

DETERMINATION OF THE QUANTUM YIELDS OF PHOTOCHEMICAL REACTIONS BY MEANS OF ABSORPTION SATURATION MEASUREMENTS

II: QUANTUM YIELDS OF PHOTOCHEMICAL INTRAMOLECULAR PROTON TRANSFER REACTIONS IN 2-(*o*-HYDROXYARYL)AZOLE SOLUTIONS

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Summary

In absorption saturation measurements the reaction quantum yield can be calculated from the dependence of the probe beam transmission on the energy of the exciting pulses provided that the probing is performed at wavelengths in the photoproduct absorption band and that excitation is at the absorption wavelengths of the substrate. This approach was used to determine the reaction quantum yields of light-induced intramolecular proton transfer reactions.

1. Introduction

2-(*o*-hydroxyaryl)azole compounds show an anomalous Stokes shift of at least 7000 cm^{-1} in their fluorescence spectra which is due to an intramolecular proton transfer in the excited state from hydroxyaryl oxygen (enol form) to azole nitrogen (coloured form) [1, 2].

In earlier work we have investigated 2-(1'-hydroxy-2'-naphthyl)benzimidazole (A), 2-(1'-hydroxy-2'-naphthyl)benzoxazole (B) and 2-(1'-hydroxy-2'-naphthyl)benzthiazole (C) using nanosecond laser flash photolysis [3] and picosecond probe beam absorption spectroscopy [4, 5]. It has been shown that two coloured transients are produced when polar solutions of A are flashed and we have assumed that these are the *cis* and *trans* rotamers of the coloured form. Only the *cis* coloured form was observed when solutions of B and C were flashed.

In this paper we describe the method used to measure the reaction quantum yields for the photochemical transition from the enol form to the coloured form for three azole compounds.

2. Experimental details

2.1. Materials

The three compounds A, B and C investigated are shown in Fig. 1. They were synthesized by H. Hartmann and A. Graness and their purity was

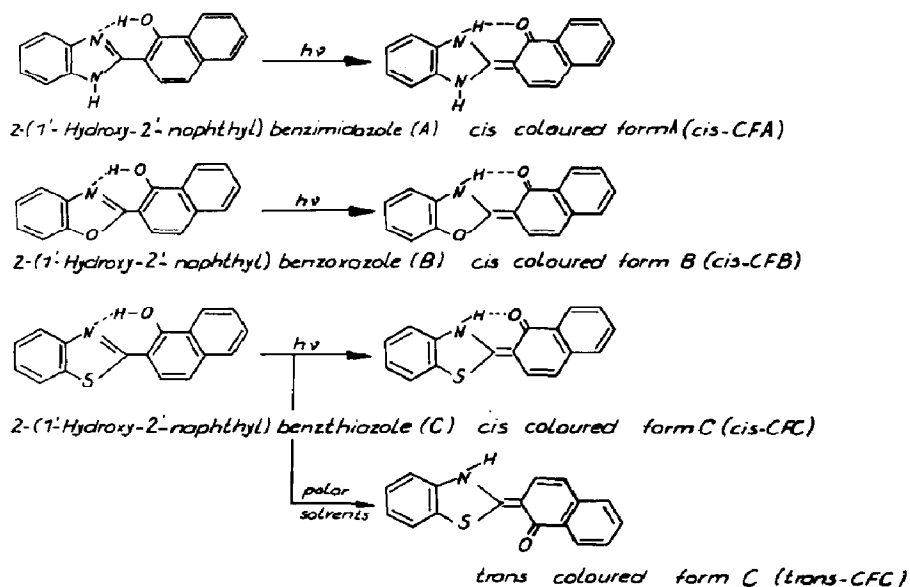


Fig. 1. Structures of the compounds investigated.

checked using thin layer chromatography and elementary analysis. The solvents were purified according to standard procedures.

2.2. Apparatus

The experimental apparatus has been described in detail elsewhere [3, 5]. The samples were irradiated using the second harmonic of a Q-switched ruby laser ($\lambda = 347$ nm; pulse duration, about 14 ns; pulse energy, less than about 50 mJ). The absorption of the transients (coloured forms) was probed using light from a flashlamp and from a continuous-wave high pressure xenon lamp. The transient spectra were observed using a normal monochromator-photomultiplier recording system. The energies of the excitation pulses were measured using a calibrated calorimeter.

3. Results

We measured the dependence of the test light transmission T (probed at wavelengths in the photoproducts' absorption band) on the energy E of the excitation pulses (wavelength, 347 nm). Typical $\ln T$ - E curves are shown in Fig. 2. Similar measurements were carried out for *n*-hexane and acetonitrile solvents.

The absorption cross sections σ_F of the $S_1 \leftarrow S_0$ transition of the coloured forms (*cis*-CFA, *cis*-CFB and *cis*-CFC) in *n*-hexane and the value of $(\sigma_F^C \phi_C + \sigma_F^T \phi_T) / (\phi_C + \phi_T)$ for the flash-induced photochemical reaction of C in methanol and acetonitrile solutions were calculated using eqns. (A12) and (A14) (Appendix A) for excitation energies $E > 30$ mJ. The absorption cross sections were calculated for the condition $\sigma' \phi' \ll \sigma \phi$ (Appendix A). Measurements of the absorption saturation near the absorption band edge of

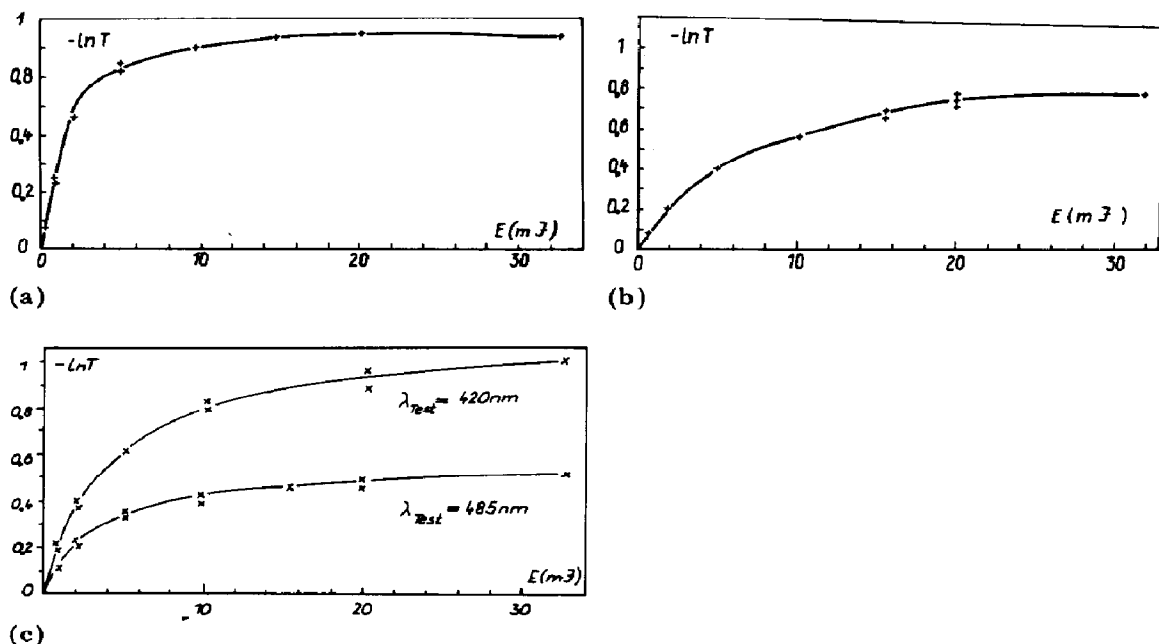


Fig. 2. $\ln T$ vs. E for methanol solutions of (a) flashed compound A ($\lambda_{\text{test}} = 460 \text{ nm}$) ($5 \times 10^{-5} \text{ mol l}^{-1}$), (b) flashed compound B ($\lambda_{\text{test}} = 460 \text{ nm}$) ($5 \times 10^{-5} \text{ mol l}^{-1}$) and (c) flashed compound C ($6 \times 10^{-5} \text{ mol l}^{-1}$).

the compounds under investigation have shown that the inequalities $\sigma' \phi' / \sigma \phi < 0.09$ and $\sigma' \phi' / \sigma(\phi_C + \phi_T) < 0.07$ hold [5].

The dependence of the absorption cross sections of the coloured forms on the wavelength are shown in Fig. 3.

The photoreaction quantum yields were calculated from the slopes of the $\ln T$ - E curves (Fig. 2) at low energy values using eqns. (A11) and (A13) (Appendix A) and are given in Table 1. The determination of ϕ_C and ϕ_T is possible because the transients *cis*-CFC and *trans*-CFC have different lifetimes [3, 5].

TABLE 1

Reaction quantum yields

Compound	Solvent	ϕ	Reaction
A	Methanol	0.46	A \rightarrow <i>cis</i> -CFA
	<i>n</i> -hexane	0.40	
B	Methanol	0.13	B \rightarrow <i>cis</i> -CFB
	<i>n</i> -hexane	0.10	
C	Methanol	0.19	C \rightarrow <i>cis</i> -CFC
		0.09	C \rightarrow <i>trans</i> -CFC
	Acetonitrile	0.15	C \rightarrow <i>cis</i> -CFC
		0.15	C \rightarrow <i>trans</i> -CFC
	<i>n</i> -hexane	0.08	C \rightarrow <i>cis</i> -CFC

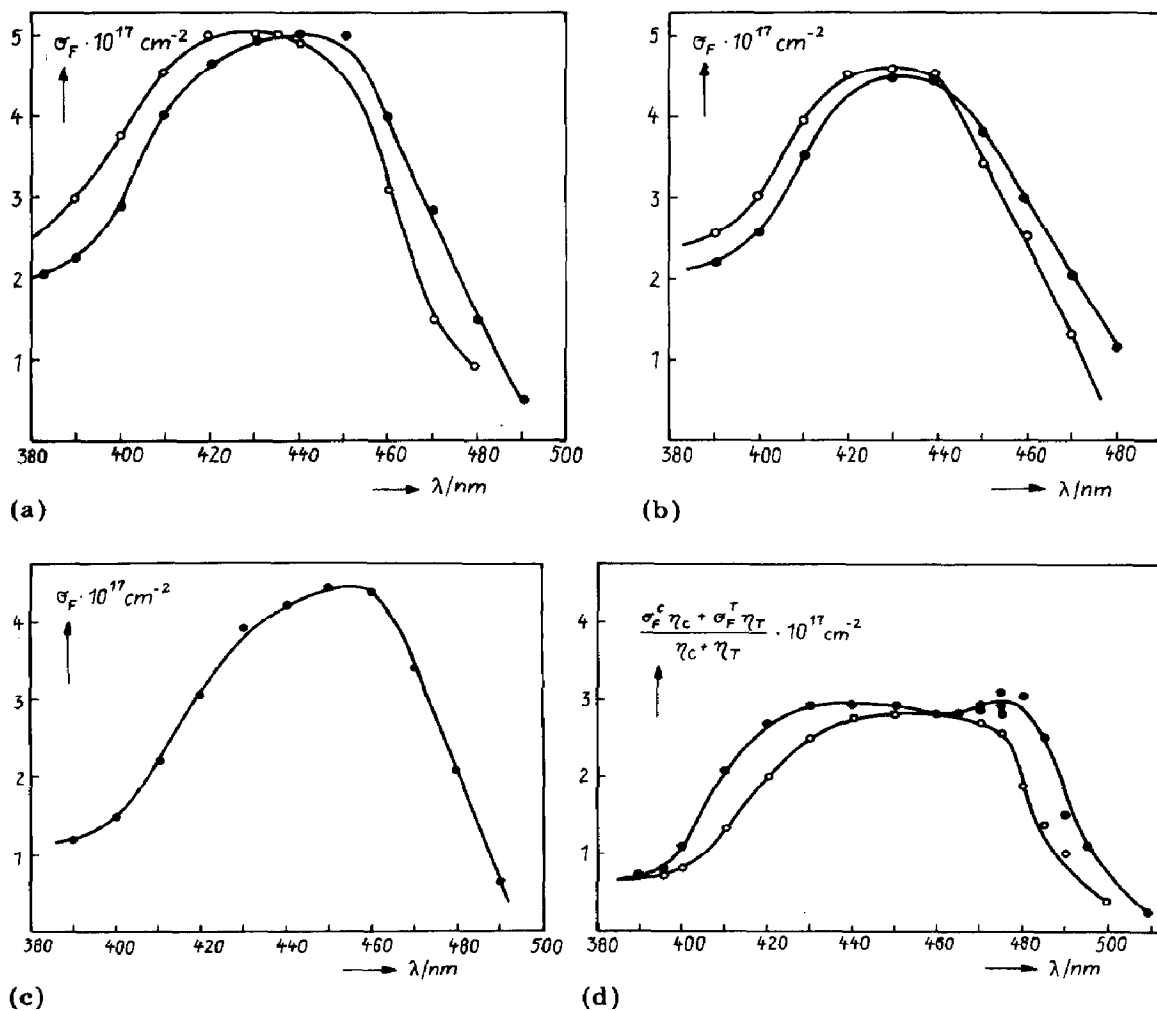


Fig. 3. Absorption cross section of $S_1 \leftarrow S_0$ transition of (a) *cis*-CFA (○, in methanol, 5×10^{-5} mol l $^{-1}$; ●, in *n*-hexane, 5×10^{-5} mol l $^{-1}$), (b) *cis*-CFB (○, in methanol, 5×10^{-5} mol l $^{-1}$; ●, in *n*-hexane, 6×10^{-5} mol l $^{-1}$), (c) *cis*-CFC (in *n*-hexane, 2.8×10^{-5} mol l $^{-1}$) and (d) flashed compound C (○, in methanol, 6×10^{-5} mol l $^{-1}$; ●, in acetonitrile, 8×10^{-5} mol l $^{-1}$).

Acknowledgment

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References

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Appendix A

We use the four-level system shown in Fig. A1 to calculate the transmission T of the test light. We denote the population number densities by N_i , the transition probabilities between states i and j by k_{ij} , the absorption cross section of the enol forms at $\lambda = 347$ nm by σ and the absorption cross section of the coloured forms at $\lambda = 347$ nm by σ' . The following assumptions are made: (1) $k_{10} + k_{12}$ and $k_{32} + k_{30}$ are much greater than the pulse length Δ ; (2) the transitions $0 \rightarrow 1$ and $2 \rightarrow 3$ are unsaturated; (3) the lifetime of the transients is much greater than Δ (the experimental lifetimes of CFA, CFB and CFC are all greater than about 100 ns).

We obtain the following equations for the population number densities:

$$\frac{\partial\{N_1(z, t)\}}{\partial t} = \sigma N_0(z, t)q(z, t) - N_1(z, t)(k_{10} + k_{12}) \quad (\text{A1})$$

$$\frac{\partial\{N_0(z, t)\}}{\partial t} = -\sigma N_0(z, t)q(z, t) + k_{10}N_1(z, t) + k_{30}N_3(z, t) \quad (\text{A2})$$

$$\frac{\partial\{N_2(z, t)\}}{\partial t} = -\sigma' N_2(z, t)q(z, t) + k_{12}N_1(z, t) + k_{32}N_3(z, t) \quad (\text{A3})$$

$$\frac{\partial\{N_3(z, t)\}}{\partial t} = \sigma' N_2(z, t)q(z, t) - N_3(z, t)(k_{30} + k_{32}) \quad (\text{A4})$$

In view of assumption (1) the inequality $N_1, N_3 \ll N_0, N_2$ holds. Therefore it is possible to simplify the system of differential equations:

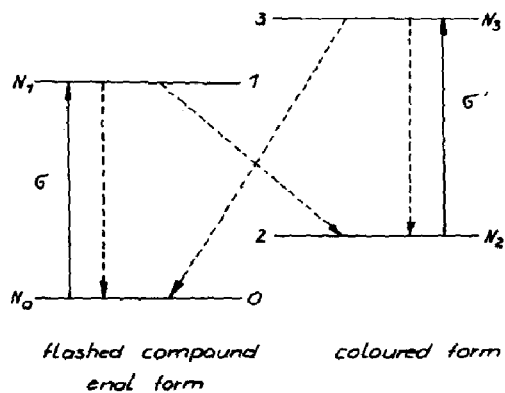


Fig. A1.

$$\frac{\partial\{N_0(z, t)\}}{\partial t} = -\sigma\phi N_0(z, t)q(z, t) + \sigma'\phi'N_2(z, t)q(z, t) \quad (\text{A5})$$

$$\frac{\partial\{N_2(z, t)\}}{\partial t} = \sigma\phi N_0(z, t)q(z, t) - \sigma'\phi'N_2(z, t)q(z, t) \quad (\text{A6})$$

where

$$\phi = \frac{k_{12}}{k_{10} + k_{12}}$$

is the quantum yield of the photochemical transition from the enol to the coloured form and

$$\phi' = \frac{k_{30}}{k_{30} + k_{32}}$$

is the quantum yield of the photochemical back reaction. The photon flux density $q(z, t)$ of the exciting radiation is given by

$$\frac{\partial\{q(z, t)\}}{\partial z} = -\sigma N_0(z, t)q(z, t) - \sigma'N_2(z, t)q(z, t) \quad (\text{A7})$$

Equations (A5) and (A6) are solved by assuming $N_0 + N_2 = N$ (where N is the number density of the molecules) and $N_0(0, z) = N$, $N_2(0, z) = 0$:

$$N_0(z, t) = N \left(e^{-x} \frac{\sigma\phi}{\sigma\phi + \sigma'\phi'} + \frac{\sigma'\phi'}{\sigma\phi + \sigma'\phi'} \right) \quad (\text{A8})$$

$$N_2(z, t) = N \frac{\sigma\phi}{\sigma\phi + \sigma'\phi'} (1 - e^{-x}) \quad (\text{A9})$$

where

$$x = \int_0^t q(z, t')(\sigma\phi + \sigma'\phi') dt'$$

The photon flux density q_T of the test light is given by

$$\frac{\partial q_T}{\partial z} = -\sigma_F N_2 q_T \quad (\text{A10})$$

where σ_F is the absorption cross section of the coloured form in the absorption band $400 \text{ nm} \leq \lambda \leq 500 \text{ nm}$ (Fig. 3).

The transmission of the test light was measured immediately after excitation ($t \approx \Delta$).

Equation (A10) was solved for very small excitation energies $x(\Delta, z) \ll 1$ and very high excitation energies $\exp\{-x(\Delta, z)\} \ll 1$.

When $x(\Delta, z) \ll 1$, $N_2(\Delta, z) \ll N_0(\Delta, z)$ and $N_0 \approx N$. We obtain the following equations from eqns. (A7) and (A9):

$$N_2(\Delta, z) = N \frac{\sigma\phi x(\Delta, z)}{\sigma\phi + \sigma'\phi'} \frac{\partial q}{\partial z} = -\sigma N_q$$

The transmission of the test light is given by

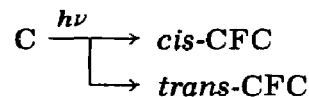
$$-\ln\{T_T(\Delta, L)\} = \sigma_F \phi \frac{E}{h\nu F} \{1 - \exp(-\sigma NL)\} \quad (\text{A11})$$

where E is the energy of the exciting pulses, F is the cross section of the exciting beam on entering the sample and L is the length of the cell.

When $\exp\{-x(\Delta, z)\} \ll 1$, N_2 is independent of the pulse energy E . We obtain from eqns. (A9) and (A10) the relation

$$-\ln\{T_T(\Delta, L)\} = \sigma_F N \frac{\sigma\phi}{\sigma\phi + \sigma'\phi'} L \quad (\text{A12})$$

A similar calculation was carried out for the photochemical reaction



and the following relations were obtained:

$$-\ln\{T_T(\Delta, L)\} = (\phi_C + \phi_T) \left(\frac{\sigma_F^C \phi_C + \sigma_F^T \phi_T}{\phi_C + \phi_T} \right) \frac{E}{h\nu F} \{1 - \exp(-\sigma NL)\} \quad (\text{A13})$$

for $\int_0^\Delta q(z, t') \{(\phi_C + \phi_T)\sigma + \sigma'\phi'\} dt' \ll 1$ and

$$-\ln\{T_T(\Delta, L)\} = \frac{\sigma_F^C \phi_C + \sigma_F^T \phi_T}{\phi_C + \phi_T} \frac{\sigma(\phi_C + \phi_T)}{\sigma(\phi_C + \phi_T) + \sigma'\phi'} NL \quad (\text{A14})$$

for $\exp[-\int_0^\Delta q(z, t') \{(\phi_C + \phi_T)\sigma + \sigma'\phi'\} dt'] \ll 1$ where ϕ_C and ϕ_T are the quantum yields of photochemical production of *cis*-CFC and *trans*-CFC respectively and σ_F^C and σ_F^T are the absorption cross sections of *cis*-CFC and *trans*-CFC respectively at the test wavelength.