

**THERMOCHROMISM AND PHOTOCHROMISM OF ARYL-SUBSTITUTED ACYCLIC AZINES
VII: SOLVENT EFFECT ON PHOTOCHEMICAL *E-Z* ISOMERIZATION**

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Summary

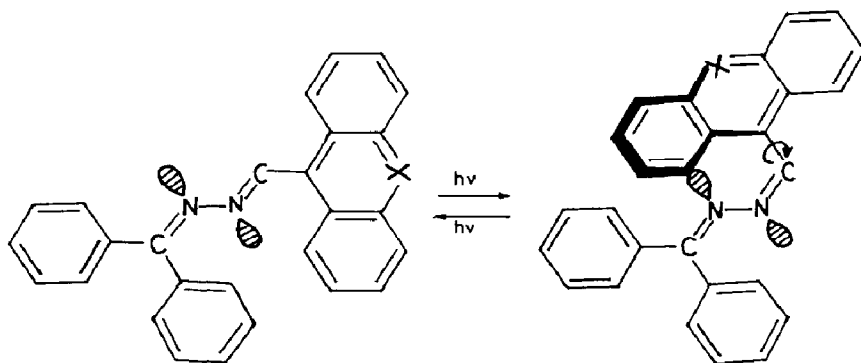
In the *E-Z* isomerization of benzophenone-9-anthraldazine and benzophenone-9-acridinealdazine there is a significant relation between $\phi_{E \rightarrow Z}$ and the solvent acceptor number AN, whereas a significant relation between $\phi_{Z \rightarrow E}$ and AN could not be detected. These results are interpreted in terms of the effect of solvent polarity on the energy levels of the *E-Z* isomers of the azine.

1. Introduction

Our investigations of the aryl-substituted 2,3-diazabutadienes (azines) $R_1R_2C=N-N=CR_3R_4$ have shown that photochromism based on *E-Z* isomerization about the C=N bond is a general property of this class of compounds [1]. We have studied the mechanism of both the photochemical [2, 3] and the thermal [4, 5] isomerization of the azines. To investigate the mechanism of the thermal isomerization we studied the solvent effect on the kinetics of the thermal reactions. We have also found that the quantum yields of the *E-Z* isomerization of these compounds show a solvent effect. Only a few examples of the solvent effect on photochemical *E-Z* isomerization have been reported to date [6] and no relation between the quantum yield and the solvent parameters has been demonstrated.

We have investigated the solvent effect on the quantum yield of the photochemical *E* \rightarrow *Z* and *Z* \rightarrow *E* isomerization of benzophenone-9-anthraldazine (BPhAA) and benzophenone-9-acridinealdazine (BPhAcA). Only two isomers are possible for azines of this structure [1] (Fig. 1).

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E *Z*
 Fig. 1. The *E*-*Z* isomers of BPhAA ($X \equiv \text{CH}$) and BPhAcA ($X \equiv \text{N}$).

2. Experimental details

The preparation of the *E* isomers *E*-BPhAA and *E*-BPhAcA is reported elsewhere [7]. The solvents used were purified by standard methods [8].

The absorption spectra were recorded using a Cary model 17 spectrometer (Varian, U.S.A.). The azine concentrations were in the range 2×10^{-5} - 9×10^{-5} M.

The irradiation wavelength for the *E* \rightarrow *Z* reaction was $\lambda' = 436$ nm. A high pressure mercury lamp (HBO 200 (VEB Narva, Berlin)) was used as the light source, and monochromatic radiation was selected using an HgMon 436 filter (VEB Carl Zeiss, Jena). The irradiation wavelength for the *Z* \rightarrow *E* photoisomerization was $\lambda' = 365$ nm (selected using an HgMon 365 filter (VEB Carl Zeiss, Jena)). This reaction was studied by starting with the photostationary state established by irradiation of the *Z* isomer after photochemical enrichment varying from 1.5×10^{-5} to 7×10^{-5} M.

The quantum yields were determined (a) by the formal integration method [9] and (b) from the initial slope [10].

(a) The change $d[E]$ in the concentration of the *E* isomer as a result of the *E* \rightarrow *Z* photoisomerization induced by monochromatic irradiation is given by [9]

$$\frac{d[E]}{dt} = -\phi_{E \rightarrow Z} \epsilon_E' I_0 [E] \frac{1 - 10^{-A'}}{A'} + \phi_{Z \rightarrow E} \epsilon_Z' I_0 [Z] \frac{1 - 10^{-A'}}{A'} \quad (1)$$

Substituting $[Z] = [E]_0 - [E]$ gives the following relation:

$$\frac{d[E]}{dt} = -(\phi_{E \rightarrow Z} \epsilon_E' + \phi_{Z \rightarrow E} \epsilon_Z') I_0 \frac{1 - 10^{-A'}}{A'} [E] + \phi_{Z \rightarrow E} \epsilon_Z' I_0 \frac{1 - 10^{-A'}}{A'} [E]_0 \quad (2)$$

and on integration this becomes

$$\frac{\int d[E]}{\int \{(1 - 10^{-A'})/A'\} dt} = -(\phi_{E \rightarrow Z} \epsilon_{E'} + \phi_{Z \rightarrow E} \epsilon_{Z'}) I_0 \frac{\int \{(1 - 10^{-A'})/A'\} [E] dt}{\int \{(1 - 10^{-A'})/A'\} dt} + \phi_{Z \rightarrow E} \epsilon_{E'} [E]_0 I_0 \quad (3)$$

where A' is the absorbance, ϵ' is the extinction coefficient and I_0 is the incident light intensity at the irradiation wavelength λ' . The quantum yields $\phi_{E \rightarrow Z}$ and $\phi_{Z \rightarrow E}$ of the photoreactions $E \rightarrow Z$ and $Z \rightarrow E$ respectively are determined either graphically (a plot of

$$\frac{\int d[E]}{\int \{(1 - 10^{-A'})/A'\} dt} \quad \text{versus} \quad \frac{\int \{(1 - 10^{-A'})/A'\} [E] dt}{\int \{(1 - 10^{-A'})/A'\} dt}$$

gives a straight line with intercept $\phi_{Z \rightarrow E} \epsilon_{Z'} [E]_0 I_0$ and slope $-(\phi_{E \rightarrow Z} \epsilon_{E'} + \phi_{Z \rightarrow E} \epsilon_{Z'}) I_0$ or by numerical evaluation [9] using a computer program [11].

(b) When eqn. (3) is employed to evaluate $\phi_{E \rightarrow Z}$ and $\phi_{Z \rightarrow E}$, $\epsilon_{Z'}$ must be determined in every solvent used. Therefore we have developed a simple method for determining $\phi_{E \rightarrow Z}$ [10]. If $\epsilon_{E'}$ is much less than $\epsilon_{Z'}$ and $A_{Z'} \approx 0$ (no absorption of the photoproduct Z during the initial period of the photoreaction), eqn. (1) can be simplified as follows:

$$\frac{d[E]}{dt} = - \frac{I_0(1 - 10^{-A'})\phi_{E \rightarrow Z}}{d} \quad (4)$$

from which the relation

$$A' + \log(1 - 10^{-A'}) = -\phi_{E \rightarrow Z} \epsilon_{E'} I_0 t + K \quad (5)$$

can be derived. A graph of $F(A')$ versus t is linear in the initial region and $\phi_{E \rightarrow Z}$ can be directly obtained from the slope if I_0 and $\epsilon_{E'}$ are known.

3. Results and discussion

The $E \rightarrow Z$ isomerization results in a hypsochromic shift of the longest wavelength absorption band (Figs. 2 and 3). Although the solvent effect can barely be detected in the main peak of this band, a hypsochromic shift with increasing solvent polarity is observed in the shoulder (Fig. 2). Thus the lowest excited energy transition of the E isomer is an n, π^* transition [2, 12].

The quantum yields $\phi_{E \rightarrow Z}$ and $\phi_{Z \rightarrow E}$ for the E - Z isomerization of BPhAA and BPhAcA in various solvents are summarized in Table 1. Simple linear regression analysis [13] was used to determine whether there was a relation between the quantum yield and the solvent parameters. The Gutmann solvent acceptor number AN and solvent donor number DN [14] were adopted as solvent parameters.

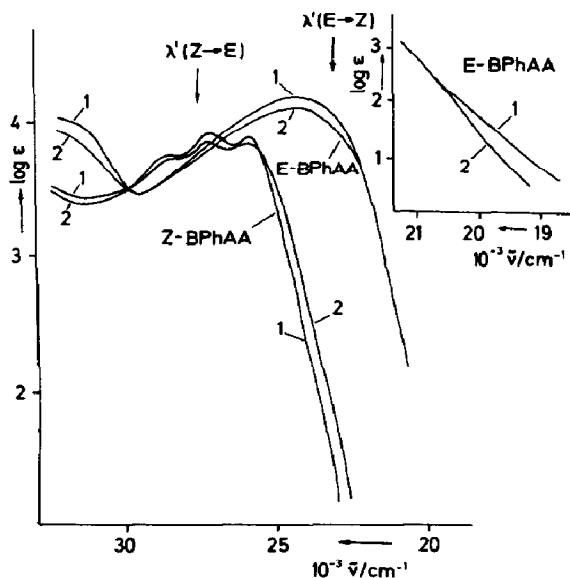


Fig. 2. The solvent effect on the longest wavelength absorption band in the $E-Z$ isomerization of BPhAA and on the longest wavelength shoulder of E -BPhAA: curves 1, in cyclohexane; curves 2, in ethanol.

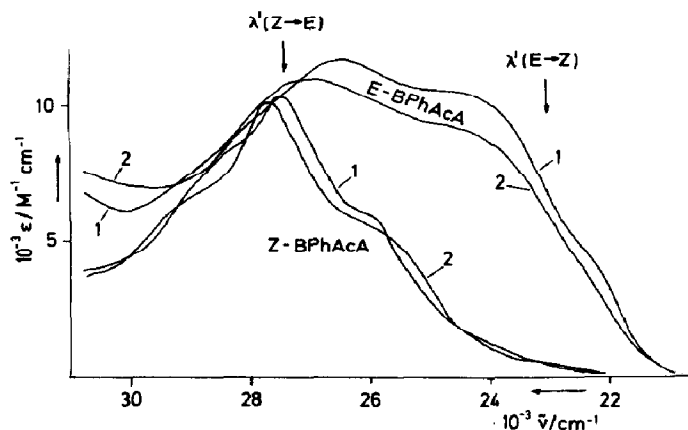


Fig. 3. The solvent effect on the longest wavelength absorption bands of E -BPhAcA and Z -BPhAcA: curves 1, in toluene; curves 2, in ethanol.

For $E \rightarrow Z$ isomerization there was a significant relation between $\phi_{E \rightarrow Z}$ and AN for both azines (Table 2). Multiple linear regression analysis which included AN and DN as well as the viscosity of the solvent showed no other significant relations. Therefore the solvent dependence of the quantum yield $\phi_{E \rightarrow Z}$ is due only to the acceptor ability of the solvent. The following quantitative relations were found:

$$\phi_{E \rightarrow Z} = (3.88 + 0.136AN) \times 10^{-3}$$

for BPhAA and

$$\phi_{E \rightarrow Z} = (2.48 + 0.102AN) \times 10^{-3}$$

TABLE 1

Solvent effect on the quantum yields of the photochemical *E-Z* isomerization of benzophenone-9-anthraldazine and benzophenone-9-acridinealdazine

Solvent	BPhAA		BPhAcA	
	$\phi_{E \rightarrow Z} \times 10^3$	$\phi_{Z \rightarrow E}$	$\phi_{E \rightarrow Z} \times 10^3$	$\phi_{Z \rightarrow E}$
Cyclohexane	3.1	0.20	1.5	0.35
<i>n</i> -decane	3.2			
Ether	3.8			
Tetrahydrofuran	5.5		3.9	
Benzene	5.3			
Toluene	5.3	0.21	3.5	0.15
Acetone	5.5		3.4	
Dimethylformamide	6.9		4.2	
Acetonitrile			4.3	
Dimethyl sulphoxide	7.5	0.18	6.1	
Chloroform	6.9		4.3	
Isopropanol	8.0			
Ethanol	7.7	0.19	5.7	0.13
Methanol	9.2	0.15		

TABLE 2

Simple linear regression analysis for the relation between the quantum yield $\phi = a + bX$ and the acceptor number AN and the donor number DN

Reaction	X	BPhAA		BPhAcA	
		<i>t</i> test	<i>t</i> (<i>P</i> = 0.95; <i>f</i>) [15]	<i>t</i> test	<i>t</i> (<i>P</i> = 0.95; <i>f</i>) [15]
<i>E</i> → <i>Z</i>	AN	8.16	3.17	3.70	3.50
<i>E</i> → <i>Z</i>	DN	2.00	3.17	2.29	3.50
<i>Z</i> → <i>E</i>	AN	2.05	5.84	1.05	63.66
<i>Z</i> → <i>E</i>	DN	1.07	5.84	0.70	63.66

for BPhAcA. No significant relations were detected for the *Z* → *E* isomerization.

Since the quantum yield depends on the lifetime of the excited state and the rate constant of the isomerization the interpretation of the solvent effect is generally rather difficult. Consideration of the solvent effect on the excited states which predominate on isomerization enables the solvent effect on the quantum yield of the *E* → *Z* photoreaction to be understood. The energy level scheme for *E*-BPhAA given in Fig. 4 is supported by the absorption spectra [12], the photochemical behaviour [2] and the luminescence properties [12] of this compound. The intersystem crossing to the $T_n(\pi, \pi^*)$ state is the most effective competitive process for the photoisomerization [2]. The difference between the $S_1(n, \pi^*)$ and the $T_n(\pi, \pi^*)$ states with increasing solvent polarity should result in a decrease in the rate constant of

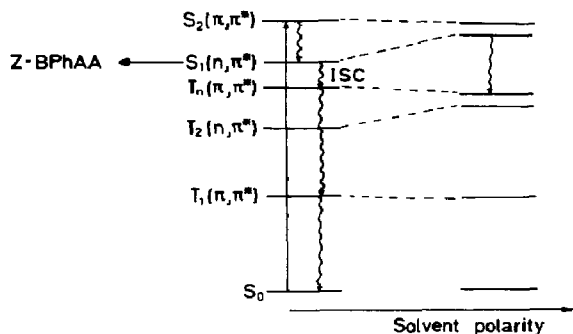


Fig. 4. The effect of solvent polarity on the energy levels of *E*-BPhAA. (Increasing solvent polarity increases the difference between the $S_1(n, \pi^*)$ and $T_n(\pi, \pi^*)$ states and decreases the intersystem crossing (ISC) which is the most effective process competing with the photoisomerization.)

the competing intersystem crossing. This explains the relation found between the quantum yield $\phi_{E \rightarrow Z}$ and AN.

The lowest energy state of the *Z* isomer of BPhAA has a dominant π, π^* nature [2, 12] which is essentially less solvent dependent. Therefore a solvent effect for the quantum yield of the $Z \rightarrow E$ isomerization is not found.

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