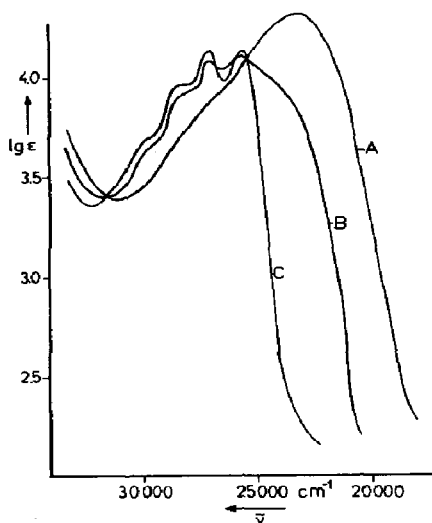


Fig. 5. Absorption spectra of the three isomers of IX in toluene: A, *EE* isomer; B, *EZ* isomer; C, *ZZ* isomer.

Not all the isosbestic points are preserved in the course of the photo-reaction. Three components can be detected by TLC in the photostationary state. The ED diagram is not linear but the EDQ diagram is, as expected. Consequently, the reaction in question is not unitary [16]. With radiation of wavelength $\lambda' = 480 \text{ nm}$ an $A \rightleftharpoons B$ reaction can be selectively induced. The isosbestic points remain unchanged and the ED diagram is linear. The con-

centration *versus* time diagram derived from the E diagram yields a survey of the total course of the photoreaction (Fig. 6).

For a three-component system the differential photokinetic equations needed for the evaluation of the partial quantum yields depend on the reaction mechanism. There are conceivably 24 reasonable reaction mechanisms for a photochemical three-component system. For these mechanisms the following three fundamental types of differential equations exist [16]:

$$\dot{c}_i = I_0 \left(\frac{1 - 10^{-E'}}{E'} \right) (x_1 c_i + x_2 c_j + x_3 c_k) \quad (1)$$

$$\dot{c}_j = I_0 \left(\frac{1 - 10^{-E'}}{E'} \right) (x_1 c_i + x_2 c_k) \quad (2)$$

$$\dot{c}_k = I_0 \left(\frac{1 - 10^{-E'}}{E'} \right) (x_1 c_i) \quad (3)$$

where c_i , c_j and c_k are the concentrations of the isomers, I_0 is the irradiation intensity, E' is the molar absorbance at the irradiation wavelength, and x_1 , x_2 and x_3 are constants of the differential equations for the evaluation of the partial quantum yields.

Equation (1) can be solved using a computer program [18]; eqns. (2) and (3) are solved graphically in the simplest manner. The reaction mechanism assumed is rejected if the partial quantum yields calculated from the x_i values are negative, or if the plot of the functions calculated using formal integration deviate from linearity.

Using this procedure 23 of the 24 possible mechanisms can be eliminated. The remaining mechanism is a reversible consecutive photoreaction:



Three further criteria prove this reaction mechanism.

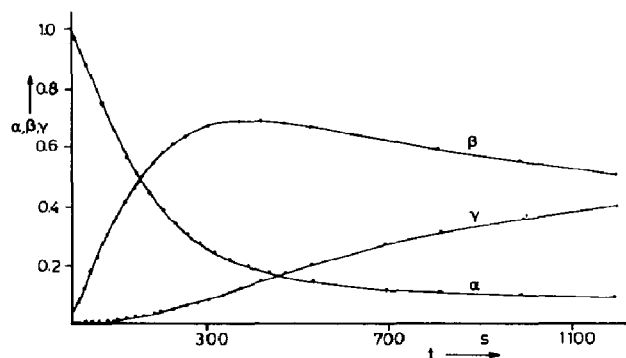


Fig. 6. A reduced concentration-time diagram for the photoreaction of IX (form A) ($\lambda = 436 \text{ nm}$).

(1) Starting from the photoproduct B a parallel photoreaction should be observable if this reaction course is correct. The ED diagram of the TLC-isolated product B is non-linear ($\lambda' = 436$ nm). The linearity of the EDQ diagram confirms two linear independent partial reactions of a parallel photoreaction.

(2) The initial slope $\Delta\alpha/\Delta\gamma$ of the photoreaction of substance A derived from the reduced concentration diagram (Fig. 7) is $-\infty$. This gives strong evidence for a consecutive photoreaction [16]. For product B, however, a finite initial slope $\Delta\alpha/\Delta\gamma = 1.41$ is found which agrees well with the theoretical value ($(da/dc)_{t \rightarrow \infty} = 1.46$) of a parallel photoreaction calculated from the differential equations.

(3) For both the consecutive photoreaction and the parallel photoreaction the same photostationary state is obtained. The concentrations in the photostationary state can be calculated from the differential equations and can be compared with the experimental results. The comparison of these values provides a sensitive criterion for checking the kinetic data and the reaction mechanisms.

To continue Mauser's work [16] *, starting from the differential equations for the system of type 2

$$\dot{a} = -I_0\varphi_B^A\epsilon'_A a \frac{1 - 10^{-E'}}{E'} + I_0\varphi_A^B\epsilon'_B b \frac{1 - 10^{-E'}}{E'} \quad (4)$$

$$\dot{c} = +I_0\varphi_C^B\epsilon'_B b \frac{1 - 10^{-E'}}{E'} - I_0\varphi_B^C\epsilon'_C c \frac{1 - 10^{-E'}}{E'} \quad (5)$$

$$C_0 = a + b + c = a_\infty + b_\infty + c_\infty \quad (6)$$

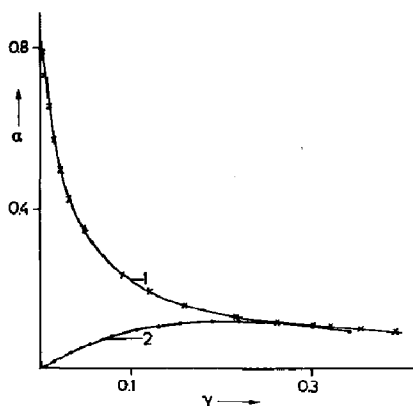


Fig. 7. A reduced concentration diagram of the photoreaction of IX in toluene ($\lambda' = 436$ nm): 1, consecutive photoreaction of the form A; 2, parallel photoreaction of the form B.

*For an explanation of the symbols used for concentrations and all photokinetic parameters see ref. 16.

and the assumption that, if $t \rightarrow \infty$ then $\dot{a} = \dot{c} = 0$ applies, the following equations for the calculation of a_∞ and c_∞ can be derived:

$$a_\infty = \frac{\epsilon'_B \varphi_A^B \epsilon'_C \varphi_B^C C_0}{\epsilon'_A \varphi_B^A \epsilon'_B \varphi_C^B + \epsilon'_B \varphi_A^B \epsilon'_C \varphi_B^C + \epsilon'_A \varphi_B^A \epsilon'_C \varphi_B^C} \quad (7)$$

$$c_\infty = \frac{\epsilon'_A \varphi_C^B \epsilon'_B \varphi_B^A C_0}{\epsilon'_A \varphi_B^A \epsilon'_B \varphi_C^B + \epsilon'_B \varphi_A^B \epsilon'_C \varphi_B^C + \epsilon'_A \varphi_B^A \epsilon'_C \varphi_B^C} \quad (8)$$

b_∞ is calculated from eqn. (6).

It should be noted that eqns. (7) and (8) of a three-component system correspond to the Zimmerman equation for a two-component system [19].

In Table 3 the photostationary concentrations calculated from eqns. (6) - (8) are compared with the experimental concentrations.

The partial quantum yields necessary for eqns. (6) - (8) are provided by the constants x_i in the differential equations eqns. (1) - (3). For azine IX in air-saturated toluene they amount to

$$\varphi_B^A = 0.02_4 \quad \varphi_A^B = 0.01_5 \quad \varphi_C^B = 0.01_0 \quad \varphi_B^C = 0.2_3$$

The assumed reaction mechanism of type 2 as well as the kinetic data are confirmed by the satisfactory correspondence of the values in Table 3.

Similar to azine IX, mesitylaldehyde azine (X) and 9-anthranil-9-acridinealdehyde azine (XVI) show photokinetics of type 2. Upon irradiation into the longest wavelength absorption band (X, $\lambda' = 300$ nm; XVI, $\lambda' = 436$ nm) linear ED diagrams are obtained only in the initial stage of the photoreaction. The linear EDQ diagrams confirm the two linearly independent partial reactions of a consecutive photoreaction of type 2.

In contrast with IX, the derivatives substituted in the 10 position, 10-methyl-9-anthraldehyde azine (XIV) and 10-methoxy-9-anthraldehyde azine (XV), as well as 9-acridinealdehyde azine (XVII) which is sterically very similar to IX, show photokinetics of type 1. The same photokinetic behaviour is also observed with 9-anthranil-1-naphthaldehyde azine (XII) and 9-anthranil-3-quinolinealdehyde azine (XIII). Upon irradiation ($\lambda' = 436$ nm) linear ED diagrams are obtained for the entire reaction course, and in the photostationary state only two isomers are detectable by TLC. With light of wavelength $\lambda' = 365$ nm the initial compounds are regenerated until the photostationary state is reached. The partial quantum yields evaluated are given in Table 4.

TABLE 3

Calculated and experimental photostationary concentrations of the isomers A, B and C of the azine IX

Concentration	Theoretical	Experimental
$\alpha_\infty = a_\infty/C_0$	0.069	0.062
$\beta_\infty = b_\infty/C_0$	0.409	0.380
$\gamma_\infty = c_\infty/C_0$	0.524	0.558

TABLE 4

Partial quantum yields of the photoisomerization of the azines XII, XIII and XVII

Compound	φ_B^A	φ_A^B
XII	0.01 ₃	0.05 ₂
XIII	0.01 ₉	0.08 ₄
XVII	0.008 ₀	0.02 ₃

Hitherto only irreversible photoreactions were known [12] for benzophenone benzaldehyde azine (III). We found that III as well as its derivatives benzophenone mesitylaldehyde azine (IV), benzophenone *p*-nitrobenzaldehyde azine (V) and benzophenone *p*-dimethylaminobenzaldehyde azine (VI) are also photochromic. The spectral changes which can be achieved upon irradiation into the corresponding longest wavelength absorption bands decrease significantly in the series IV–V–VI–III (Fig. 8), and with III they are only observable under optimized detection conditions. The ED diagrams are linear over the entire course of the photochemical forward and back reactions. Thus, all four azines exhibit a complicated unitary photoreaction of type 1. Evaluation of the quantum yields failed because of the unsuccessful TLC separation of the photoisomers.

In the literature there are contradictory results for benzaldehyde azine (I). According to several authors [9, 20] I is photoinactive, whereas Binkley [12] has reported irreversible photolytic decomposition. We can confirm

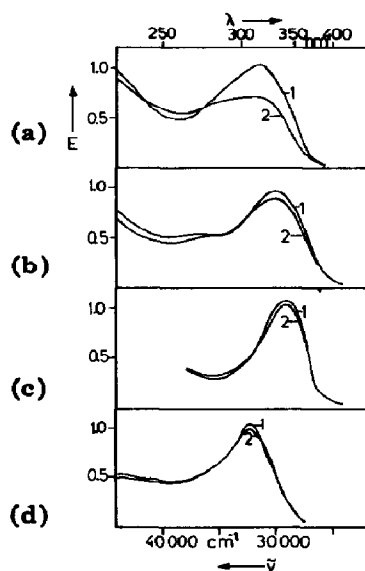


Fig. 8. Absorption spectra of the azines in cyclohexane (1, initial form; 2, photostationary state): (a) IV, $\lambda' = 333$ nm; (b) V, $\lambda' = 365$ nm; (c) VI, $\lambda' = 405$ nm; (d) III, $\lambda' = 333$ nm.

Binkley's results. I is not photochromic, neither in air-saturated nor in de-gassed solution. Upon irradiation with light of wavelength $\lambda' > 300$ nm (HBO 200, glass optics, glass filter UG 11) a decrease of the long-wavelength absorption band occurs. Isosbestic points are not detectable in either stage of the reaction. Neither the ED diagrams nor the EDQ diagrams are linear. The formal kinetic behaviour can be assigned neither to type 1 nor to type 2.

Even upon prolonged irradiation benzophenone azine (II) does not show spectral changes; II is not photochromic, as expected if the photochromism is based on the *E-Z* isomerization about the C=N bond. Irradiation at shorter wavelengths causes fast decomposition.

4. Discussion

All the acyclic aryl-substituted azines we investigated are photochromic as far as this is possible with respect to their structure. Benzaldehyde azine (I) is an exception. However, the azines vary with respect to their reaction mechanism. This different behaviour of the azines can be realized if a photochemically induced *E-Z* isomerization about the C=N bond is assumed. Thus, from the point of view of formal kinetics, the azines can be divided into four reaction types depending on the substituents R_i (Table 5).

The correspondence of the expected formal kinetic behaviour of the azines in Table 5 with the experimental results is a direct proof of a photochemical *E-Z* isomerization of these compounds. If the photochromism of the azines is the result of an *E-Z* isomerization then no representatives with substituents $R_1 = R_2$ and $R_3 = R_4$ can be photochromic (reaction type 0). This has been experimentally verified by azine II. Thus the photoproducts A, B and C correspond to *E-Z* isomers about the C=N bond. For instance in the case of azine IX the following photoisomerization proceeds:

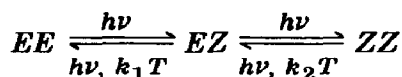


TABLE 5

Classifications of the azines according to formal kinetics

Reaction type	Substituents (see Fig. 1)	Isomers	Photo-reaction	Experimentally verified representatives
0	$R_1 = R_2, R_3 = R_4$	1	None	II
1	$R_1 = R_2, R_3 \neq R_4$	2 <i>E-Z</i>	Complicated unitary	III, IV, V, VI, VII, VIII, XI
2	$R_1 \neq R_2, R_3 \neq R_4$ $R_1 = R_4, R_2 = R_3$	3 <i>EE-EZ-ZZ</i>	Complicated, not unitary	IX, X
3	$R_1 \neq R_2, R_3 \neq R_4$ $R_1 \neq R_4$ or $R_2 \neq R_3$	4 <i>EE-EZ(1)-EZ(2)-ZZ</i>	Complicated not unitary	Hitherto no example known

Therefore the spectra of the twisted forms *EZ* and *ZZ* especially (see Fig. 5) are closely similar to that of 9-butylanthracene [21].

A direct isomerization of the form A (isomer *EE*) to the product C (*ZZ* isomer) could not be detected. Thus, the two-bond isomerism discussed with butadiene derivatives [22] can be ruled out in the case of the 2,3-diazabuta-dienes (azines).

A number of azines are assigned according to formal kinetics to a reaction type which differs from that expected from their structure. Examples for this behaviour are given in Table 6.

The reason for the deviating formal kinetic behaviour of these azines might be a very close spectral similarity of the isomers so that one isomer becomes negligible in the formal kinetic treatment and an apparent unitary system results. This is also indicated from results on aryl-substituted butadiene derivatives [23, 24].

Of all the azines investigated in this work, azine I shows deviating behaviour because it is not at all photochromic. An estimate of the (apparent integral) quantum yields verifies Binkley's result [12] that only photolysis but no *E-Z* isomerization occurs upon irradiation into the longest wavelength absorption band. Thus, according to the results presented here, the only azine investigated in more detail in the literature is not representative of the class of compounds but is an exception to the rule. Obviously in azine I photolysis proceeds more effectively than *E-Z* isomerization.

Since photochromism based on *E-Z* isomerization was demonstrated as occurring with all the acyclic azines substituted by phenyl, higher condensed aromatic and heterocyclic substituents, this photoreaction is a general property of this class of compounds.

TABLE 6
Azines with deviating formal kinetic behaviour

<i>Reaction type</i>		<i>Examples</i>
<i>Expected</i>	<i>Observed</i>	
2	1	XIV, XV, XVII
3	1	XII, XIII
3	2	XVI

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