ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 85 (1995) 207–211

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photokinetic examination of (*Z,E,E*)-4,4′-distyrylazobenzene ☆

Günter Gauglitz [a,*], Philipp Stößel [a], Herbert Meier [b], Hermann Rau [c]

[a] *Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany*
[b] *Institut für Organische Chemie, Universität Mainz, J.-J.-Becher-Weg 18–22, 55099 Mainz, Germany*
[c] *FG Physikalische Chemie, Institut für Chemie, Hohenheim, Garbenstraße 30, 70593 Stuttgart, Germany*

Received 5 April 1994; accepted 28 June 1994

Abstract

4,4′-Distyrylazobenzenes demonstrate a photokinetic equilibrium and a superimposed thermal backward reaction in which the absorption coefficient of one of the partners in the equilibrium is principally unknown. Using the dependence of the photostationary state on the irradiation intensity, the photochemical quantum yields φ_1^A and φ_2^B were determined, as well as the thermal rate constant *k*, as a function of the irradiation and observation wavelengths. Experimental difficulties and the wavelength dependence of φ_1^A and φ_2^B are discussed.

Keywords: 4,4′-Distyrylazobenzenes; Photokinetic equilibrium

1. Introduction

Optically switchable liquid crystals require mesogenic compounds containing chromophores which are responsible for the photoactivity. Recently, the thermally and photochemically reversible (*E*) → (*Z*) isomerizations of stilbene and azobenzene systems have generated specific interest [1]. The various isomers of 4,4′-distyrylazobenzene are promising [2]. To understand and optimize the reactive pathways, the photoisomerization from (*Z,E,E*)- to (*Z,Z,E*)-4,4′-distyrylazobenzene has been examined in detail (Scheme 1, Fig. 1).

This reaction has been used as a model system for the evaluation of a recently proposed photokinetic method for the examination of photoisomerization with a superimposed thermal back reaction in which only the spectrum of the starting material is known [3]. In Ref. [3], Fischer's method [4] was used to determine the absorption coefficient ϵ_B. This method requires that the photochemical quantum yield is independent of the wavelength and can even be used if a thermal backward reaction influences the photostationary state. In this case, the thermal reaction is frozen out by working at low temperatures. Then it must be assumed that ϵ_B is temperature independent. This thermal chromism is valid for the (*Z,E,E*) isomer, but not for the (*Z,Z,E*) isomer. Even though ϵ_A and ϵ_B can be determined by temperature-dependent measurements, Fischer's method cannot be used since preliminary experiments have shown the dependence of the photochemical quantum yield φ_1^A on the wavelength. For this reason, the two isomers were separated by flash chromatography.

2. Kinetic fundamentals

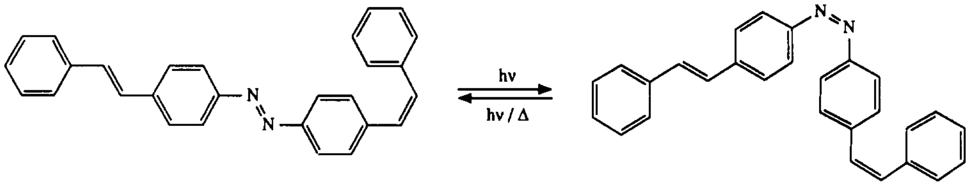
Several methods have been published which allow the evaluation of photoisomerizations [5]. However, most of these methods cannot be applied if the isomerization product B reconverts thermally to the starting material. For this reason, a method has been given which allows a graphical evaluation to be made of the linear relationship between the reciprocal of the difference between the absorbance in the photostationary state and that at the beginning of the reaction and the reciprocal of the irradiation intensity [3]. By applying Eq. (1) (see below), the photochemical quantum yield φ_1^A can be determined from the slope and φ_2^B from the intercept, if all the other values are known (especially ϵ_B and ϵ'_B) and if the following principles are fulfilled: (a) a thermal backward reaction must be superimposed on the photoisomerization process such that the pho-

---

☆ Dedicated to Prof. Dr. Heinz Mauser on the occasion of his 75th birthday.

[*] Corresponding author.

SSDI 1010-6030(94)03912-E



(Z,E,E)-4,4'-distyrylazobenzene (Z,Z,E)-4,4'-distyrylazobenzene

Scheme 1. (*Z*,*E*,*E*)-4,4'-Distyrylazobenzene → (*Z*,*Z*,*E*)-4,4'-distyrylazobenzene.

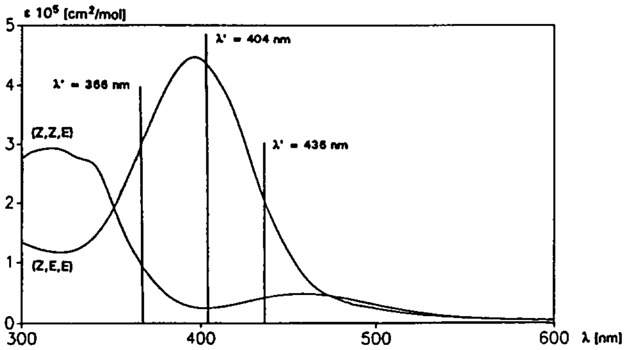


Fig. 1. Absorption spectra of (*Z*,*E*,*E*)- and (*Z*,*Z*,*E*)-4,4'-distyrylazobenzene at the indicated irradiation wavelengths.

tostationary state depends on the intensity of the irradiation source; (b) the absorbance spectra of the two isomers must overlap so that the quantum yields φ_1^A and φ_2^B can be determined; (c) the photochemical quantum yields φ_1^A and φ_2^B must be independent of the irradiation intensity in the intensity range used; (d) no other intramolecular or intermolecular reactions are allowed apart from isomerization.

$$\frac{1}{A(\mathrm{s})-A(0)} = \frac{\epsilon'_A\varphi_1^A+\epsilon'_B\varphi_2^B}{(\epsilon_B-\epsilon_A)\epsilon'_A\varphi_1^A a(0)} + \frac{kA'(\mathrm{s})}{(\epsilon_B-\epsilon_A)\epsilon'_A\varphi_1^A a(0)(1-10^{-A'(\mathrm{s})})}\,\frac{1}{I} \qquad (1)$$

where $a(0)$ is the initial concentration of the solution, $A(0)$ is the absorbance of the pure isomer A, $A(\mathrm{s})$ is the absorbance of the solution in the photostationary state, $A'(\mathrm{s})$ is the absorbance at the irradiation wavelength of the solution in the photostationary state, ϵ_A is the absorption coefficient of isomer A at the measurement wavelength, ϵ_B is the absorption coefficient of isomer B at the measurement wavelength, ϵ'_A is the absorption coefficient of isomer A at the irradiation wavelength, ϵ'_B is the absorption coefficient of isomer B at the irradiation wavelength, φ_1^A is the photochemical quantum yield of the reaction A → B at a certain wavelength λ' of irradiation, φ_2^B is the photochemical quantum yield of the backward reaction B → A at a certain wavelength λ' of irradiation, k is the rate constant of the thermal backward reaction and $I = I_0 \times 1000$ is the corrected intensity of irradiation (einstein cm dm^{-3} s^{-1}).

Of course, the absorbance in the photostationary state $A(\mathrm{s})$ depends on the irradiation wavelength. Furthermore, the left-hand side of the above equation and the photokinetic factor $[A'(\mathrm{s})/(1-10^{-A'(\mathrm{s})})]$ on the right-hand side of this equation will depend on the irradiation intensity. A graph of the left-hand side vs. the reciprocal irradiation intensity allows the determination of φ_1^A from the slope and φ_2^B from the intercept given by the first element of the equation.

An evaluation is possible only if the value of ϵ'_B can be determined, e.g. by the method of Fischer, but this requires a pure photoreaction without a superimposed thermal backward reaction. Such a reaction could be observed if it was possible to record the photostationary state in the limit of infinite intensity, since the $A(\mathrm{s})$ values of the photostationary state at infinite intensity can be obtained from the graph of the above equation by extrapolation of $1/I$ to zero. However, the method given by Fischer [4] requires irradiation at two different wavelengths and assumes that the ratio of the quantum yields φ_1^A/φ_2^B is independent of the irradiation wavelength. During the evaluation of the chosen photoreaction, it was demonstrated that this requirement is not fulfilled. For this reason, a chemical procedure to separate the two isomers was chosen.

3. Experimental details

3.1. Determination of the absorption coefficients

The absorption coefficients of the (*Z*,*E*,*E*) isomer were determined at two temperatures (15 and 50 °C) taking four concentrations (by weight). Each was diluted once. In Table 1, the results are given for four wavelengths including the absorption maximum and the errors are calculated as the standard deviation (SDV) including Student's *t*-factor for eight experiments at each temperature.

The absorption coefficients of the (*Z*,*E*,*E*) isomer show some thermochromism. Fortunately, this is not so for the (*Z*,*Z*,*E*) isomer. This isomer was isolated in pure form from a photoisomer mixture by preparative methods at very low temperature and short separation times.

Table 1
Absorption coefficients for (*Z*,*E*,*E*)-4,4′-distyrylazobenzene

λ (nm)	ϵ_A[a] (cm^2 mol^{-1})	λ (nm)	ϵ_A[b] (cm^2 mol^{-1})
366	30570 ± 820	366	32650 ± 890
396	45160 ± 1220	396	44250 ± 1180
404	43450 ± 1180	404	41320 ± 1100
436	20070 ± 520	436	17440 ± 470

[a] $T = 15$ °C.
[b] $T = 50$ °C.

Table 2
Absorption coefficients for (*Z*,*Z*,*E*)-4,4′-distyrylazobenzene

λ (nm)	ϵ_B (cm^2 mol^{-1})
366	9100 ± 320
404	2280 ± 80
436	3740 ± 130

The (*Z*,*E*,*E*) isomer (25 mg) was dissolved by stirring in 10 ml of toluene. The isomer was photoisomerized at −25 °C by irradiation at 404 nm. At the end of photoisomerization, 0.25 ml of ethylacetate was added. The isomer mixture was separated on a thermostatically controlled flash chromatography column at −60 °C using silica gel (0.063–0.2 mesh) and eluted by a mixture of toluene and ethylacetate (40:1) precooled to −70 °C. The (*Z*,*Z*,*E*) fraction, which was eluted at a retention time of 4 min, was frozen out by liquid nitrogen. This fraction is the pure (*Z*,*Z*,*E*) isomer according to thin layer chromatography.

Various samples of the separated pure (*Z*,*Z*,*E*) isomer were isomerized thermally. Using the final absorbance of these solutions and the known absorption coefficients of the (*Z*,*E*,*E*) isomer, the initial concentration of the (*Z*,*Z*,*E*) isomer was determined and the absorption coefficients ϵ_B were calculated. The results of ten different measurements are given in Table 2.

To control for any wavelength shift of the (*Z*,*Z*,*E*) isomer caused by temperature variation, some samples were spectrally examined between 0 and −40 °C. No temperature influence was detected.

Closed cells had to be used to avoid concentration reduction by evaporation. Furthermore, at high temperatures (50 °C), problems of recondensation at the top of the cell had to be excluded.

3.2. Apparatus

For observation of the thermal and photochemical reactions, a combined radiation and measurement device was used. It consisted of a mercury high-pressure arc (HBO 100/W2), with its arc arranged parallel to the optical axis. The monochromatic light beam was collimated and mirrored to the front window (3 cm^2) of the cell. A diode array spectrometer controlled by a computer was used for measurement. The cell contained a thermoelement and the solution was stirred. This apparatus results in very homogeneous irradiation with very small fluctuations (Fig. 2). The source stability was controlled by a photodiode.

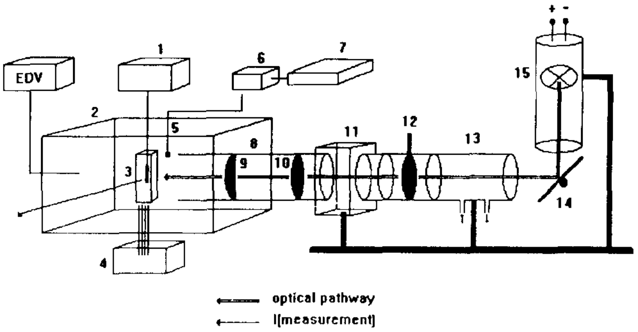


Fig. 2. Schematic diagram of experimental apparatus. (1) Thermoelement; (2) diode array spectrometer; (3) cell; (4) thermostat; (5) photodiode; (6) amplifier and millivoltmeter; (7) recorder; (8) tube; (9) convex planar lens; (10) biconvex lens; (11) filter; (12) shutter; (13) water filter; (14) mirror; (15) mercury high-pressure arc lamp.

3.3. Determination of the intensity

The irradiation intensity was continuously controlled by a photodiode. It was calibrated against Parker's solution [6] and the azobenzene actinometer [7]. After thermal equilibrium had been reached, the irradiation lamp showed less than 2% changes in intensity. Intensity fluctuations which were observed in an early set-up were omitted by arranging the light source in a vertical position. Thus the absorption spectrum stayed constant in the photostationary state.

4. Results and discussion

4.1. Thermal rate constant

The thermal backward reaction starting from (*Z*,*Z*,*E*)-4,4′-distyrylazobenzene to the (*Z*,*E*,*E*) isomer was examined using the pure (*Z*,*Z*,*E*) isomer and beginning at the photostationary state. Toluene–ethylacetate (40:1) was used as solvent mixture to give the same conditions as used for the determination of the absorption coefficients. Isosbestic points and linear absorbance diagrams [8] demonstrate that one single linear independent reaction step occurs. The rate constant was determined by linearization of the exponential equation for first-order kinetics as well as by applying a Marquardt fit to the experimental curve. At 15 °C, the thermal rate constant was determined from ten independent measurements. During nine photochemical measuring cycles at 50 °C, the thermal backward reaction starting at the photostationary state was evaluated. The spectral results are given in Fig. 3. The statistics are given in Table 3 for a 99% confidence interval for the two temperatures.

The values obtained correlate with those measured previously [9]. A change in solvent composition to *n*-hexane–diethylether caused a non-linearity in the absorbance diagrams due to peroxides in these solvents, as shown by an alkali metal iodide test. Even when the solvents were refluxed on sodium benzophenone to remove the peroxides, the long duration of the measurement cycle caused a new appearance of peroxides. The pronounced non-linearity mentioned above could be reproduced by the deliberate addition of peroxide to the solvent solution.

4.2. Photokinetic evaluation

The intensity was adjusted using neutral–grey glass filter combinations in the irradiation pathway. The intensity was determined by actinometry at the beginning of the reaction and at the photostationary state. During the reaction, this intensity was continuously controlled by a photodiode.

The stirred solution was thermostatically controlled in the cell at 50 °C excluding light. The spectrum of the solution was measured until a constant temperature was obtained. These spectra were used to determine the initial concentration. During thermostatic control and measurement the concentration may vary by evaporation. For this reason, these values were compared with those measured at the end of the photochemical measurement cycle. Furthermore, by this means, leaking of the cell becomes obvious. By monitoring at the absorbance maximum of 392 nm, the time the photostationary state is reached can be determined. In the photostationary state, the spectra were taken five times. The difference is less than 0.3% of the average value.

The neutral–grey glass filter combination was varied in order of increasing intensity. The transmissions of the filters were chosen such that the change in the final absorbance at the photostationary state was less than 0.1 absorbance units at the absorbance maximum. Thus, during such a cycle, the photostationary states were measured for all irradiation intensities. After the photostationary state had been reached for the highest irradiation intensity (without any neutral–grey glass), the thermal back reaction was measured taking the spectra every 20 s. Next, the irradiation wavelength was changed. Normally, two irradiation wavelengths were measured in one cycle. The total procedure was finished in about 12 h. Afterwards, the irradiation intensity was measured actinometrically. The data obtained were used if the irradiation intensities did not vary by more than 2% between the beginning and the end of the cycle. The measurements were made six times at the three radiation wavelengths used. By these means, all the parameters necessary to evaluate Eq. (1) were determined or known. Thus the photochemical quantum yields φ_1^A and φ_2^B could be determined for the three observation wavelengths and the three ir-

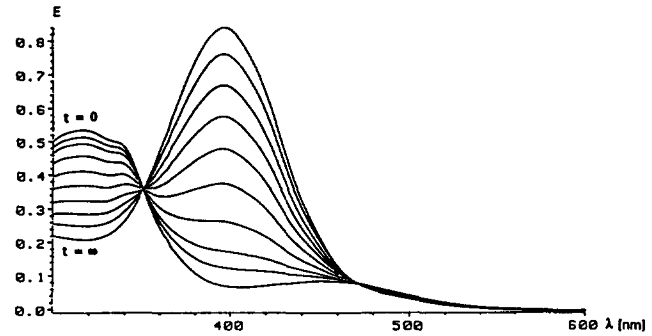


Fig. 3. Spectrum of the thermal backward reaction of the (*Z*,*Z*,*E*) isomer to the (*Z*,*E*,*E*) isomer at 15 °C in toluene–ethylacetate (40:1).

Table 3
Thermal rate constants at 15 and 50 °C

T (°C)	k_{therm} (s^{-1})	T (°C)	k_{therm} (s^{-1})
15±0.5	$1.2\times10^{-4}\pm1\times10^{-5}$	50±1	$4.4\times10^{-3}\pm4\times10^{-4}$

Table 4
Photochemical isomerization quantum yield φ_1^A

λ (measurement) (nm)	λ′ (irradiation) (nm)		
	366	404	436
366	0.085±0.001	0.099±0.001	0.109±0.002
404	0.084±0.001	0.098±0.001	0.108±0.001
436	0.084±0.001	0.098±0.001	0.107±0.001

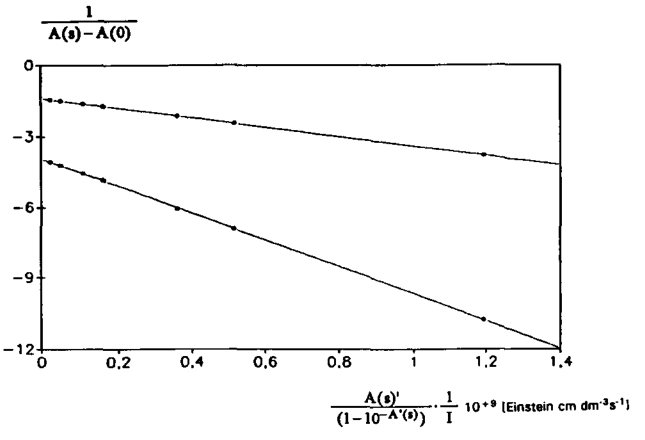


Fig. 4. Graph according to Eq. (1) at λ′ = 436 nm.

Table 5
Photochemical isomerization quantum yield φ_2^B

λ (measurement) (nm)	λ′ (irradiation) (nm)		
	366	404	436
366	0.25 ± 0.02	0.22 ± 0.02	0.36 ± 0.01
404	0.25 ± 0.01	0.25 ± 0.02	0.36 ± 0.01
436	0.26 ± 0.02	0.23 ± 0.02	0.34 ± 0.01

radiation wavelengths (Table 4) using graphs such as that shown in Fig. 4.

The photochemical quantum yields for (*E*) → (*Z*) isomerization depend on the wavelength (Table 4). The shorter the irradiation wavelength, the smaller the quantum yield becomes. Taking the absorbance spectrum of the (*Z*,*E*,*E*) isomer, we can interpret the result to indicate that, in the measured wavelength range, which exhibits a single absorption band, an $n \rightarrow \pi^*$ transition is superimposed on the $\pi \rightarrow \pi^*$ transition.

For (*Z*) → (*E*) photoisomerization (Table 5), the quantum yield of the $\pi \rightarrow \pi^*$ transition is 0.25 ($\lambda' = 366$ nm), whereas that of the $n \rightarrow \pi^*$ transition is 0.35 ($\lambda' = 436$ nm). These results fit well with the values obtained for azobenzene photoisomerization.

The overlap of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions was demonstrated by solvent-dependent spectroscopy as well as polarization spectroscopy in oriented distyrylazobenzenes. For the latter experiment, distyrylazobenzene was introduced into polyethene films by diffusion. These films were spilled by dichloromethane to dispense the films from the only adsorbed distyrylazobenzene molecules. After drying, the absorbance spectra of the stretched films were taken at different angles of polarization. The factor of orientation is larger than 0.9 and results from a change in direction of the transition moment for the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. As a consequence, the intense long-wavelength absorption band in the spectrum of (*Z*,*E*,*E*)-4,4′-distyrylazobenzene consists of two transitions. This explains the wavelength dependence of the photochemical isomerization quantum yield φ_1^A.

5. Conclusions

The evaluation method proposed allows complex photoreactions to be examined in detail, if the absorption coefficients can be determined from pure compounds obtained by flash chromatography. The application of statistics increases the significance of the values obtained.

References

[1] F. Vögtle, *Supramolekulare Chemie,* Teubner, Stuttgart, 1989; H. Meier, *Angew. Chem., 104* (1992) 1425; *Angew. Chem. Int. Ed. Engl., 31* (1992) 1399.

[2] H. Meier, F. Kosteyn, N. Hanold, H. Rau and G. Gauglitz, *Chem. Ber., 125* (1992) 889.

[3] H. Rau, G. Greiner, G. Gauglitz and H. Meier, *J. Phys. Chem., 94* (1990) 6523.

[4] E. Fischer, *J. Phys. Chem., 71* (1967) 3704.

[5] H. Rau, Azocompounds, in H. Dürr and H. Bouas-Laurent (eds.), *Photochromism,* Elsevier, Amsterdam, 1990; H. Rau and G. Greiner, *EPA Newsletter, 41* (1991) 40.

[6] C.A. Parker and C.G. Hatchard, *Trans. Faraday Soc., 57* (1961) 1894.

[7] G. Gauglitz and St. Hubig, *Z. Phys. Chem. (Wiesbaden), 139* (1984) 237.

[8] H. Mauser, *Formale Kinetik,* Bertelsmann Verlag, 1974.

[9] U. Röhrig, *Master Thesis,* Tübingen, 1989.