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Mechanistic studies on the photodegradation of azoarenes

John O. Morley [a,*], Owen J. Guy [a], Michael H. Charlton [b]

[a] *Chemistry Department, University of Wales Swansea, Singleton Park, Swansea, SA2 8PP, UK*
[b] *Evotec OAI, 111 Milton Park, Abingdon, Oxfordshire, OX14 4SD, UK*

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Abstract

The photochemical stability of a series of coloured azobenzenes and azothiophenes containing both electron donors and attractors has been explored in methanol under anaerobic conditions using a xenon light source for irradiation. 4-Dialkylaminoazobenzenes containing a nitro group in the 4′-position of the chromophore are the most stable, while those containing the same group in the 2′-position are the least stable and found to have similar lifetimes to azothiophenes. The photodegradation reaction or loss of colour in each case is attributable to the irradiation of the second absorption band alone, which leads to the formation of a reactive triplet state. This is believed to behave as a biradical and abstract hydrogen from the solvent as the relative rate of photodegradation increases sharply in moving from methanol to propan-2-ol. The reaction is inhibited by radical scavengers, such as the stable 2,2,6,6-tetramethyl-1-piperidinyloxy free radical and enhanced by photochemical radical generators such as acetone or benzophenone. A combination of steric and electronic effects are believed to be responsible for the low photochemical stability of 2′-nitroazobenzenes versus the corresponding 4′-isomers.

Keywords: Azobenzenes; Azothiophenes; Photodegradation; Mechanism

1. Introduction

There is a considerable current interest in the design and synthesis of dyes and pigments, which are resistant to fading by natural and artificial light particularly for applications in ink jet printing [1]. Unfortunately, many of the commercial dyes used for dyeing or printing textiles, paper, plastics, paints and wood, eventually fade or change colour to commercially unacceptable shades on exposure to sunlight [2]. While there have been many studies on the photodegradation or lightfastness of dyes [3,4,5–10], the mechanism of the process is still poorly understood.

The lightfastness of a dye is influenced by a number of factors including the physical structure and chemical nature of the substrate including its water content, the chemical constitution of the dye, the wavelength and intensity of the light used for fading studies, the presence or absence of oxygen and its concentration, the physical state of the adsorbed dye, and the dyeing or printing method employed. The mechanism of photofading is further complicated by the application used for the dye. For example, in textile dyeing, the photofading mechanism for a given dye may be different on cellulose, to that on a protein substrate such as wool [6].

Additionally the same dye may exhibit good lightfastness on conventional textile dyeing, but poor properties on printing using the same or a similar substrate. This apparent difference in behaviour, however, only arises because the dye layer lies at the surface and is only a few microns thick in printing, whereas the dye is distributed more homogeneously through a much thicker fibre in textile dyeing and the same degree of fading is less noticeable [7]. It follows that in applications, such as ink-jet printing, the lightfastness of the dye used is of critical importance as the dye is concentrated at the paper surface. In the latter application, which is a subject of much current interest, black, cyan, yellow and magenta dyes are used, with a combination of the last three colours producing a full colour printing spectrum. While dyes which have narrow absorption bands, high tinctorial strength, and no secondary visible absorptions are preferred as the coloured components,

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* Corresponding author. Tel.: +44 1792 295861; fax: +44 1792 295747.
E-mail address: j.o.morley@swansea.ac.uk (J.O. Morley).

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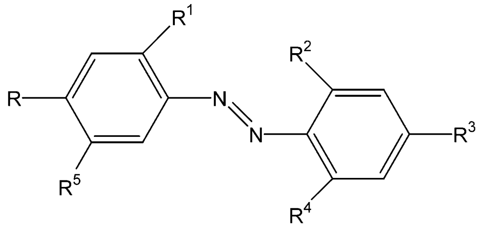
because they have a brighter colour, they often suffer from the disadvantage of poor lightfastness [2]. Many yellow and magenta dyes are based on the azobenzene skeleton, but the mechanism of the photofading process which gradually occurs on paper is not properly understood. While, several papers have proposed mechanisms for the corresponding photoreactions of azo dyes on polyamide substrates [8,9], the reaction on non-protein substrates has not been explored in detail and the fading products have not been established [10].

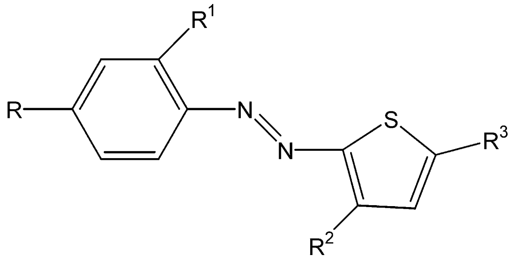
In the current studies, we have explored the lightfastness properties of a range of azobenzenes and azothiophenes by assessing their photochemical stability, and then attempted to explore the mechanisms of the photodegradation reaction. Although an understanding of the photodegradation of azo dyes on paper is of primary interest, because of the difficulties associated with (1) the quantitative measurement of fading rates on a heterogeneous substrate and (2) the addition of sensitizers and free radical scavengers to the paper surface to explore the mechanism, it was decided to model the reactions in solution [11]. Paper is a form of cellulose, which is a plant material consisting of macromolecules varying in molecular weight from several hundred to several thousand glucose units [12]: these in turn contain both primary and secondary alcohol units as well as ether linkages. Possible model solvents might therefore include propan-2-ol, methanol, ethanol, ethylene glycol or diethylene glycol. However, the solubility of the range of azobenzenes selected for this work, was found to be greatest in methanol and smallest in diethylene glycol, and accordingly it was decided to use methanol as the model solvent for the quantitative studies of the photofading process though other solvents were also used.



(1)

	R	R^1	R^2	R^3	R^4	R^5
a	$N(C_2H_5)_2$	SCH_3	H	NO_2	H	H
b	$N(C_2H_4OH)_2$	Cl	H	Cl	NO_2	H
c	$N(C_2H_4OH)(C_2H_5)$	H	H	CO_2CH_3	H	H
d	$N(C_2H_4OH)(C_2H_5)$	H	H	H	NO_2	H
e	$N(C_2H_4OH)(C_2H_5)$	CH_3	H	H	NO_2	H
f	$N(C_2H_4OH)(C_2H_5)$	H	H	Cl	NO_2	H
g	$N(C_2H_4OH)_2$	H	H	Cl	NO_2	H
h	NH_2	H	H	NO_2	H	H
i	$N(C_2H_4OH)(C_2H_5)$	H	H	NO_2	H	H
j	$N(C_2H_5)_2$	H	H	NO_2	H	H
k	$N(C_2H_4OH)_2$	H	H	NH_2	H	H
l	$N(C_2H_5)(C_2H_4CN)$	H	H	NO_2	H	H
m	$N(C_2H_4OH)(C_2H_5)$	H	H	NO_2	Cl	H
n	$N(C_2H_4OH)_2$	H	H	H	H	H
o	$N(C_2H_4OCOCH_3)_2$	CH_3	CN	NO_2	Br	H
p	$N(CH_3)_2$	H	H	NO_2	H	H
q	$N(C_2H_5)_2$	H	H	OCH_3	H	H
r	$N(C_2H_5)_2$	H	H	$N(C_2H_5)_2$	H	H
s	$N(C_2H_4OH)N(C_2H_4CN)$	$NHCOCH_3$	NO_2	H	Br	OCH_3
t	$N(C_2H_4OH)N(C_2H_4CN)$	$NHCOCH_3$	CN	H	Br	OCH_3
u	$N(C_2H_4OH)N(C_2H_4CN)$	$NHCOCH_3$	NO_2	H	Cl	OCH_3
v	$N(C_2H_4OH)_2$	H	H	H	NO_2	H
w	$N(CH_3)_2$	H	H	NO_2	NO_2	H

Scheme 1.



(2)

	R	R^1	R^2	R^3
a	$N(C_2H_4OCOCH_3)_2$	H	NO_2	NO_2
b	$N(C_2H_5)_2$	$NHCOCH_3$	NO_2	NO_2
c	$N(C_2H_5)$ $(C_2H_4OCOCH_3)$	CH_3	$COCH_3$	NO_2
d	$N(C_2H_4OCOCH_3)_2$	CH_3	$COOC_2H_5$	NO_2
e	NMe_2	H	H	NO_2
f	NO_2	H	H	NMe_2

Scheme 2.

The azo compounds selected for these studies were based mainly on azobenzenes (**1**), but phenylazothiophenes (**2**) were also considered, with both types containing a variety of donor and acceptor groups in each of the aromatic rings. The position of the acceptor group in the azo dye is known to strongly influence its photochemical stability, and to assess this important effect, two isomeric azobenzenes, 4-(*N*-(β-hydroxyethyl)-*N*-ethyl)amino-2′-nitroazobenzene (**1d**) and 4-(*N*-(β-hydroxyethyl)-*N*-ethyl)amino-4′-nitroazobenzene (**1i**), were directly compared. A total of 19 dyes were assessed in these studies (Schemes 1 and 2).

A 1000 W xenon arc lamp was selected as the irradiation source for photofading studies as it has a similar irradiation profile to the sun in the visible region, unlike the spiked output of an alternative mercury lamp, and should therefore imitate conditions under which natural solar fading would occur [13]. As the emission profile of the lamp over the 250–700 nm range is fairly constant, each dye was irradiated at the same concentration in methanol (1×10^{-4} mol dm^{-3}) to give a direct comparison of the effect of substituents on the photochemical stability.

2. Results and discussion

2.1. Absorption spectra

Both the azobenzenes (**1**) and azothiophenes (**2**) generally show two absorptions in the 250–600 nm region of the spectrum (Table 1). For example, the spectrum of 4-(*N*-

Table 1
The absorption spectra, lifetimes and half-lives of the azo dyes (**1**) and (**2**) in deoxygenated and oxygenated methanol solution[a]

Dye	λ_1	λ_2	τ (h)	$\tau_{1/2}$ (h)	τ^{o} (h)	$\tau_{1/2}{}^{o}$ (h)
1a	513.4	307.0	1.61	1.11	23.1	11.6
1b	455.9	291.4	0.92	0.69	7.91	3.83
1c	444.7	276.8	3.61	1.80	25.3	12.4
1d	447.8	274.4	1.37	0.87	7.11	3.52
1e	495.2	288.6	2.26	1.44	9.55	4.77
1f	464.7	278.8	0.93	0.65	4.79	2.34
1g	438.1	286.9	1.18	0.86	7.97	3.84
1h	435.9	275.0	2.07	1.06	20.8	10.5
1i	481.9	285.9	4.46	1.12	18.8	12.7
1j	487.8	285.3	6.60	1.48	NM	NM
1k	445.2	317.7	4.00	1.96	31.2	15.5
1l	455.8	281.2	4.36	1.08	23.5	16.5
1m	500.3	285.8	2.95	1.08	21.2	13.6
1n	408.6	258.7	2.76	1.38	16.3	8.33
1o	580.2	306.7	0.89	0.44	14.7	2.72
2a	618.8	286.8	1.36	0.70	4.37	1.82
2b	613.1	275.6	1.42	0.72	6.00	3.47
2c	612.1	280.3	1.71	0.84	NM	NM
2d	615.2	286.7	1.15	0.34	NM	NM

[a] $\lambda_{1,}$ and λ_2 are the main absorption bands in nm; τ and $\tau_{1/2}$ the lifetimes and half-lives of the dyes in methanol under anaerobic conditions (all at a concentration of 1×10^{-4} mol dm^{-3}); τ^{o} and $\tau_{1/2}{}^{o}$ are the corresponding lifetimes and half-lives of dyes in oxygenated methanol. NM, not measured.

(β-hydroxyethyl)-*N*-ethyl)amino-4′-nitroazobenzene (**1i**) in methanol shows a strong absorption at 482 nm and a weaker one at 286 nm (Fig. 1).

Generally, the simple donor acceptor azobenzenes (**1a**–**m**) range in colour from yellow to red in methanol with absorption maxima ranging from 436 to 513 nm [14], though the heavily substituted azo dye (**1o**) is violet and absorbs at 580 nm. The presence or absence of an acceptor substituent in the right hand ring of the azobenzene strongly influences the position of the long wave absorption. Thus (**1n**), which has no acceptor substituent absorbs at 409 nm, whereas related structures such as (**1i**) and (**1m**) which contain electron attractors absorb at 482 and 500 nm, respectively.

The long wavelength absorption band of the azothiophene dyes (**2**) in methanol occurs at longer wavelengths of around 600–630 nm than the donor acceptor azobenzene dyes, which absorb around 450–580 nm. Although the thiophene ring itself has been considered as an electron attractor because of its vacant d orbitals [15], both the theoretical and experimental absorption bands of the two isomeric azothiophenes (**2e**) and (**2f**) which contain a dimethylamino group in either the benzene ring or the thiophene ring with the nitro group positioned in the other ring are similar [4,16]. The bathochromic shift found in moving from the absorption of the donor–acceptor azobenzene (**1p**) at 479 nm to the absorptions of the azothiophenes (**2e**) and (**2f**) at 553 and 561 nm, respectively, [16] suggest that the thiophene ring is simply functioning as a more efficient conjugation path between the donor and acceptor groups, which allows the electrons to move more easily between them on excitation [16].

The position of the second absorption band, which occurs in the region of 275–307 nm for most of the dyes in methanol (Table 1), is influenced less by substituents or structure than the long wavelength absorption band. For example, in moving from the structure of the azobenzene (**1m**) to the azothiophene (**2a**), a marked bathochromic shift is observed in the first absorption band from 500 to 619 nm, respectively, but significantly the second absorption band shows virtually no shift and occurs at about 286 nm in both cases (Table 1).

2.2. Identification of the absorption responsible for photofading

In principle, either the long or short wavelength absorption bands (or both) are responsible for the observed photofading properties of the azobenzenes and azothiophenes in sunlight.

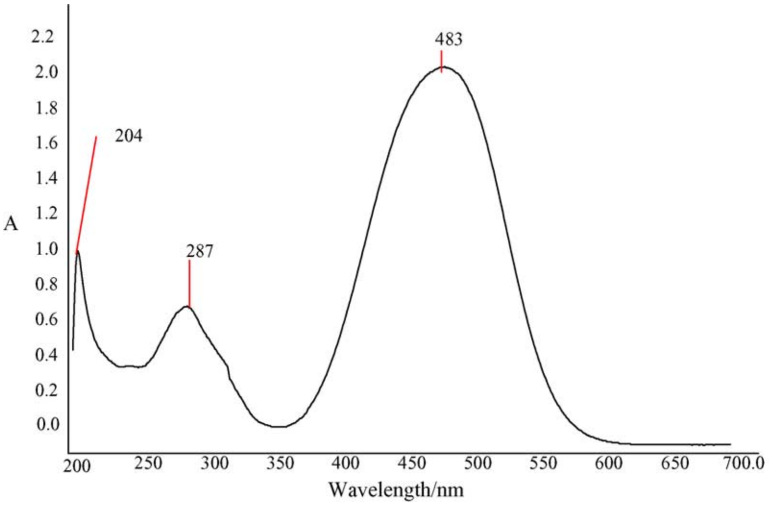


Fig. 1. The UV–vis absorption spectrum of (**1i**) in methanol (*A* is the absorbance).

A previous study [17] has shown that irradiation of the long wavelength absorption band of 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene (**1j**) in methanol has no permanent effect and photofading begins to occur only, when irradiation is carried out with ultraviolet light of 312 nm and at shorter wavelengths. To explore this effect more fully with the more complex range of azo dyes considered in these studies, methanolic solutions of the dyes (all at a concentration of 1×10^{-4} mol dm^{-3}) were irradiated in the presence and absence of an Oriel UV filter, which cuts out all light between 200 and 345 nm, using the 1000 W xenon arc lamp arrangement described in Section 3.

Irradiation of a methanolic solution of 4-(*N*-(β-hydroxyethyl)-*N*-ethyl)amino-4′-nitroazobenzene (**1i**) which had been de-aerated with argon, in a quartz cuvette, results in almost complete loss of colour after 4.46 h. Other azobenzenes such as (**1a**) and (**1g**) lose colour even faster. However, when a UV filter is employed, which removes all light below 345 nm, no fading is observed for (**1i**) even after 12 h irradiation. Furthermore, if a methanolic solution of the same dye, (**1i**), is irradiated for 8 h with an argon ion laser emitting solely at 514.5 nm, where the dye shows a significant absorption (Fig. 1), no fading is observed. It follows that the short wavelength absorption is entirely responsible for the photofading process [18] as originally found by Pietra et al. [17,9].

Quantitatively, the rate of photofading under anaerobic conditions in methanol using argon varies according to dye structure. While the photofading of the simple azobenzenes (**1k**) and (**1n**) shows an approximately linear relationship with time, implying zero-order kinetics, that of (**1a**) and (**1e**) show a quadratic relationship with time, but others such as (**1d**) are more complex (Fig. 2). Since it is not possible to directly compare the rates of reaction for linear and polynomial photofading curves, it was decided to measure the half-lives and lifetimes of the dyes, where the former ($\tau_{1/2}$) is defined as is the time taken for the absorbance *A* of the dye at its long wave maximum to reduce to half its initial value, and the latter (τ) is the time at which the absorbance of the dye solution becomes zero. The lifetimes and half-lives of all the dyes measured are summarized in Table 1.

An analysis of the data shows that dyes containing a nitro group in the 2-position of the acceptor ring (**1b**) and (**1d–g**), all show similar lifetimes which are relatively short compared to the corresponding dyes containing a nitro group in the 4-position of same ring. Although the behaviour of 4-amino-4′-nitroazobenzene (**1h**) appears to be anomalous, with a much shorter lifetime than expected from data on the other 4′-nitroazobenzenes, this is probably due to the absence of stabilising alkyl groups on the amino nitrogen. 4-*N*,*N*-diethylamino-4′-nitroazobenzene(**1j**), which like the corresponding 4-*N*,*N*-dimethylamino derivative (**1p**) [19,20] would be expected to be planar [21–23], is the most stable dye found under these conditions with a lifetime of 6.60 h. The replacement of one hydrogen atom of the ethyl group by an hydroxyl group to give (**1i**) results in significant reduction in the photostability with a lifetime now of 4.46 h. When the nitro group is moved from the 4′-position to the 2′-position of the ring to give the isomeric 2′-nitro derivative (**1d**), the lifetime falls to 1.37 h. The introduction of other substituents into the *ortho* positions of the donor ring, which can induce non-planarity, also result in a drastic reduction in the photostability. Thus the azobenzene (**1a**) which contains a thiomethyl group at the 2-position of the donor ring, and (**1o**), which contains a methyl group at the same position of the donor ring, and cyano and bromo substituents at the 2′- and 6′-positions of the acceptor ring have comparatively short lifetimes of 1.61 and 0.89 h, respectively (Table 1).

All the azothiophene dyes (**2**) contain acceptor groups adjacent to the azo linkage, and have lifetimes of around 1.15–1.71 h, which are similar to the related azobenzenes containing a nitro group in the 2′-position of the acceptor ring. The relative instability of the azothiophenes (**2**) and the 2′-substituted azobenzenes such as (**1f**) and (**1g**) under anaerobic conditions may be attributed to differences in the

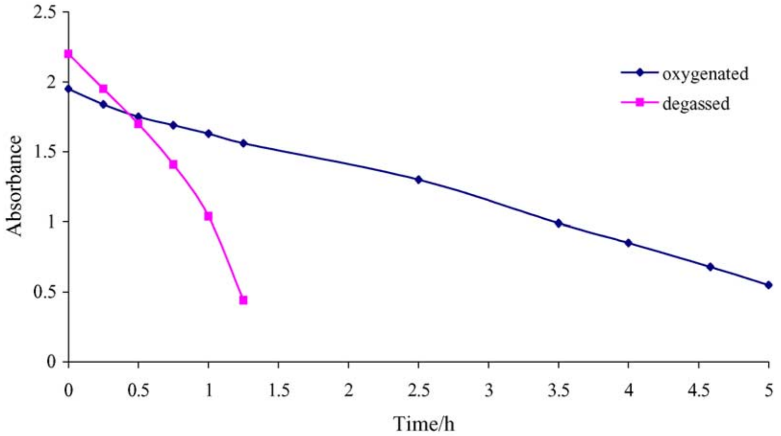


Fig. 2. The change in the absorbance of a methanol solution of azobenzene (**1d**) at its absorption maximum with irradiation time under de-aerated and oxygenated conditions.

strength of the azo bond induced by both steric [24] and electronic factors [25] (see later).

2.3. *Effect of oxygen on the rate of photofading*

Oxygen greatly retards the rate of photofading of all of the dyes studied in methanol, when the solutions are saturated with oxygen for 10 min prior to irradiation, though not all of the dyes show the same pattern of fading under oxygenated conditions. For example, the azobenzene (**1d**), fades rapidly under de-aerated conditions (argon), but the rate slows markedly in the presence of oxygen to give an approximately linear relationship between the irradiation time and the absorbance of the dye at 448 nm, with a fairly constant rate of fading which follows zero-order kinetics (Fig. 2). There is no initial induction period, and no sudden changes in the rate of fading. These factors suggest that even though oxygen slows down the photofading reaction, some photoreaction still occurs at a constant rate, resulting in the constant loss of intensity of the long wavelength absorption peak. The projected lifetime of this dye in the presence of oxygen, calculated from the straight line equation, is $\tau = 7.11$ h (Fig. 2) with a corresponding half-life of $\tau_{1/2} = 3.52$ h. Oxygenation of the solution, therefore increases the half-life and lifetime of this dye by a factor of 4.1 and 5.2 times over the values obtained under argon (Table 1).

The order of photofading for the 19 dyes in oxygenated methanol is similar to the order under de-aerated conditions, with dyes that contain the 2′-nitro substituent on the acceptor ring showing half-lives and lifetimes, which are approximately three to four times shorter than the more stable dyes containing the 4′-nitro substituent on the same ring (Table 1). Thus, the 2′-nitroazobenzenes (**1d–g**) have half-lives which range from 2.34 to 4.77 h while the corresponding 4′-nitro derivatives (**1h–i**, **1l–m**) have values which range from 10.5 to 16.5 h. The azothiophene (**2a**) is the least stable of all the dyes examined with a half-life of 1.82 h, though both the related azothiophene (**2b**) and the heavily substituted 2-acetylamino-4-diethylamino-2′-cyano-4′-nitro-6′-bromoazo-benzene (**1o**) also possess relatively short half-lives of 3.47 and 2.72 h, respectively.

While oxygen greatly retards the rate of photofading of all the dyes examined in this work, some dyes are stabilized to a greater extent than others. For example, while the lifetimes and half-lives of the nitroazobenzenes (**1a**) and (**1o**) are greatly stabilized by oxygen, those of (**1d**) and (**1e**) are not (Table 1). The least stabilized dyes are the azothiophenes (**2a**) and (**2b**), where oxygen appears to have the smallest effect on their lifetimes (Table 1).

2.4. *Nature of the excited states*

Light absorption by each of the dyes results in the initial formation of an excited singlet state and rearrangement of the electrons. Relaxation of the geometry follows quickly via a vibrational cascade to generate a relaxed singlet state (S_1R), which can then either return to its ground state by internal conversion (IC) or by fluorescence. Alternatively, the singlet state can change to an excited triplet state by intersystem crossing followed by a vibrational cascade and rearrangement of the geometry to form a relaxed triplet state (T_1R). The latter then reverts to the ground state either by intersystem crossing or by phosphorescence [26].

The excited singlet states of azobenzenes have been studied extensively by steady state spectroscopic and photochemical methods including UV–vis [27–30], and Raman [31–33] spectroscopy and also theoretical modelling [34–37]. Several studies have looked at the detailed mechanism of the *trans–cis* photoisomerisation reactions of azobenzenes, which are of current interest because of their uses in optical switching and image storage devices [38–40].

Fluorescence in simple azobenzenes appears to depend on the position of the n–π* and π–π* absorption bands. If the n–π* singlet transition is lower in energy than the π–π* singlet transition, then fluorescence may be observed. This condition holds for some sterically hindered substituted monoazobenzenes, where the very weak luminescence has been interpreted as fluorescence from the S_1R n–π* state [41,42]. However, if the n–π* transition is higher in energy than the π–π* transition then no fluorescence is observed though coupling of the n–π* and π–π* states leads to fluorescence in the case of the azo dye 4-dimethylamino-4′-nitroazobenzene (**1p**). The relative character and energy of the triplet state also determines whether or not fluorescence occurs. For example, the triplet state of 4-*N*,*N*-diethylamino-4′-methoxyazobenzene (**1q**), is n–π* in character, but that of 4-*N*,*N*-diethylamino-4′-nitroazobenzene (**1j**) is π–π* in character. The only azobenzenes that show strong fluorescence are those containing donor groups at either side of the azo linkage, such as bis-4,4′-diethylaminoazobenzene (**1r**), which fluoresces strongly in glassy MTHF solution [43].

However, for most donor–acceptor azobenzenes, such as those explored in these studies, the main deactivation of the singlet state is believed to occur by internal conversion caused by changes in geometry which bring the S_1R and ground state S_0 potential energy surfaces closer together. Less is known about the properties of the triplet states of azobenzenes as little phosphorescence is observed. For example, the lowest triplet state T_1 of azobenzene [44,45] does not phosphoresce [34], though the energy of T_1R has been estimated to lie between 35 and at 45 kcal mol^{-1} using flash kinetic spectroscopy and energy transfer from the triplet states of aromatic hydrocarbons to the triplet state of the dye [44,45]. Other estimates of the triplet energy of *trans* azobenzene have been derived from a magneto optical rotary dispersion experiment, [46] and from MO calculations [47]. The lowest triplet state T_1 of some donor acceptor azobenzenes, including (**1s–1u**), has been explored using laser flash spectroscopy and absorption and emission spectroscopy and found to lie around 40 kcal mol^{-1} above the ground state [48]. This excited state (T_1R) is implicated in the reversible isomerization of the azobenzene backbone from the *trans* conformer to the higher energy *cis* conformer [17,48].

In the results reported here, however, the first excited states of the azo dyes (1) and (2) do not appear to be directly involved in photofading as ultraviolet filters inhibit the reaction and no photodegradation is observed on laser irradiation of the first absorption band alone which might be expected to yield some of the triplet species by intersystem crossing. Furthermore, previous irradiation studies on 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene (**1j**), also in methanol, have shown that benzene and fluorene are effective triplet photosensitizers for the degradation reaction, while anthracene is wholly ineffective [17]. We have calculated [49] the second triplet state (T_2R) energy of the azobenzene (**1j**) at 62.3 kcal mol^{-1} and shown that it lies below the experimental triplet energies of benzene and fluorene at 84 and 68 kcal mol^{-1}, respectively [50], but above the experimental triplet energy of anthracene [50] at 47 kcal mol^{-1}. Our calculations also place the first triplet state [49] of (**1j**) at 28.5 kcal mol^{-1} and well below the corresponding triplet states of all three aromatics. It follows that the first triplet state is probably not implicated in the photofading reaction as anthracene would be expected to also act as a photosensitizer. That it does not act in this way, coupled with our observation that irradiation of the first absorption band produces no degradation, strongly suggests that the second triplet state is initially responsible for the photochemical degradation reaction.

2.5. Solvent effects

Previous studies on (**1j**) have shown that the rate of photofading increases in moving from methanol to propan-2-ol [17]. In these studies, a variety of different alcohols were explored to examine the effect of the length of the alkyl chain and also the effect of branching on rates of fading of azo dyes under argon using 4-(*N*-(β-hydroxyethyl)-*N*-ethyl)amino-4′-nitroazobenzene (**1i**) as a typical example.

Our results show that the rate of fading using straight chain primary alcohols increases sharply with increasing alkyl chain length of the solvent. Compared with methanol, the reaction in ethanol is around 4.6 times faster, that in butan-1-ol is 10.1 times faster, while that in heptan-1-ol is 23.5 times faster (Table 2). Secondary alcohols also facilitate the photofading reaction. The corresponding lifetime of the azobenzene (**1i**) in the secondary alcohol, propan-2-ol, is approximately seven times shorter than that in the primary alcohol, propan-1-ol. Cyclohexanol shows a similar effect. Branching of the alkyl chain seems to have little effect at positions other than the α-carbon adjacent to the hydroxy group, as the rate of fading of 2-methylpropan-1-ol and the unbranched butan-1-ol are comparable (Table 2). However, there is a dramatic change to both the lifetime and half-life of (**1i**) in moving from butan-1-ol to *t*-butanol with a 10-fold increase observed in the latter. Indeed, the lifetime and half-life of the dye in *t*-butanol are comparable to those found in methanol.

Table 2
The lifetimes and half-lives of azobenzene (**1i**) (at a concentration of 1×10^{-4} mol dm^{-3}) in different alcohols under anaerobic conditions

Solvent	Alcohol type	Lifetime (h)	Half-life (h)	Relative rate[a]
Methanol	Primary	4.46	1.12	1.00
Ethanol	Primary	0.98	0.49	4.55
Propan-1-ol	Primary	0.80	0.40	5.58
2-Methylpropan-1-ol	Primary	0.58	0.29	7.69
Butan-1-ol	Primary	0.44	0.22	10.1
Heptan-1-ol	Primary	0.19	0.10	23.5
Propan-2-ol	Secondary	0.11	0.06	40.5
Cyclohexanol	Secondary	0.22	0.11	20.2
t-Butanol	Tertiary	4.73	2.36	0.94

[a] Relative rate based on the lifetime data and relative to methanol.

2.6. Mechanism of the photofading reaction

2.6.1. Anaerobic conditions

The triplet states of polar organic molecules are well known to react with hydroxylic solvents and abstract hydrogen. For example, the triplet state of benzophenone readily abstracts hydrogen from propan-2-ol to form a ketyl radical (Eq. (1)) which can either dimerize to form benzpinacol (Eq. (2)) or abstract another hydrogen atom from the solvent to form benzhydrol (Eq. (3)) [51].

$$[\mathrm{Ph_2C{=}O}]^{3*} + \mathrm{CMe_3OH} \rightarrow [\mathrm{Ph_2COH}]^{\bullet} + {}^{\bullet}\mathrm{CMe_2OH} \qquad (1)$$

$$[\mathrm{Ph_2COH}]^{\bullet} \rightarrow [\mathrm{Ph_2COH}]_2 \qquad (2)$$

$$[\mathrm{Ph_2COH}]^{\bullet} + \mathrm{CMe_3OH} \rightarrow [\mathrm{Ph_2CHOH}] + {}^{\bullet}\mathrm{CMe_2OH} \qquad (3)$$

The initial hydrogen transfer reaction is facilitated because the unpaired electron on the resulting benzohydryl radical is stabilized by resonance with the two phenyl rings.

The observation that triplet sensitizers promote the photodegradation reaction of 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene (**1j**) [17] coupled with the isolation of the corresponding hydrazobenzene as an intermediate product upon irradiation in methanol in the absence of air [17] suggests that azobenzenes behave in a similar way to benzophenone in Eqs. (1) and (3). Further photodegradation of (**1j**) eventually results in the formation of 4-(*N*,*N*-diethylamino)aniline and 4-nitroaniline [17]. A similar result is obtained on irradiation of the second absorption band of 4-diethylamino-4′-methoxyazobenzene (**1q**) at 254 nm to give the corresponding hydrazobenzene [52], but irradiation of the first absorption band at 434 nm results only in reversible *trans*–*cis* isomerization [52].

It is thought therefore that the triplet states of the azo dyes (**1**) and (**2**) react in a similar way to benzophenone and abstract hydrogen from the solvent to form less coloured hydrazo radicals and hydroxymethyl radicals. However, because the azo dyes are unsymmetrical, two radicals are possible (where, R^1 and R^2 are the donor and acceptor rings, respectively).

$$[R^1\text{–N=N–}R^2]^{3*} + CH_3OH \rightarrow R^1\text{–NH–N}^{\bullet}\text{–}R^2 + {}^{\bullet}CH_2OH \tag{4a}$$

$$[R^1\text{–N=N–}R^2]^{3*} + CH_3OH \rightarrow R^1\text{–N}^{\bullet}\text{–NH–}R^2 + {}^{\bullet}CH_2OH \tag{4b}$$

Both reactions are facilitated because the unpaired electrons on the azo nitrogens are stabilized by resonance with the two phenyl rings in a similar way to the benzhydryl radical discussed above. However, the first reaction is likely to be more favoured (Eq. (4a)) as the resulting radical is better stabilized by resonance with the phenyl ring containing electron attracting groups. Once formed, the hydrazo radicals would be expected to further abstract hydrogen from the solvent to form the hydrazobenzenes which have been identified for (**1j**) and (**1q**).

$$R^1\text{–NH–N}^{\bullet}\text{–}R^2 + CH_3OH \rightarrow R^1\text{–NH–NH–}R^2 + {}^{\bullet}CH_2OH \tag{5}$$

The differences found for the rate of photofading of (**1i**) in the various alcohols is compatible with the mechanisms shown above with the fastest reactions expected and found in those alcohols, which have the easiest abstractable hydrogen atoms. These processes (Eqs. (4–5)) will be affected by the strength of the C–H bond of the alcohol and also by the stability of the radical formed after abstraction of hydrogen. The more alkyl groups attached to the α-carbon radical centre the greater the stability arising from their inductive or hyperconjugative effect. For example, methanol has no alkyl groups to stabilize the resulting radical after abstraction (Eqs. (4a) and (4b)), whereas ethanol has one methyl group, and propan-2-ol has two. Consequently, the rate of photofading appears to be related to the radical stability as the relative rates of photofading for the three alcohols are 1.00:4.55:40.5, respectively (Table 2), or if the number of available abstractable hydrogens at the α-carbon are considered, the relative rates are 1:9.10:122. However, the rate of photofading increases with the increasing length of the alkyl chain connected to the α-carbon. Thus, the relative rates increases along the sequence ethanol (4.55) < propan-1-ol (5.58) < butan-1-ol (10.1) < heptan-1-ol (23.5), suggesting that the alkyl groups are stabilizing the α-carbon radical by an inductive effect rather than a hyperconjugative effect which would be expected to operate in the reverse order. In contrast to the other alcohols studied, the rate of fading of the dye in *t*-butanol is relatively slow but comparable to that in methanol (Table 2). There are no hydrogens available on the α-carbon in *t*-butanol, and consequently only radicals involving the β-carbon can be formed in this case. That this alcohol also facilitates the photofading reaction suggests that the increased rates observed for the long chain alcohols may also arise from the formation of radicals at centres other than the α-carbon.

2.6.2. Aerobic conditions

The observation that oxygen, which is a triplet in its ground state, retards the rate of photofading suggests that it quenches the excited triplet state of the azo dye to form the ground state (S_0) and generates singlet oxygen, i.e.

$$[R^1\text{–N=N–}R^2]^{3*} + {O_2}^3 \rightarrow R^1\text{–N=N–}R^2 + {O_2}^1 \tag{6}$$

Pietra et al. have argued that because of the short lifetime of the second triplet state and the low concentration of oxygen, this process is unlikely to compete with the reaction of the triplet state with the solvent, which is present in large excess [17]. Furthermore, their results imply that the retarding effect of oxygen on the photofading may be due in part to oxidation of the hydrazobenzene formed and regeneration of the original azobenzene [17,52]. However, the solubility of oxygen saturated methanol has been reported recently [53] as 0.95×10^{-2} mol dm^{-3}, which is almost 100 times larger than the concentration of azo dyes used in our studies at 1×10^{-4} mol dm^{-3}. This data suggests therefore that there is sufficient oxygen available in solution to quench the excited triplet state of the molecule in line with Eq. (6). Confusingly, other studies [54,55] on the photolysis of 4-dimethylamino-2′,4′-dinitroazobenzene (**1w**) in aerated 2-propanol have shown that that the azo linkage is oxidised under these conditions to give 4-dimethylamino-2′,4′-dinitro-ONN-azoxybenzene. The same compound is obtained, when the azobenzene (**1w**) is heated with hydrogen peroxide [54]. Similar results are obtained from the photochemical and thermal reactions of 4-dimethylamino-4′-dinitroazobenzene (**1p**) [54]. These results mainly on heavily substituted azobenzenes suggest that the singlet oxygen generated by Eq. (6) or from the decomposition of hydrogen peroxide possibly reacts with the ground state of the respective dye to form the azoxybenzenes.

2.7. Effect of radical scavengers and generators

The photofading reaction of 4-(*N*-(β-hydroxyethyl)-*N*-ethyl)amino-4′-nitroazobenzene (**1i**) is also inhibited in methanol (at a concentration of 1×10^{-4} mol dm^{-3}) by radical scavengers such as 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO), 1,4-diazabicyclo[2,2,2]octane (DABCO) and 2,6-di(*t*-butyl)phenol (TBP). For example, the presence of TEMPO (at a concentration of 1000×10^{-4} mol dm^{-3}) increases the half-life of the photofading reaction of the dye in methanol alone from 1.12 to 4.12 h, to give a relative rate of 0.27 (Table 3), but this effect is not as large as the effect of oxygen which

Table 3
The half-lives ($\tau_{1/2}$) of the azo dyes (**1i**), (**1d**) and (**2a**) in methanol (at a concentration of 1×10^{-4} mol dm^{-3}) in the presence of ketones and TEMPO under anaerobic conditions

Azo dye	Ketone	Concentration (mol dm^{-3})	TEMPO[a] (mol dm^{-3})	$\tau_{1/2}$ (h)	Relative rate[b]
1i	None		None	1.120	1.00
1i	None		0.10	4.120	0.27
1i	Benzophenone	10×10^{-5}	None	0.001	1120
1i	Acetone	3.4×10^{-6}	None	0.007	160.0
1i	Acetone	6.8×10^{-5}	None	0.002	560.0
1i	Acetone	6.8×10^{-5}	0.10	3.550	0.32
1d	None		None	0.870	1.00
1d	Acetone	3.4×10^{-6}	None	0.022	39.5
1d	Acetone	3.4×10^{-6}	0.10	0.830	1.05
2a	None		None	0.700	1.00
2a	Acetone	3.4×10^{-6}	None	0.014	50.0
2a	Acetone	3.4×10^{-6}	0.10	0.400	1.75

[a] TEMPO is 2,2,6,6-tetramethyl-1-piperidinyloxy free radical.
[b] Relative rate refers to the rate of photofading in the absence of both sensitizer and scavenger.

increases the half-life to 12.7 h (Table 1). A similar effect has been reported for (**1j**), where the addition of 3,3,4,4-tetramethyl-diazetine 1,2-dioxide, a known triplet quencher, and 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxide, a well known radical trap, both inhibit the reaction [17].

The radical scavenger is thought to act by reacting with the intermediate hydrazo radicals formed by the processes shown in Eqs. (4a) and (4b). However, if the rate of photofading or loss of colour is due simply to the formation and reaction of hydrazo radicals alone then the scavenger would exert little influence as it would simply trap the less coloured radicals already formed. The four-fold increase in lifetime found for the azobenzene in the presence of TEMPO under anaerobic conditions strongly suggests that it is preventing other radical reactions from occurring. In the photolysis of benzophenone, the triplet state of the ketone abstracts hydrogen from propan-2-ol (Eq. (1)) and dimerizes (Eq. (2)) [51]. However, the quantum yield for the disappearance of benzophenone is found to be around 2 under favourable conditions [51], which has been attributed to a further reaction between the isopropyl radical formed initially (Eq. (1)) and a molecule of ground state benzophenone to produce acetone and another benzhydrol radical which subsequently dimerizes (Eq. (7)) [51].

$$\mathrm{Ph_2C{=}O} + {}^{\bullet}\mathrm{CMe_2OH} \rightarrow [\mathrm{Ph_2COH}]^{\bullet} + \mathrm{Me_2C{=}O} \qquad (7)$$

By analogy, it is possible that the more reactive hydroxymethyl radical generated by the processes shown in Eqs. (4a), (4b) and (5), behaves in a similar way, and reacts with a molecule of the ground state azobenzene (**1i**) to lose hydrogen and form formaldehyde and the hydrazobenzene radical (Eq. (8)). The corresponding but faster reaction in propan-2-ol (Table 2) would generate acetone as a by-product in line with Eq. (7).

$$\mathrm{R^1{-}N{=}N{-}R^2} + {}^{\bullet}\mathrm{CH_2OH} \rightarrow \mathrm{R^1{-}NH{-}N^{\bullet}{-}R^2} + \mathrm{CH_2O} \qquad (8)$$

It follows that the initial reaction of the azobenzene triplet leads to the formation of two hydroxymethyl radicals (Eqs. (4a), (4b) and (5) which can react further and may result in the loss of colour of up to three dye molecules by the secondary reaction shown above (Eq. (8)). The efficacy of TEMPO in increasing the lifetime of the dye may therefore be due to its ability to effectively trap the hydroxymethyl radicals formed in Eqs. (4a), (4b) and (5).

The addition of photochemical radical generators such as acetone and benzophenone, which are known to generate radicals under the reaction conditions (Eq. (9)) have the opposite effect on the rate of photodegradation. For example, the addition of acetone, at a concentration ranging from 3.4 to 6.8×10^{-5} mol dm^{-3}, to a solution of the dye (**1i**) in methanol under anaerobic conditions, increases the rate of photofading by 160–560 relative to the reaction in its absence (Table 3). Benzophenone shows an even greater effect on the rate of photofading at around the same concentration (10×10^{-5}mol dm^{-3}) with a rate increase here of 1120 (Table 3).

$$[\mathrm{R_2C{=}O}]^{3*} + \mathrm{CH_3OH} \rightarrow [\mathrm{R_2COH}]^{\bullet} + {}^{\bullet}\mathrm{CH_2OH} \qquad (9)$$

If the free radical TEMPO functions by trapping the hydroxymethyl radicals generated in Eqs. (4a), (4b) and (5), it would also be expected to exert a strong effect on the acetone sensitized reactions also. The experimental results are fully supportive with the relative rate of photofading falling from 560 in the presence of acetone alone to 0.32, when TEMPO is added. As the latter rate is comparable to that found for the photolysis in the presence of TEMPO and absence of acetone at 0.27, it suggests that the scavenger is highly effective at trapping almost all the hydroxymethyl radicals in solution.

Similar effects are found in the photosensitized fading reactions of 4-(*N*-(β-hydroxyethyl)-*N*-ethyl)amino-2′-nitroazobenzene (**1d**) and 2-(4-*N*,*N*-bis(β-acetoxyethyl)aminophenylazo-3,5-dinitro-thiophene (**2a**), where acetone at a concentration of 3.4×10^{-6}mol dm^{-3} increases their rates of photofading by 39.5 and 50.0, respectively, relative to the non-sensitized reactions (Table 3). In both cases, the addition of TEMPO nullifies the effect of the ketone and gives rates, which are comparable to those found in the absence of acetone (Table 3). The smaller rate enhancement found for the photosensitized reaction in these two cases versus the corresponding reactions of (**1i**) is possibly a reflection of the steric effect of a nitro group present on the phenyl or thiophene ring, which may prevent the nearby azo nitrogen atom from abstracting a hydrogen atom from the solvent (Eq. (4b)).

The alternative possibility that acetone (and benzophenone) photosensitize the photofading reactions by energy transfer from the excited triplet state of the ketone to the ground state of the azo dyes (in the same way as benzene and fluorene discussed earlier), can be discounted. First of all, as the concentration of the ketone is much smaller than that of the azo dye (Table 3), the concentration of the ketone triplet state is even smaller. Secondly, the lifetime of the ketone triplet state is known to be very short in alcohols because of the facile abstraction reaction [51] (Eqs. (1) and (9)). It follows that energy transfer by a spin allowed collision process is unlikely to compete at all with the abstraction reaction.

2.8. *Structural effects on the photochemical stability*

It is well established that good lightfastness in azobenzenes results from a combination of an electron donor in one ring, such as a 4-dialkylamino group and an electron acceptor, such as a 4′-nitro or 2′- and/or 4′-cyano group, in the other [9,24,25,56–58]. However, the very poor lightfastness found for the corresponding 2′-nitro derivatives has been attributed to steric interactions between the substituent and the adjacent azo nitrogen [24,58]. Improved lightfastness results, when electron attracting groups are attached to one or both alkyl chains of the dialkylamino group of 4,4′-disubstituted derivatives which reduce the amino nitrogen basicity [5]. Related studies have shown a linear relationship between the inductive effect of substituents, attached to the alkylamino nitrogen, and the fading rate [59].

The results found here for the 2′-nitro derivatives (**1b**) and (**1d–g**) reflect the expected experimental trends for lightfastness with all showing a low photochemical stability relative to the corresponding 4-nitro derivatives (Table 1). The explanation for this behaviour is almost certainly attributable to structural and electronic differences between the isomers. We have previously discussed the differences between the calculated and experimentally derived structures and spectra of 4-dialkylamino-4′-nitroazobenzenes which are planar, and 4-dialkylamino-2′-nitroazobenzenes, which are not [19]. The evidence available suggests that not only is the nitro group twisted relative to the aromatic ring, but also that the acceptor ring itself may be twisted relative to the plane of the other phenylazo component. For example, in the crystal structure of 4-(*N*,*N*-di-(β-hydroxyethyl)amino)-2′-nitroazobenzene (**1v**), the acceptor ring is twisted by 44.5° relative to the plane of the phenylazo group and the nitro group is twisted by a further 27.6° relative to the plane of the acceptor ring [19]. In solution these torsion angles may be less pronounced, but nonetheless, the molecule is essentially non-planar because of the large electronic and repulsive interaction between the lone pair of electrons residing on one of the oxygen atoms of the nitro group, and those residing on the nearby nitrogen atom of the azo linkage.

We have carried out spectroscopic calculations of the electron spin densities at the AM1/MECI level in methanol on the triplet state of the 2′-nitro derivatives (**1d–g**) and the azothiophene (2**a**) and showed that the two unpaired electrons are heavily localized on the azo nitrogen bridge [49]. Consequently, the biradical can readily abstract a hydrogen atom from the solvent in the way shown in Eqs. (4a) and (4b). In contrast, in the 4′-nitro derivatives (**1h–k**), the distribution of the two unpaired electrons at the azo nitrogen is much

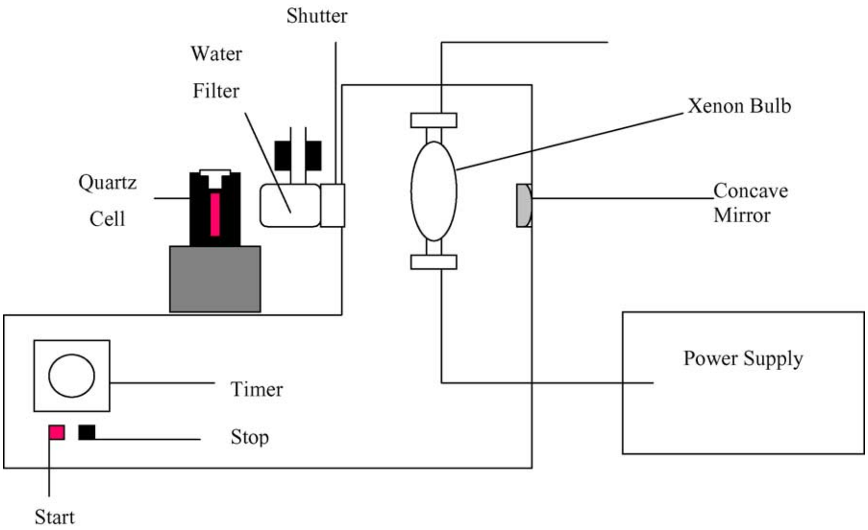


Fig. 3. Diagrammatic representation of the 1000 W xenon arc lamp apparatus for the photofading of dye solutions in a quartz spectrophotometric cuvette.

reduced and spread more uniformly over all of the heavy atoms in both rings [49]. These results help to explain why the 2′-nitro derivatives show a much higher photochemical reactivity than the more stable 4′-nitro derivatives. However, the enhanced photochemical stability of 4-diethylamino-4-nitroazobenzene (**1j**) over related derivatives containing hydroxyethyl groups at nitrogen such as (**1i**) and (**1m**), or one cyanoethyl group at nitrogen such as (**1l**), is more difficult to explain as experimental evidence from lightfastness studies suggests the opposite [5]. One possible explanation is that the polar groups are able to bind the azo dye more firmly to the heterogeneous substrate and stabilize it in a rigid conformation.

3. Experimental

The spectra of all the dyes were recorded at room temperature on a Perkin-Elmer Lambda 19 Spectrophotometer in quartz cuvettes with a 10 mm pathlength. Kinetic experiments on the photofading process were also carried out at room temperature (25°) in the same spectrophotometer quartz cuvettes, which were made air tight with a teflon stopper. The methanol solutions of the dyes (concentration $1 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) were photofaded using the 1000 W xenon arc lamp arrangement shown in Fig. 3. The lamp consisted of a 1000 W bulb obtained from Oriel [60] housed in a steel casing which was fan cooled. To maximize the output of the lamp, a concave rear reflector mirror was used to focus the light through an opening, which was 30 mm × 20 mm in size. The bulb was aligned to allow a maximum output of light through the opening. A shutter, which is either open or shut, controlled the light allowed out of the lamp housing. This shutter was linked to timer so the exposure time of the sample to irradiation was controlled. The minimum exposure time allowed by the timer was 1 s.

A water filter was placed in front of the opening so that the infrared emission from the Xe lamp was absorbed to prevent heating of the dye solution. The sample, contained in the quartz cell was then placed directly in line with the opening to allow maximum exposure to irradiation. De-aerated solutions of the dyes in a quartz cell faded quickly, with complete loss of colour in less than 2 h for (**1d**).

Laser irradiation of samples were performed using a coherent air-cooled continuous wave argon ion laser emitting at 514.5 nm with a 1 mm beam width and an operating power of 15 mW (BS Industries, Columbus, OH).

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