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Photochemical Degradation of Some Aminoazobenzene and Related 3-Amino-5-nitro(2,1)benzisothiazole-based Dyes in Ethanolic Solution

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ABSTRACT

This paper reports some kinetic measurements of the photofading in ethanol of some aminoazobenzene and related 3-amino-5-nitro(2,1)benzisothiazole-based disperse dyes derived from, as coupling components, derivatives of N-*benzyl*-N-*phenyl-β-alanine with different substituents in the benzyl or phenyl residue. A fair linear relationship between the measured fading rate and* σ_0 *constants of* ortho *substituents in the phenyl ring was found. The influence of substituents in the benzyl group on the rate of fading was not noticeable.*

1 INTRODUCTION

Dyes based on 4-aminoazobenzene and related heterocyclic compounds have been the subject of many studies in respect to their colouristic and fastness properties.

One of the most important properties of the dye is its fastness to light and many efforts have been made to correlate this with the structure of the dye.[1,2] The photodegradation of dyes has been concluded to involve (depending on the experimental conditions) photoisomerization, photocyclisation, photooxidation and photoreduction.[3-8] Most experimental investigations have dealt with the influence of different substituents in the diazo components[9] or of different terminal amino group in the coupling components[10] on the photofading of azobenzene disperse dyes.

Little has been reported about the influence of substituents *ortho* to the azo linkage in the coupling components.

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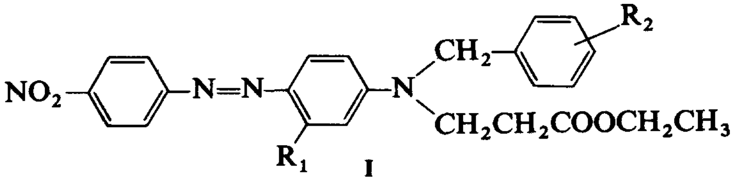
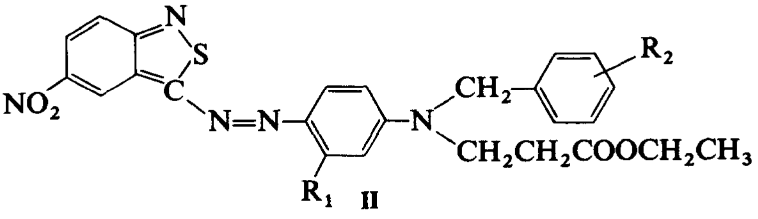


I



II

Dye	*R_1*	*R_2*
Ia, IIa	H	H
Ib, IIb	CH_3	H
Ic, IIc	OCH_3	H
Id, IId	H	p-CH_3
Ie, IIe	H	p-OCH_3
If, IIf	H	m-NO_2

This paper reports some kinetic measurements of the photofading of aminoazobenzenes (**I**) and 3-amino-5-nitro(2,1)benzisothiazole-based analogues (**II**) in which, as coupling components, some ethyl esters of *N*-benzyl-*N*-phenyl-*β*-alanine were used.

The measurements were carried out in ethanolic solution and represent a preliminary stage in the investigations of fading of these dyes on polyester fibres.

2 EXPERIMENTAL

The azo dyes were prepared as previously described[11–13] and purified by crystallization. Ethanolic solutions (96·2% rectified ethanol) of the dyes ($2{\cdot}5 \times 10^{-5}$ mol/litre) were faded in a Rayomet photolytic reactor RPR-100 equipped with 16 300-nm lamps under unaerobic conditions which were achieved by bubbling dry nitrogen into the solution for 30 min before irradiation. The kinetics were followed by measuring the absorbance at regular intervals of time. The concentration of dyes was determined spectrophotometrically using a Specord M-40 UV-VIS spectrophotometer (C. Zeiss, Jena, Germany) (the dyes solutions obeyed Lambert–Beer law at the concentrations used). Visible spectra data for dyes **I** are given in Table 1; those for dyes **II** have been previously reported.[12,13]

TABLE 1
Visible Spectra of Dyes I in Ethanol

Dye	λ_{max} (*nm*)	ε ($\times 10^{-4}$)
Ia	463	3·20
Ib	474	2·88
Ic	483	3·10
Id	467	3·15
Ie	469	3·05
If	450	2·60

3 RESULTS AND DISCUSSION

The first important conclusion resulting from the obervation of the absorption of the irradiated dyes solutions is that the position of their λ_{max} remains the same during the fading process. This indicates that measurements presented pertain to the photolytic degradation of the dyes in the monomeric form, and that dealkylation does not occur.

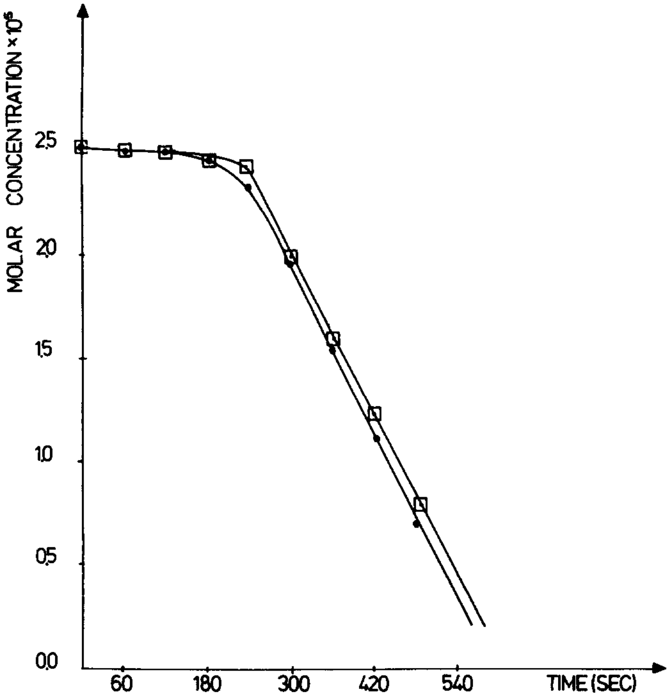


Fig. 1. Fading rate curves for dyes **Ia** (●) and **Ic** (⊡).

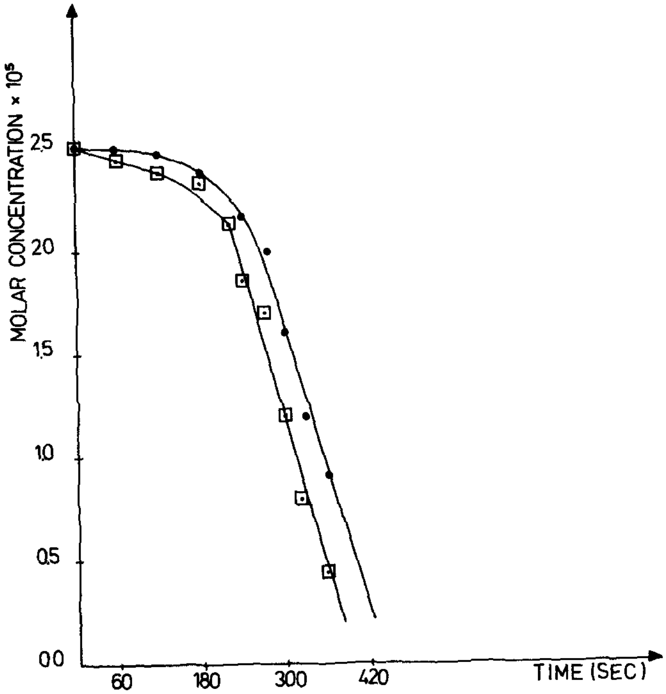
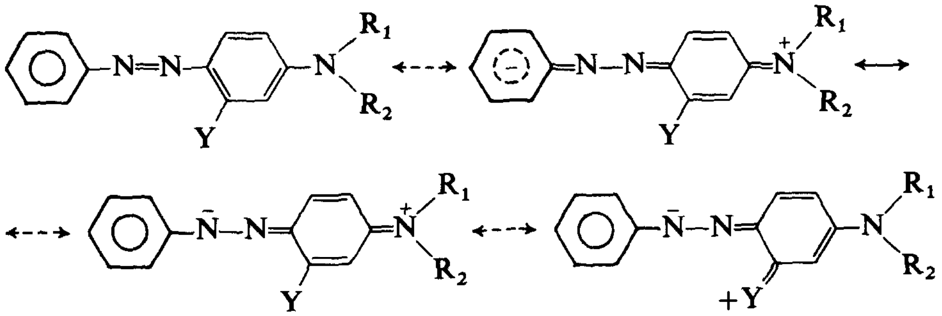


Fig. 2. Fading rate curves for dyes **IIa** (●) and **IIc** (⊡).

In this present work the general shape of the fading curves is shown in Figs 1 and 2, and they are in accord with results reported by Bridgeman and Peters[14] for photodegradation of some aminoazobenzene dyes in ethanolic solutions.

In the initial stage of irradiation the extent of dye degradation is small. After an 'induction' period, the rate of photodegradation increases rapidly and the relationship between dye concentration and time is linear, according to zero-order reaction. Fading rates calculated for dyes **I** and **II** are presented in Table 2.



Scheme 1. Resonance-contributing structures to the hybrid.

TABLE 2
Fading Rates[a] for Photofading of Dyes I and II

Dye	$k_0 \times 10^9$ *(mol/litre s)*	$lg\,k_0$	*Light-fastness of 0·5% polyester dyeings*
Ia	7·20	−8·142	5
Ib	6·80	−8·167	4–5
Ic	6·35	−8·197	4
Id	7·14	−8·146	5
Ie	7·11	−8·147	5
If	7·15	−8·145	5
IIa	11·90	−7·924	6
IIb	12·80	−7·892	5
IIc	13·00	−7·886	5–6
IId	11·97	−7·921	5–6
IIe	12·20	−7·913	5
IIf	12·15	−7·915	5

[a] Average values from at least three determinations.

It is generally observed that under the described conditions, the degradation of 3-amino-5-nitro(2,1)benzisothiazole-based dyes is faster than that of their azobenzene analogues.

It is well known[10] for 4-aminoazobenzene dyes that amino group substituents influence the electron density of azo linkage according to their electronic effects (Scheme 1).

Since, in the case of azobenzene derivatives, it is more likely that photolytic degradation involves the azo linkage,[10] this is an indication that *ortho* substituents may also affect the rate of fading. Results obtained here clearly confirm this suggestion. In the azobenzene dyes (**I**) the presence of *ortho* electron-donating substituents decreases the rate of fading, whereas in 3-amino-5-nitro(2,1)benzisothiazole dyes (**II**) the influence is the opposite.

Additionally, from kinetic measurements, it is apparent that there is no influence of the benzyl group substituents on the rate of fading. The benzyl group is isolated from the amino group and its substituents do not affect the electron density of the azo linkage.

As a measure of the electronic effects of the *ortho* substituents their σ_0 polar constants were correlated with $1\,gk_0$ (Ref. 15) of the dye fading. These results are given in Figs 3 and 4.

The plot of the rate of photodegradation versus σ_0 (Ref. 16) demonstrates that there is the tendency towards a good linear relationship in azobenzenes (**I**) (correlation coefficient: 0·99) and also in the heterocyclic derivatives (**II**) (correlation coefficient: 0·94) as well.

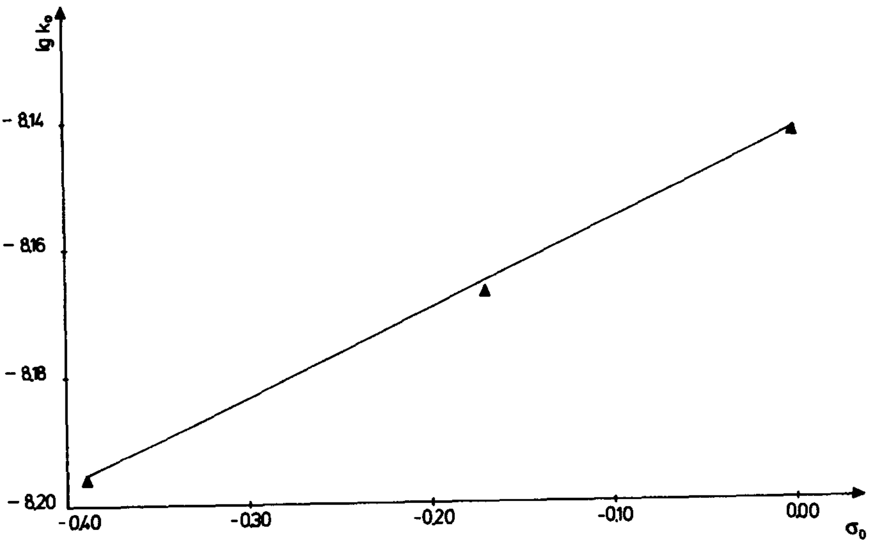


Fig. 3. Relationship between electronic effect of substituents and the rate of fading of dyes I.

Least-squares analysis of the relevant data gave the relationship, for the azobenzenes (**I**, eqn (1)):

$$\lg k_0 = -8{\cdot}142 + 0{\cdot}138\sigma_0 \tag{1}$$

and, for the 3-amino-5-nitro(2,1)benzisothiazole dyes (**II**, eqn (2)):

$$\lg k_0 = -7{\cdot}915 - 0{\cdot}0998\sigma_0 \tag{2}$$

A not too significant slope of the line in eqn (1) is an indication of a small but clear influence of the *ortho* substituents on the fading rate of dyes **I**. A similar decrease of the rate of fading of aminoazobenzenes was also found by Bridgeman and Peters[17] for (arylazo)-*N*,*N*-bis-β-cyanoethylaniline derivatives, when in their coupling components, the *ortho* H substituent was replaced by an *ortho* CH_3 group.

It is also worth noting that in the case of 4-aminoazobenzenes (**I**), in contrast to the related heterocyclic dyes (**II**), the value of the slope is positive, which implies that the fading is accelerated by a decrease of electron density of the azo linkage, confirming their reductive degradation in ethanolic solution.

The very low (negative) slope of the line in eqn (2) suggests a very small influence of the *ortho* substituents in the coupling components on the fading rate of benzisothiazole derivatives. This indicates that the photostability of these dyes in alcoholic solution is to some extent determined by the heterocyclic residue. For comparison, additional kinetic measurements were carried out for dye **III** under the same conditions; its rate of photofading is

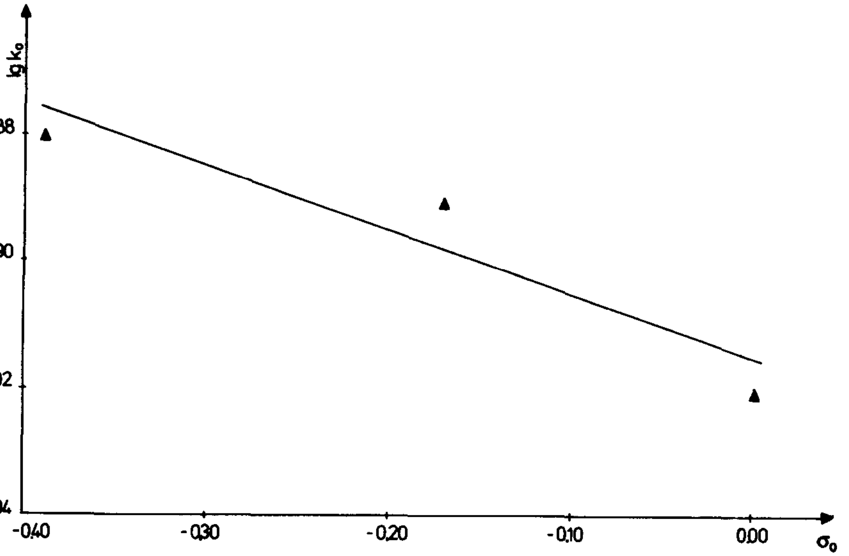
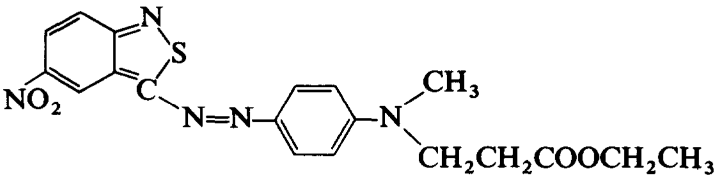


Fig. 4. Relationship between electronic effect of substituents and the rate of fading of dyes **II**.

characterized by $k_0 = 1{\cdot}20 \times 10^{-8}$ mol/litres which is very close to those calculated for some of the dyes **II**.



III

It is thus apparent from these investigations that there is a lack of relationship between the fading rates of dyes **I** and **II** in ethanolic solutions and their light-fastness on polyester fabric. This indicates that the mechanisms of their destruction in these media are different.

Future investigations in this area will include the measure of the change of colour parameters of dyed polyester fibres as a function of irradiation time, and correlation of these results with the structure of the dyes.

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