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Photochemical *Trans–Cis* Isomerization of some 4-Diethylaminoazobenzenes

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ABSTRACT

The quantum yields for the trans–cis *(Φ_1) and* cis–trans *(Φ_2) photoisomerization reaction of 4′-X-4-diethylaminoazobenzenes ($X = H$, OCH_3, CN, NO_2) have been measured in cyclohexane,* N,N-*dimethylformamide and diethyleneglycol dimethyl ether by irradiation at 415 nm. The corresponding visible absorption spectra of the* cis *isomers have been determined. The sum of Φ_1 and Φ_2 is equal to unity, within the limits of experimental error, for all the investigated dyes in all solvents. Electron-withdrawing 4′-substituents increase Φ_1. The same effect is brought about by increasing solvent polarity. The experimental data suggest that photoisomerization proceeds in the singlet manifold along an inversion path.*

1 INTRODUCTION

The photochemical behaviour of azobenzene has been extensively studied as a function of many parameters such as temperature, solvent, irradiation

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wavelength, etc., as well as in the presence of sensitizers and of oxidizing and reducing agents.[1-10] Despite the wide commercial importance of azo dyes, only a few photochemical investigations have been carried out on them.[11-14] Nevertheless, it is now well established that these compounds when irradiated by visible light undergo, almost exclusively, *trans–cis* isomerization in all media. The *cis* form then reverts progressively to the thermodynamically more stable *trans* isomer following either a photochemical or a thermal path.[15-19]

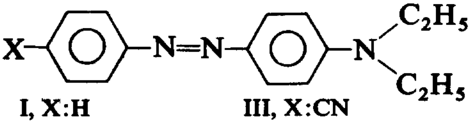
The good photostability shown by azo dyes, either in solution or in polymer matrices, is clearly connected with the high efficiency of these photochemical processes and in conjunction with the thermal isomerization reaction, which usually occurs at a rate much higher than that of the parent compound, especially in polar media or when electron-withdrawing substituents are present on the benzene rings.[18] In this way, azo dyes are able to dissipate rapidly the excitation energy, thus lowering the lifetime and hence the reactivity of the excited states generated by irradiation.

On the other hand, a detailed knowledge of the photochemical behaviour of dyes is important in order to assess the photodegradation phenomenon in more than simple qualitative terms.

The photofading of dyes on fibres or in polymer matrices is a complex phenomenon, affected by many factors, either external to the dye–matrix system (such as the spectral distribution of the light source, the atmospheric composition, humidity, or temperature), or internal to the system (including the chemical and physical structure both of the dye and of the medium, dye aggregation, diffusion and energy transfer processes, the presence of other molecules or, finally, the dyeing procedure).[20]

As a part of our research programme, in our previous papers several aspects of the physical and chemical behaviour of azo dyes have been studied, namely the acid–base and tautomeric equilibria,[21,22] solvatochromism,[22,23] the solvent effect on the kinetics of the thermal *cis–trans* isomerization,[18] and the influence of polymer matrix morphology on geometrical isomerization and on photofading.[23-28] The physical and chemical behaviour of these dyes appears to be quite sensitive to even small changes in their structure and in the medium and is determined by the action of many interrelated factors.

In this paper we report a study on the effect of the solvent and substituent



I, X:H III, X:CN
II, X:OCH$_3$ IV, X:NO$_2$

Scheme 1

on the photochemical *trans–cis* isomerization of some 4-diethylaminoazobenzenes I–IV (see Scheme 1), as an initial approach to the investigation of their photochemical behaviour on fibres and polymers.

2 EXPERIMENTAL

2.1 Materials

The azobenzene derivatives I–IV were supplied by ACNA SpA and purified by repeated crystallization from 1-butanol. Spectrograde solvents (Fluka AG) were used. A small amount of diethylamine (*c.* 0·5%) was added to sample solutions in order to avoid the adventitious catalytic effect of acidic impurities, which can seriously affect measurement reproducibility.

2.2 Measurements

Trans–cis photoisomerization quantum yields were measured using equipment designed in our laboratories. The irradiation source was a 100-W tungsten lamp and the excitation wavelength was isolated using an Oriel interferential filter. The light energy impinging on the sample solution, contained in a quartz 1 cm fluorescence cell, was determined by ferrioxalate actinometry;[29] comparison tests which were carried out using azobenzene actinometry, according to Gauglitz & Hubig,[7] gave substantially identical results. The sample cuvette was contained in a thermostated (±0·1°C) cell holder and the temperature inside the cell was continuously checked using a thermocouple. The reaction progress was followed spectrophotometrically, by measuring the absorbance change of the sample at a suitable wavelength as a function of time. This measurement was carried out using a system consisting of a tungsten lamp, a monochromator and a photomultiplier arranged perpendicularly to the irradiation path. The intensity of the analytical light beam was found to be negligible with respect to the exciting beam. The total dye concentrations of the samples ranged between 5×10^{-6} M and 2×10^{-5} M. All the dyes observed the Lambert–Beer law over a wide concentration range.

The solutions to be studied were introduced into the cuvette and kept in the dark, at the temperature of the experiment, for a period long enough to exclude the presence of *cis* isomer.[18] It was assumed that, at equilibrium, only the *trans* form was present, as is generally accepted.[19] The sample was suddenly exposed to the exciting radiation and the consequent absorbance change monitored for a period at least four times longer than that necessary to reach the photostationary state. Finally, the irradiation unit was turned off and the thermal return monitored in the same apparatus. It was always found that the absorbance at the end of the experiment was coincident with that measured initially. This was considered proof that no irreversible secondary reactions took place.

2.3 Quantum yield determination

Quantum yields were calculated from the experimental absorbance vs time curves on the basis of the following mechanistic scheme:

$$\mathrm{T}\ \underset{\xleftarrow[k]{}}{\underset{\Phi_2}{\overset{\Phi_1}{\rightleftarrows}}}\ \mathrm{C}$$

where T and C represent the *trans* and the *cis* form of the dye, respectively; Φ_1 is the quantum yield of the photochemical *trans–cis* conversion, while Φ_2 refers to the opposite photochemical reaction; k is the kinetic constant of the thermal *cis–trans* return.

This model is described kinetically by the following equation,

$$-\frac{\mathrm{d}[\mathrm{T}]}{\mathrm{d}t}=\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t}=\Phi_1 I_{\mathrm{T}}-\Phi_2 I_{\mathrm{C}}-k[\mathrm{C}] \tag{1}$$

where I_{C} and I_{T} are the light intensities absorbed by *cis* and *trans* isomers, respectively; square brackets indicate the concentrations of each species. Equation (1) can also be written as

$$\frac{\mathrm{d}y}{\mathrm{d}t}=I^0\varepsilon_{\mathrm{T}}\Phi_1(1-y)/F-I^0\varepsilon_{\mathrm{C}}\Phi_2 y/F-ky \tag{2}$$

where $y=[C]/C^0$ (C^0 being the total dye concentration); I^0 is the light intensity impinging on the cuvette; $F=A'/(1-10^{-A'})$, A' being the sample absorbance at the irradiation wavelength; ε_{T} and ε_{C} are the absorptivities of the *trans* and *cis* form, respectively.

At the photostationary state $\mathrm{d}y/\mathrm{d}t=0$ and $y=y_{\mathrm{ss}}$; thus

$$\frac{1-y_{\mathrm{ss}}}{y_{\mathrm{ss}}}=kF/(I^0\varepsilon_{\mathrm{T}}\Phi_1)+(\varepsilon_{\mathrm{C}}\Phi_2)/(\varepsilon_{\mathrm{T}}\Phi_1) \tag{3}$$

Application of eqn (3), for different dye concentrations, allowed us to calculate $\varepsilon_{\mathrm{C}}\Phi_2/\varepsilon_{\mathrm{T}}\Phi_1$; as expected from k values obtained by thermal return experiments, the term $k/\varepsilon_{\mathrm{T}}\Phi_1$ is generally small.

When the thermal term could be neglected, the spectrum of the *cis* isomer, which cannot be physically isolated, was calculated according to Fischer's method.[30] For dyes characterized by fast thermal back-reaction, Fischer's method was still used, but the corresponding equations were modifed to take

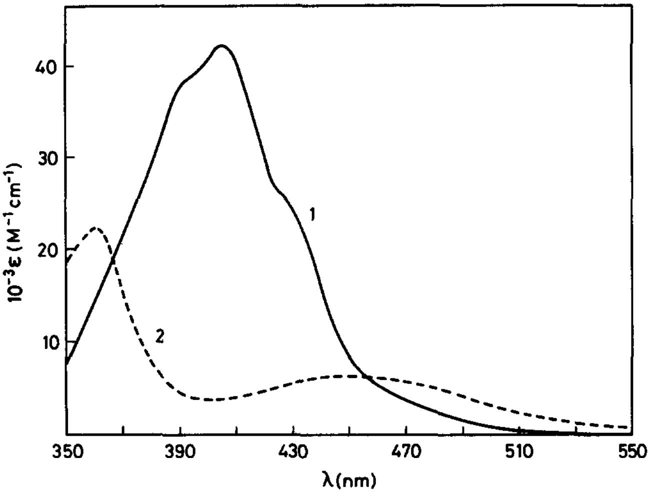


Fig. 1. Absorptivities ε ($M^{-1}\,cm^{-1}$) of 4-diethylaminoazobenzene as a function of wavelength λ (nm) in cyclohexane. Curves 1 and 2 refer to the measured spectrum of the *trans* isomer and to the extrapolated spectrum of the *cis* isomer respectively.

into account the thermal kinetic term and solved numerically with the help of a personal computer. The calculated spectra of the *cis* forms of dyes I–III in cyclohexane are reported in Figs 1–3 and are in good agreement with those expected on the basis of literature data.[19]

Finally, using the values of the ratios Φ_2/Φ_1 obtained from photostationary states and the corresponding rate constants k, Φ_1 and Φ_2 were determined individually by applying eqn (2) to absorbance vs time

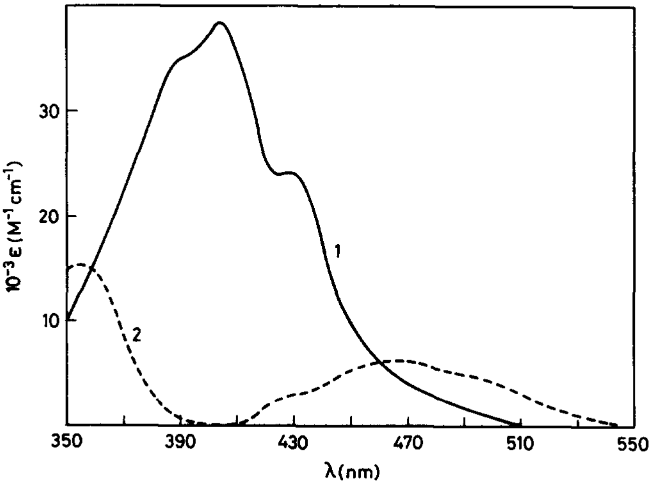


Fig. 2. Absorptivities ε ($M^{-1}\,cm^{-1}$) of 4′-methoxy-4-diethylaminoazobenzene as a function of wavelength λ (nm) in cyclohexane. Curves 1 and 2 refer to the measured spectrum of the *trans* isomer and to the extrapolated spectrum of the *cis* isomer respectively.

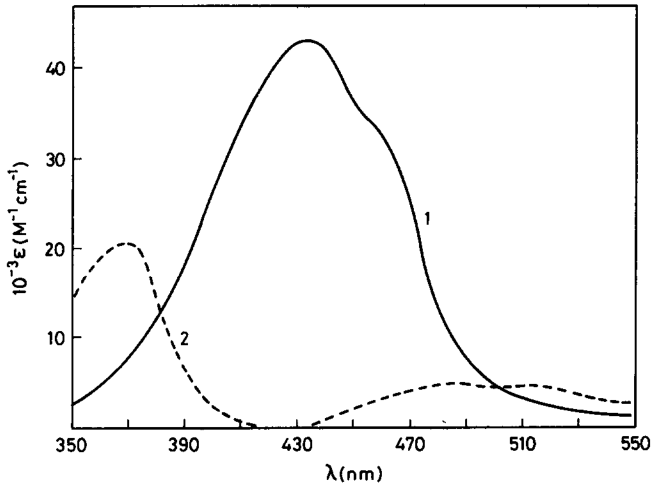


Fig. 3. Absorptivities ε (M^{-1} cm^{-1}) of 4′-cyano-4-diethylaminoazobenzene as a function of wavelength λ (nm) in cyclohexane. Curves 1 and 2 refer to the measured spectrum of the *trans* isomer and to the extrapolated spectrum of the *cis* isomer respectively.

experimental curves with the help of a simple computer program. The good agreement between experimental data and computed values is shown in Fig. 4 for one case.

Quantum yields of the dyes I–IV in various solvents are collected in Table 1; the values are the average of at least three separate determinations.

The irradiation wavelength was 415 nm and the temperature at which all experiments were carried out was 25°C. The absorbance values used in eqn (2) were measured by means of the detection system described above and corrected for the large bandwidth of the irradiation filter.[31]

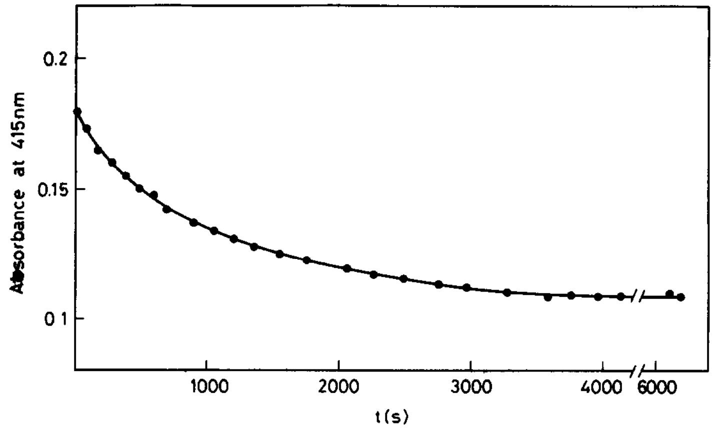


Fig. 4. Absorbance (at 415 nm) change of a cyclohexane solution of 4-diethylaminoazobenzene ($5{\cdot}2 \times 10^{-6}$ M) as a function of irradiation (at 415 nm) time. The solid line is calculated from the measured Φ_1, Φ_2 and k values on the basis of eqn (2).

TABLE 1

Trans–Cis and *Cis–Trans* Photoisomerization Quantum Yields (Φ_1 and Φ_2, Respectively) of Dyes I–IV in Various Solvents

Solvent		*Dye*			
		I	*II*	*III*	*IV*
Cyclohexane	Φ_1	0·086 ± 0·009	0·025 ± 0·005	0·25 ± 0·03	
	Φ_2	0·81 ± 0·08	0·97 ± 0·08	0·64 ± 0·05	
Diethyleneglycol/ dimethyl ether	Φ_1	0·26 ± 0·03	0·15 ± 0·02	0·27 ± 0·03	
	Φ_2	0·70 ± 0·07	0·70 ± 0·08	0·64 ± 0·05	
N,*N*-Dimethyl- formamide	Φ_1	0·38 ± 0·03	0·24 ± 0·02	0·24 ± 0·03	0·38 ± 0·03
	Φ_2	0·61 ± 0·06	0·76 ± 0·08	0·70 ± 0·06	0·60 ± 0·07

3 RESULTS AND DISCUSSION

Irradiation within the visible absorption band of dyes **I–IV** results invariably in *trans–cis* isomerization. No significant difference was observed when carrying out experiments on samples subjected to nitrogen purging or when they were exposed to radiation of different wavelength within the visible absorption band. When irradiation stopped, the dyes always reverted, at different rates, to the initial spectrum allowing us to exclude the presence of irreversible simultaneous photochemical reactions. In fact, as discussed above, application of the mechanistic scheme represented by eqn (1) always resulted in very good agreement with the experimental data.

Check experiments have shown that other reactions, such as photoreduction, occur only by irradiating at shorter wavelength with higher light intensities; photoreduction quantum yields could be estimated to be always smaller than 10^{-3}, in agreement with the literature.[13]

Values of Φ_1 and Φ_2 in different solvents for dyes **I–IV** are collected in Table 1. The values measured in the case of **II** and **III** in cyclohexane are in good agreement with those reported in the literature,[13] bearing in mind the differences in the methods of evaluation of data and in the experimental conditions adopted by other research groups.

Inspection of Table 1 leads to some general conclusions. Thus, $(\Phi_1 + \Phi_2)$ is practically constant and close to unity, within the limits of experimental error, for all dyes and in all solvents. Variations of Φ_1 and of Φ_2 are always coupled: increase of one leads to the decrease of the other. These experimental observations show that the only dissipative path operative is represented by geometrical isomerization and suggest that this process proceeds through an excited state common to both isomers. On the other hand, triplet sensitized quantum yields have been found to be significantly lower than those of the direct process,[13] indicating that, by irradiation in the visible absorption band, photoisomerization occurs in the singlet manifold.

As far as the effect of 4′-substituents is concerned, an increase of the electron-withdrawing properties of this group produces an increase of Φ_1 and a corresponding decrease of Φ_2. On the other hand, if we consider dye **I**, an increase in solvent polarity or in solvent ability to interact with electron lone pairs of the azo nitrogen atoms, as in *N,N*-dimethylformamide, produces a regular increase in Φ_1 and a decrease in Φ_2. Such behaviour is also observed in the case of **II**, although not so clearly, while it disappears in the case of **III**, where solvent variation has only a slight influence on quantum yields.

The above considerations can be rationalized assuming that both *trans* and *cis* singlet excited states decay to a distorted intermediate in the singlet manifold: changes in substituents and in solvent polarity modify the relative energy levels of the different excited states and, in parallel, the respective probabilities of radiationless transitions from excited to ground state. Therefore it is not surprising to find a parallelism between substituent and solvent effects on the photoisomerization of these molecules and their solvatochromism. In previous papers[22,23] it was shown that the extent of the bathochromic shift caused by an increase in solvent polarity decreases steadily with the electron-accepting properties of the 4′-substituents, as the result of the less extensive solvent rearrangement required by the electronic transition. The same effect is likely to be operative in photoisomerization, where, as cited above, Φ_1 and Φ_2 of dye **III** are practically independent of solvent while dyes **I** and **II** are more sensitive to the medium.

Substitution and solvent variation may affect the energy levels of the ground and excited states both of the *trans* and *cis* forms in different ways, as well as those of the intermediate state, the nature of which has been the object of much discussion. In principle, the photoisomerization process may proceed through a rotational or an inversion (shift-in-plane) path; this latter hypothesis seems to be now generally accepted for azobenzene, on the basis of various experimental data[9,32] and theoretical calculations.[33,34] This should also be true for 4-diethylaminoazobenzenes; in fact their photochemical behaviour appears to be qualitatively analogous to that observed in the parent compound, azobenzene,[5] even if, in the present case, excitation involves a π–π^* transition with charge-transfer character, while in azobenzene it is a forbidden n–π^* transition. On the other hand, in the case of the *cis* isomer, due to the large deviation from planarity, the lowest energy band is n–π^* in character. As shown by Figs 1–3 and by literature data,[19] introduction of electron-withdrawing groups in the 4′-position causes a large red shift in the visible spectrum of the *cis* form, which may be attributed to a combined electronic and geometric effect: electron acceptor 4′-

substituents increase the *s*-character of the nitrogen–phenyl carbon bond and increase the angle between the azo group and the phenyl ring, thus leading to an increase of the energy of the corresponding molecular orbitals and also to the well-known decrease in the activation energies of the thermal *cis–trans* isomerization;[18,35] polar solvents give the same result possibly because they contribute to lowering the electrostatic repulsion between the nitrogen lone pairs. Therefore, the experimental data appear to be in agreement with a potential energy curve for the lowest singlet excited state which presents a shallow minimum along the inversion reaction coordinate, as also suggested by analogy with azobenzene.[33] The low values of Φ_1 for **I** and **II** in cyclohexane indicate that the minimum is likely to be shifted to a position which delivers preferentially the *trans* ground form; this is equivalent to saying that the intermediate state is more *trans*-like than *cis*-like. Therefore, substituents and solvents which favour more polar forms lower the energy level of the excited singlet state of the *trans*-4-diethylaminoazobenzenes, as well as, although less markedly, that of the inversion intermediate state; on the contrary, in the case of the *cis* isomers, the same agents increase the energy of the ground state while the singlet excited state is likely to be further stiffened. As a consequence, the potential energy curve is displaced to lower levels and the minimum to a more central position along the reaction coordinate, which corresponds to the N=N—C angle; thus Φ_1 is favoured and Φ_2 relatively depressed on increasing polarity both of the solute and of the solvent.

In conclusion our results seem to support, for all the dyes here studied, and probably for all 4-diethylaminoazobenzenes, the hypothesis that photoisomerization occurs through an inversion path in the singlet manifold and through a unique intermediate state. The efficiency of this dissipative path, coupled with the high thermal conversion rate, is the main reason for the photostability of azo dyes: only very high radiation intensity or any matrix effect able to block the mechanism can stimulate photodegradation, which is predominantly attributable to photoreduction.

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