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The Role of Azo–Hydrazone Tautomerism in the Photofading of 1-Phenylazo-4-naphthol in Polymer Substrates

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SUMMARY

The photofading of 1-phenylazo-4-naphthol has been studied in films of cellulose acetate and cellulose triacetate. The relative rates of fading of the azo and hydrazone tautomers were monitored by resolving the visible absorbance spectrum of the dye into two overlapping bands corresponding to each tautomer. Permanent photofading of 1-phenylazo-4-naphthol was found to be due to oxidative attack on the ground state hydrazone tautomer of the dye by singlet excited oxygen. The lowest excited triplet state of the hydrazone tautomer was responsible for sensitizing singlet oxygen. The azo tautomer was resistant to permanent photofading, but its concentration was depleted during irradiation while it temporarily existed in the hydrazone form. As well as thermal tautomeric interchange, tautomeric conversion following trans → cis isomerization of the azo tautomer could have been responsible for this temporary existence. Relative fading rates were influenced by the nature of the polymer concerned, and the method used to incorporate the dye. Temporary fading occurred as a result of isomeric and conformational changes in each tautomer.

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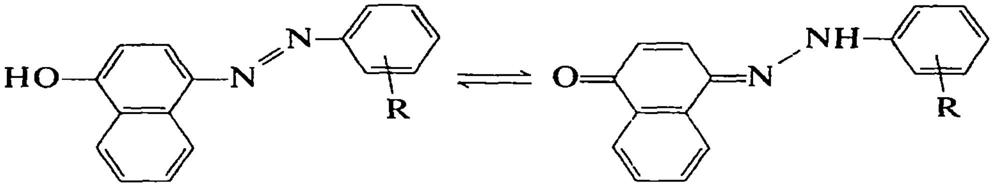
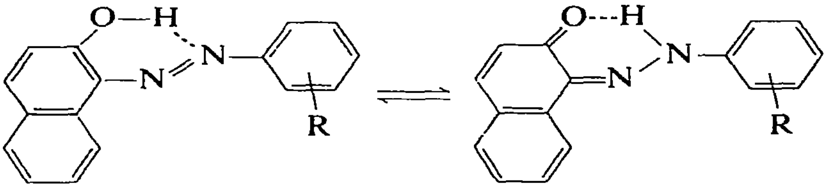
1. INTRODUCTION

The importance of azo dyes as commercial colorants has meant that extensive studies of their photofading behaviour have been made.[1-6] However, the role played by azo–hydrazone tautomerism[7] (see **I** and **II**) remains a point of conjecture.



I 4-Phenylazo-1-naphthol



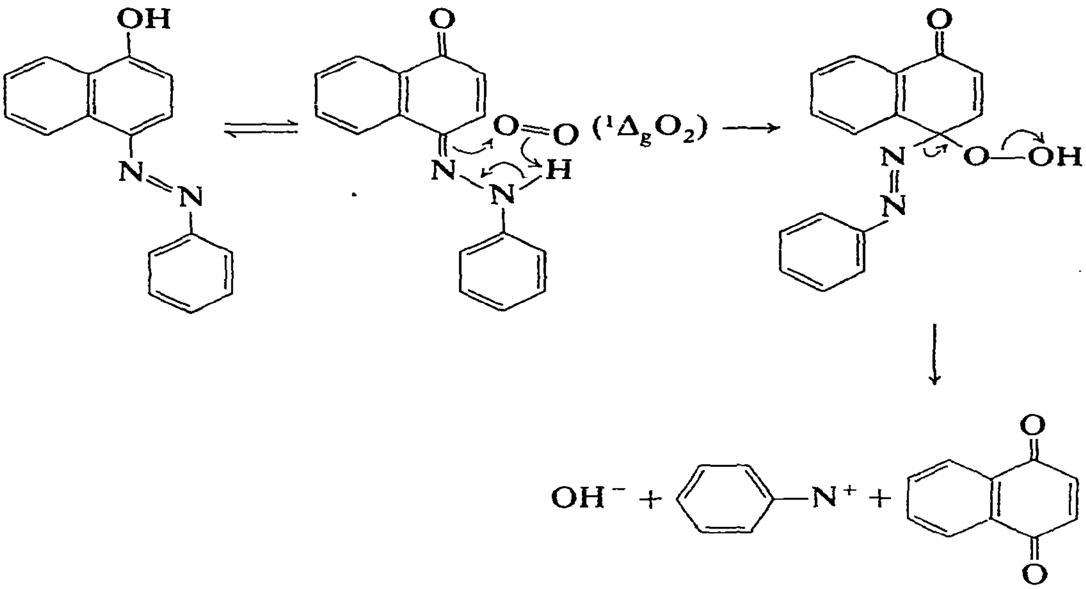
II 1-Phenylazo-2-naphthol

Studies by a variety of workers have shown singlet oxygen to be capable of decolorizing solutions of tautomeric hydroxyazo dyes. Griffiths and Hawkins[8-10] first proposed a mechanism involving attack of the hydrazone such as that shown in Scheme 1.

Subsequently, other groups who have examined the photofading of hydroxyazo dyes in solution have reported corroborative findings,[11-14] although other possible reactions have been proposed (e.g. ref. 15).

Studies of hydroxyazo dye fading in polymer substrates have noted degradation of the dye via the singlet oxygen mechanism (Scheme 1) in some cases,[16] but other reactions, possibly free radical, have also been observed.[17,18] Incorporating singlet oxygen quenching groups (*N*,*N*-dialkylaminomethyl-) within the chromophore of derivatives of **II** actually increased their fading susceptibility in polypropylene and polyester films by giving rise to favourable free radical degradation pathways.[19]

Derivatives of **II** were found by Mallet and Newbold[20] to fade reductively when incorporated in polypropylene and irradiated under



Scheme 1. Reaction of hydrazone tautomer of **I** with singlet excited oxygen.

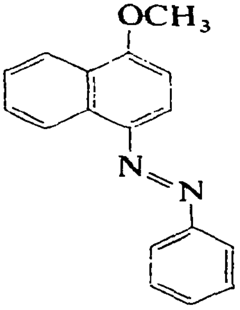
nitrogen. As substituents increased the concentration of hydrazone tautomer, the relative fading rate was seen to rise in proportion. Thus photoreduction of the hydrazone form was indicated. When the experiment was repeated under oxygen, the correlation between relative fading rate and the azo–hydrazone ratio was lost. Dual competing oxidative and reductive fading mechanisms were probably responsible. Dyes of general structure **I** (R = *para*-substituent) incorporated in polyamide film also exhibited fading characteristics that depended on the state of the tautomeric equilibrium.[21] For derivatives of **I** in which the spectral band overlap of the two tautomers was said to be small (i.e. **I**, R = p-OCH_3, p-CH_3, H) fading rates of each of the tautomers present could be evaluated. Under Xenotest irradiation of the dyed nylon films, it was found that the azo tautomers faded oxidatively while the hydrazone tautomers were photoreduced.[21] The fading of dyes ***II*** in polyamide film was also consistent with photoreduction of the hydrazone tautomer, but considerable overlap of the azo and hydrazone bands prevented information regarding fading of the azo tautomer from being obtained.[21]

This report describes an examination of the photofading of 1-phenylazo-4-naphthol, **I** (R = H), in cellulose acetate and triacetate polymer films. An assessment has been made of the relative susceptibilities of each tautomer to photofading and the way in which the polymer substrates inhibit free tautomeric exchange.

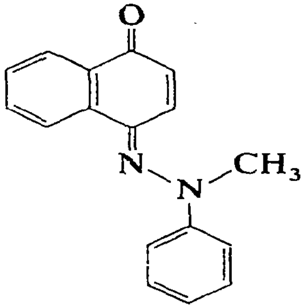
2. EXPERIMENTAL

2.1. Dyes

1-Phenylazo-4-naphthol, **I**(R = H), was synthesized by coupling benzene diazonium chloride with 1-naphthol. The *O*-methyl ether, **III**, was prepared by treating a methanolic solution of **I**(R = H) with a solution of diazomethane in ether. Compound **IV** was synthesized by reducing *N*-nitroso-*N*-methylaniline to *N*,*N*-methylphenylhydrazine according to Enders,[22] then condensing with 1,4-naphthoquinone.[23] In each case, preparative column chromatography using silica gel and methylene chloride as eluent was used to purify the dyes.



III



IV

2.2. Polymers

Purum grade cellulose acetate and cellulose triacetate were supplied in the form of small flakes by Fluka AG. Dyed films were made by dissolving the polymers (0·9 g) and the required amounts of dye and other additives in a suitable solvent. Chloroform (50 g) was used for cellulose triacetate films, and acetone (30 g) for cellulose acetate. The solutions were then poured on to level glass plates 145 mm square and allowed to dry.

Disperse-dyed cellulose triacetate films were prepared by immersing blank films in an aqueous dye suspension. The suspension was formed by adding a few millilitres of a solution of dye in acetone to 400 ml of water then boiling off excess acetone (indicated by boiling point >99 °C). Dyeing was continued at the boil until an absorbance of approximately 0·3 was obtained. The dyed films were thoroughly rinsed in cold aqueous ethanol (50/50 v/v). Cellulose acetate films were dyed in the same way, but the dyebath temperature was restricted to 70 °C.

2.3. Irradiation by 310 nm light

A sample 9·5 × 50 mm^2, cut from the required film, was placed inside a quartz tube, supported vertically in the centre of an Oliphant irradiation chamber and connected to a gas supply (oxygen or pure nitrogen) via a heat exchanger. A slurry of ice in acetone was placed around the heat exchanger and the gas flow rate adjusted to a value of 2–3 litre min^{-1} so that the temperature of the film sample in the tube was 20 ± 2 °C, as measured by a thermocouple. The 25 cm diameter Oliphant irradiation chamber contained 16 vertically mounted 8 W fluorescent tubes (Oliphant FL & E and Clemco 9008) with a maximum intensity at 310 nm.

2.4. Absorbance measurement

The film sample being studied was rinsed for 10–15 s in cold demineralized water, then placed in a water-filled 1·0 mm quartz cell for measurement on a Cary model 210 double beam recording spectrophotometer. The water treatment was necessary for two reasons. Firstly, it eliminated the optical interface between the polymer film and the air and thereby prevented an interface pattern being superimposed on the recorded spectra. Secondly, it caused temporary fading effects to revert quickly, thus ensuring that only permanent fading was observed. After absorbance measurement, excess surface moisture was removed with a clean dry tissue, then the film was thoroughly dried by placing it under a dry gas stream in the dark for at least 20 min. This gas was the same as that used during irradiation. Wetting the films caused slight spectral alterations, but these were fully reversible for up to 15 wet–dry cycles carried out in the dark. Thus the low temperature conditions and the brief duration of immersion did not allow dye molecules in the polymer to migrate to new locations which might have altered their tautomeric structure.

For the non-tautomeric dyes **III** and **IV**, only the absorbance at the wavelength of maximum absorbance was measured. Because of reversible fading of **III** which did not fully revert within 15 s of immersion in water, films containing this dye were stored for 16–24 h in the dark before absorbance measurements. For the tautomeric dye **I**(R = H), the full visible absorption spectrum was recorded and the underlying band maxima found by spectral curve resolution.

2.5. Spectral curve resolution

The visible absorption spectrum of **I**(R = H) was modelled by a linear combination of the spectra of the methylated derivatives **III** and **IV**. A program[24] was used in a Hewlett-Packard 41C calculator with peripheral printer to perform the spectral resolution. The program aimed to find the regression coefficients a, b and c in eqn (1) by solving the linear equations in eqn (2).

$$t = a + bx + cy \tag{1}$$

$$\begin{bmatrix} n & \Sigma x_i & \Sigma y_i \\ \Sigma x_i & \Sigma(x_i)^2 & \Sigma(x_i y_i) \\ \Sigma y_i & \Sigma(y_i x_i) & \Sigma(y_i)^2 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} \Sigma t_i \\ \Sigma x_i t_i \\ \Sigma y_i t_i \end{bmatrix} \tag{2}$$

where t = absorbance of **I**(R = H) at λ_i; x = absorbance of **III** at λ_i; y = absorbance of **IV** at λ_i; n = number of data points = i_{max}.

To perform the regression, absorbance values for the tautomeric dye **I**(R = H) and the methylated compounds **III** and **IV** were recorded under identical conditions at 10 nm intervals between approximately 400 and 500 nm. This wavelength range was chosen because it includes each of the band maxima, but is sufficiently short to subdue any band narrowing or widening effects which may have been operating. The spectra of the representative methylated compounds were normalized to an absorbance maximum of 1·000. The spectra of the methylated compounds had to be manually red-shifted before the regression yielded a good agreement between predicted and experimentally determined absorbances. The hypsochromic absorbances of the methylated compounds relative to the azo and hydrazone tautomers of **I**(R = H) which they were representing could have been due to steric crowding caused by reduced molecular planarity. In addition, hydrogen bonding to the substrate polymer by the azo and hydrazone tautomers of **I**(R = H) would increase the donor strength of the —OH and —NH groups respectively and thereby result in a slight bathochromic shift. The unnecessary regression coefficient a in eqn (1) was effectively removed by forcing the regression through zero. In this way, spectra of **I**(R = H) in cellulose acetate and cellulose triacetate were resolved into two overlapping absorption bands corresponding to the azo and hydrazone tautomers as shown in Figs. 1 and 2.

2.6. Measurement of fading rates

The relative rates of fading of the dyes were determined by measuring the initial film absorbance, then conditioning the film to the temperature and atmosphere of the irradiation chamber and irradiating for a known time interval. The absorbance was then recorded and the procedure repeated. Each sample was subjected to 7–10 irradiation periods of 5–20 min duration, depending on how rapidly fading occurred. The measured absorbances were converted to values of the proportion of dye remaining and these values were then plotted as $\log_e$ (percentage of dye remaining) versus time. Apparent first-order kinetics were indicated by the linearity of these plots. The relative fading rates were determined as the gradient of the semi-logarithmic plots as calculated by linear regression.

2.7. Selective irradiation

To excite selectively the azo and hydrazone tautomers of **I**(R = H) and the singlet oxygen sensitizer, Methylene Blue, the polymer films were

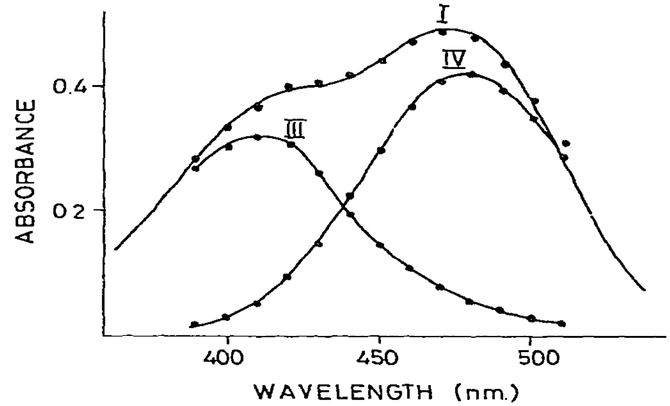


Fig. 1. Absorption band resolution of **I**(R = H) in cellulose acetate film: ——, Measured absorption curve; ●, predicted absorbance values. Curve III, optimized azo absorbance (8 nm red shift); IV, optimized hydrazo absorbance (14 nm red shift).

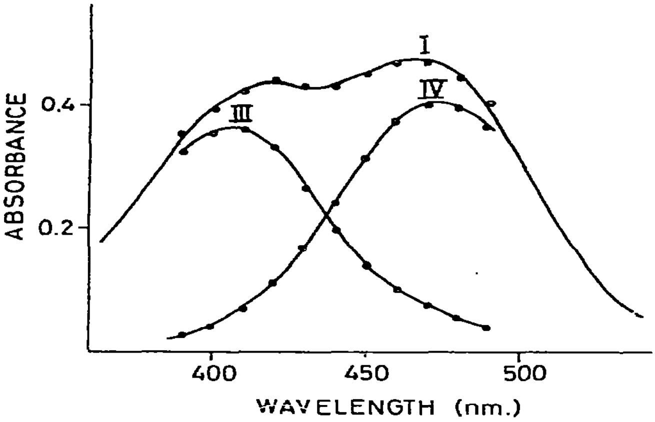


Fig. 2. Absorption band resolution of I(R = H) in cellulose triacetate film: ——, Measured absorption curve; ●, predicted absorbance values. Curve III, optimized azo absorbance (6 nm red shift); IV, optimized hydrazo absorbance (14 nm red shift).

irradiated by narrow radiation bands, with bandwidths less than 40 nm at half peak height, obtained by passing light from a 150 W high-pressure xenon lamp through a Bausch and Lomb grating monochromator.

In order to observe temporary fading, both irradiation and measurement were performed on films conditioned to the laboratory atmosphere.

3. RESULTS AND DISCUSSIONS

3.1. Dye fading under 310 nm irradiation

By irradiating polymer films containing I(R = H) ($1{\cdot}2 \times 10^{-5}$ mol per g of polymer), the relative fading rate constants shown in Table 1 were obtained. Statistically significant differences between the azo and hydrazone fading rates were found, except for irradiations carried out in a nitrogen atmosphere, and for cellulose triacetate dyed by casting from a common solvent and irradiated in air.

The most salient feature of these fading rates is that oxygen is an essential intermediate. Further experiments demonstrated that singlet excited oxygen appears to be the species responsible. In dyed cellulose triacetate films containing 1,4-diazabicyclo(2.2.2)octane ($2{\cdot}4 \times 10^{-5}$ mol per g of polymer), a known singlet oxygen quencher,[25] the relative fading

TABLE 1
Relative Fading Rate Constants (Apparent First Order) for 1-Phenylazo-4-naphthol ($1{\cdot}2 \times 10^{-5}$ mol per g Polymer) in Polymer Films

	Cast from common solvent				*Disperse dyed*	
	Nitrogen		*Air*		*Air*	
	Azo	*Hydrazone*	*Azo*	*Hydrazone*	*Azo*	*Hydrazone*
Cellulose acetate	$< 1{\cdot}0$	$< 1{\cdot}0$	15·3	18·4	19·4	25·3
Cellulose triacetate	$< 1{\cdot}0$	$< 1{\cdot}0$	28·5	28·6	33·7	39·2
Cellulose triacetate + DCO[a]	—	—	6·0	6·0	—	—
Cellulose triacetate + MB[b]	$< 1{\cdot}0$	$< 1{\cdot}0$	123	123	—	—

[a] DCO, 1,4-diazabicyclo(2.2.2)octane ($2{\cdot}4 \times 10^{-5}$ mol per g polymer).
[b] MB, Methylene Blue ($5{\cdot}6 \times 10^{-7}$ mol per g polymer).

rate constant of each tautomer of I(R = H) decreased from 28·6 to 6·0. On the other hand, incorporating Methylene Blue ($5{\cdot}6 \times 10^{-7}$ mol per g of polymer), an efficient sensitizer of singlet oxygen, increased the relative fading rate constant of each tautomer of I(R = H) in cellulose triacetate to 123. It has been reported[6,15] that Methylene Blue is able to play an active role in the fading of hydroxyazo dyes, rather than the passive role of merely sensitizing the formation of singlet oxygen. However, such free radical modes of decomposition should still be observable in the absence of oxygen. When cellulose triacetate films containing I(R = H) and Methylene Blue were irradiated under a nitrogen atmosphere, no fading occurred. Thus Methylene Blue was acting solely as a sensitizer of singlet excited oxygen in these experiments.

Another feature of the fading characteristics of I(R = H) which supports the intermediacy of singlet oxygen is the more rapid fading rates found in cellulose triacetate than in cellulose acetate. This is in spite of the fact that the former polymer is regarded as having a more ordered structure than the latter, thereby restricting oxygen diffusion. The explanation may be that the greater number of hydroxyl groups in cellulose acetate shortens the lifetime of singlet oxygen in that polymer. The lifetime of singlet oxygen is reduced when it is incorporated in solvents which contain hydroxyl groups. This is attributed to the efficiency of electronic energy transfer to the vibrational energy levels of the O—H moiety.[26] For example, the lifetime of singlet oxygen is reported to be $(19 \pm 3) \times 10^{-6}$ s in ethanol and $(47 \pm 15) \times 10^{-6}$ s in ethyl acetate.[27] Thus it is likely that a similar effect reduces the lifetime of singlet oxygen in cellulose acetate relative to cellulose triacetate.

Another important feature of the results given in Table 1 is the dependence of the degradation rate on the method of incorporation of the dye **I**(R = H) in the polymer. For both cellulose acetate and triacetate, more rapid degradation of **I**(R = H) was observed if the dye has been applied by disperse dyeing rather than casting from a common solvent. The increased degradation rate obtained for the disperse dyed films is to be expected if oxygen is an active intermediate. This is because a certain proportion of dye incorporated by casting from a common solvent is likely to be accommodated in voids which are surrounded by ordered regions that protect the dye by retarding the diffusion of oxygen. For the disperse dyed films, all the dye molecules must enter the polymer via pores. The much smaller oxygen molecules would also be able to diffuse through these pores unless the depth of dyeing were so great that large aggregates of dye built up and blocked them. At the depths of dyeing employed in this study (maximum absorbance of approximately 0·3), significant aggregation was extremely unlikely.

3.2. Selective excitation of the azo tautomer

For the azo tautomer of **I**(R = H) the temporary spectral changes caused by 390 nm radiation have already been described.[28] There was no significant qualitative difference in behaviour between films dyed by casting from a common solvent or disperse dyeing.

Permanent fading of **I**(R = H) in either cellulose acetate or cellulose triacetate did not occur to a significant extent following irradiation with 390 nm light. This is shown by the almost complete recovery of the original spectra following storage in the dark. Thus, although temporary fading of **I**(R = H) can occur as a result of excitation of the azo tautomer, it is not the species responsible for major permanent photofading.

A well populated triplet state is necessary to cause appreciable sensitization of singlet oxygen. For non-tautomeric azo compounds, the only direct observation of a triplet state reported in the literature was made recently by using laser flash photolysis.[29] Further examination of a number of these compounds revealed that they were capable of sensitizing singlet oxygen, with the singlet oxygen yield increasing as the triplet yield increased.[30] However, it appears that a criterion for a triplet state to be detectable is that substitution should cause the lowest triplet state to have (π, π^*) rather than (η, π^*) character.[29] This is unlikely for the azo tautomer of **I**(R = H) since, by analogy with the results of Gorner *et al.*[29] and Gruen *et al.*,[30] extremely powerful donor–acceptor substitution is necessary to cause the $^3(\pi, \pi^*)$ state to become lower in energy than the $^3(\eta, \pi^*)$ state. The fact that selective excitation of the azo tautomer of **I**(R = H) did not cause permanent photofading provides experimental evidence that the azo tautomer does not possess a lowest excited triplet state of sufficient population or longevity to be capable of sensitizing singlet oxygen.

3.3. Selective excitation of the hydrazone tautomer

Selective excitation of the hydrazone tautomer of **I**(R = H) in cellulose acetate and cellulose triacetate films by 490 nm radiation caused both temporary and permanent fading (see Figs. 3 and 4). As for selective excitation of the azo tautomer of **I**(R = H), the rate of recovery of the temporary component of the light-induced fading could be greatly accelerated by immersing the irradiated film in water. There was no significant qualitative difference between films dyed in a disperse dyebath and those formed by casting from a common solvent.

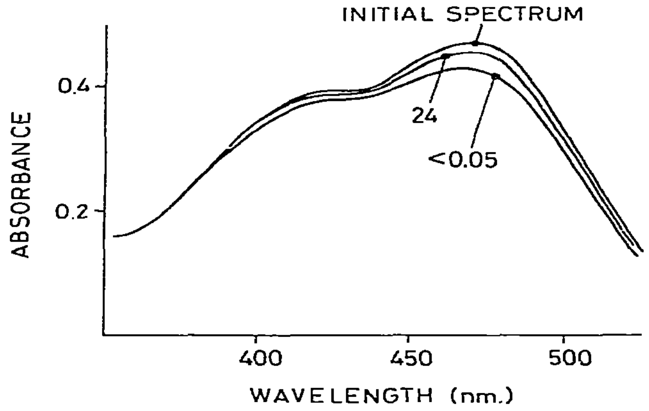


Fig. 3. Spectral changes in cellulose acetate film containing **I**(R = H) (cast from common solvent) following irradiation for 16 h at 490 nm. Numbers indicate the time (h) after irradiation had ceased.

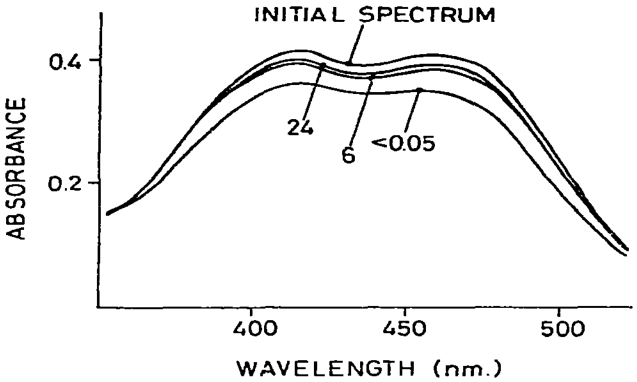


Fig. 4. As for Fig. 3 with cellulose triacetate.

The temporary bleaching of I(R = H) caused by 490 nm radiation did not occur to the same extent as noted for 390 nm radiation.[28] This is not surprising, as the hydrazone tautomer does not have the same opportunity to undergo photochemical stereoisomerization as the azo tautomer does. Two previous studies[31,32] have, however, reported that the hydrazone tautomer of II(R = H) is susceptible to viscosity-dependent, thermally-reversible conformation changes following excitation by light. It is likely that the hydrazone tautomer of I(R = H) is similarly susceptible and that the restricted molecular motion of the dye in the polymer substrates prolongs the lifetime of the conformers formed in this way. In addition to the temporary fading, selective illumination of the hydrazone of I(R = H) resulted in some permanent fading. The ability of 490 nm light to cause permanent fading demonstrates that the excited hydrazone is instrumental in causing the photodegradation of I(R = H).

Like those of azo compounds, the triplet states of hydrazone compounds are spectroscopically elusive. However, deactivation of the lowest excited singlet state of hydrazones can occur by intersystem crossing to the triplet manifold,[33] as well as by conformational changes[32] and fluorescence.[34] The lowest energy ($\pi \rightarrow \pi^*$) transition of the hydrazone tautomer occurs at about 470 nm and elevates the energy of the ground state molecule by about 255 kJ mol^{-1}. Since the lower $^1\Delta_g^*$ state of singlet oxygen has an energy of 92 kJ mol^{-1},[35] the lowest $^3(\pi, \pi^*)$ state of the hydrazone tautomer would be capable of being quenched by ground state triplet oxygen, as singlet–triplet splitting is not likely to exceed 80–90 kJ mol^{-1}.

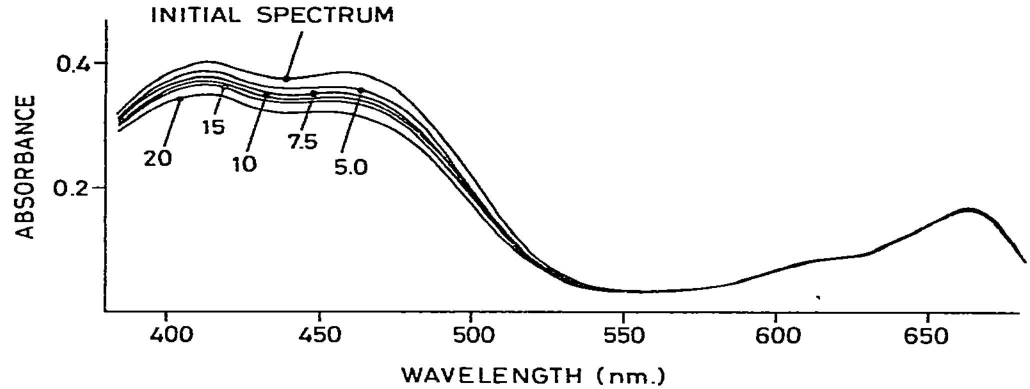


Fig. 5. Special changes in cellulose triacetate film containing I(R = H) and Methylene Blue following irradiation at 665 nm. Numbers indicate time of irradiation in minutes.

This postulate is supported by the fact that selective excitation of the hydrazone tautomer of I(R = H) in air resulted in permanent fading of the dye.

The susceptibility of the hydrazone tautomer of I(R = H) to attack by singlet oxygen was demonstrated by irradiating cellulose acetate and cellulose triacetate films containing I(R = H) and Methylene Blue with a narrow radiation band centred about 665 nm. Under these conditions, singlet oxygen is produced by Methylene Blue, but I(R = H) remains in its ground state. Thus any effects arising from photo-induced tautomeric,[36,37] isomeric and conformational changes[31,32] of I(R = H) were essentially eliminated. The spectral changes observed are displayed in Figs. 5 and 6. There is a clear preference for degradation of the hydrazone tautomer.

3.4. Maintenance of tautomeric equilibrium in polymer substrates

It has been shown that it is the hydrazone tautomer of I(R = H) which is both responsible for sensitizing and susceptible to degradation by singlet oxygen. However, the azo tautomer concentration is also depleted as a result of consumption of the hydrazone tautomer. This is likely to be due to the azo tautomer temporarily existing in the hydrazone configuration and therefore susceptible to attack. Becker and Franz[13] showed that in solution in methanol, the rate of tautomeric interchange is much greater than the rate of reaction of the hydrazone tautomer with singlet oxygen. However, in polymer substrates, free tautomeric interchange is inhibited

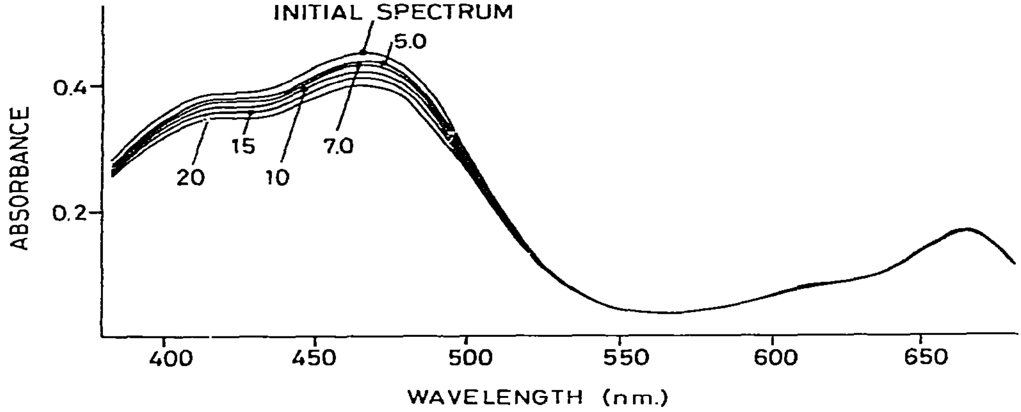
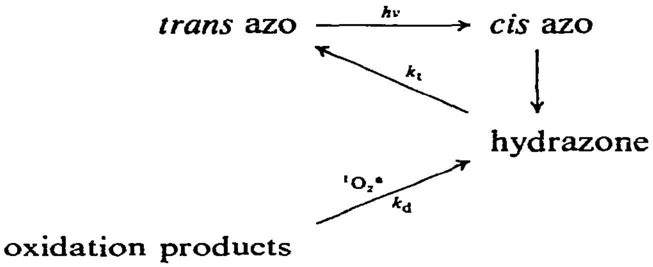


Fig. 6. As for Fig. 5 with cellulose acetate.

by the establishment of specific interactions which preferentially stabilize a particular tautomer at a given location.[28] Thus, the rate of consumption of the hydrazone tautomer by singlet oxygen can exceed the rate of the azo–hydrazone tautomeric exchange. The degree to which the two rates differ depends on the polymer concerned and the method used to incorporate the dye. In this study, it has been shown that cellulose acetate inhibits tautomeric exchange more than cellulose triacetate, and that disperse dyeing instead of casting from a common solvent also has this effect.

A second possibility for tautomeric interchange occurs following *trans* → *cis* isomerization of the azo tautomer. For hydroxyazo compounds capable of azo–hydrazone tautomerism, thermal reversion of the *cis* azo isomer to the *trans* configuration occurs via the hydrazone tautomer.[38] A previous study[28] has demonstrated that the lifetime of the photochemically produced *cis* isomer is greatly prolonged in polymer substrates relative to liquid solvents. This implied that the two-step reversion process (*cis* azo → hydrazone → *trans* azo) was inhibited by the rigid polymer environment. However, since some tautomeric interchange can occur between *trans* azo and hydrazone (see Figs. 5 and 6, where consumption of hydrazone by singlet oxygen is accompanied by a decrease in *trans* azo concentration), it is even more likely to occur between *cis* azo and hydrazone, where the greater potential energy difference would provide added incentive. The reaction pathway envisaged is shown in Scheme 2.



Scheme 2. Consumption of azo tautomer of I(R=H) by a hydrazone-specific reaction (attack by singlet oxygen).

If rate constant k_d is at least similar in magnitude to k_t, the degradative reaction route will become significant. The lifetime of the hydrazone formed in this way is a point of conjecture. Hydrazone absorbance does not increase unduly during thermal reversion of the *cis* azo isomer,[28] thereby demonstrating that its lifetime is not prolonged. If previous solution studies are taken as a guide, the lifetime of the temporarily formed hydrazone could be of the order of 10^{-4} s.[13] On the other hand, that of singlet oxygen could be as short as 10^{-6} s.[27] These figures demonstrate that the degradative pathway shown in Scheme 2 is feasible. The fact that cellulose triacetate shows less difference between the relative fading rates of the azo and hydrazone tautomers of I(R = H) than cellulose acetate could be due to degradation via Scheme 2. Cellulose triacetate is able to support a higher concentration of *cis* azo isomer in the photostationary state than cellulose acetate,[28] thus providing more opportunity for *cis* azo → hydrazone conversion.

3.5. Photofading of methylated compounds III and IV

The relative fading rate constants (apparent first order) of **III** and **IV** are shown in Table 2. The relative rates of fading of **III** on cellulose acetate and cellulose triacetate are quite comparable under both air and nitrogen. Thus photo-oxidation is not an important reaction for **III** although it is for I(R = H). Additional evidence for this was found by irradiating **III** in cellulose triacetate with Methylene Blue. This actually improved the fading resistance of the azo compound. Thus **III** appears to be highly resistant to singlet oxygen attack. The increased lightfastness of **III** in the presence of Methylene Blue may be due to a radiation screening effect by

TABLE 2

Relative Fading Rate Constants (Apparent First Order) for Methylated Derivatives **III** and **IV** (both $1{\cdot}2 \times 10^{-5}$ mol per g Polymer) in Polymer Films

	Cellulose acetate		*Cellulose triacetate*	
	Air	*Nitrogen*	*Air*	*Nitrogen*
III	5·2 ± 0·7[a]	7·3 ± 1·0	7·7 ± 1·1	8·2 ± 0·9
III + MB[b]	—	—	3·5 ± 0·8	3·1 ± 1·1
IV	2·4 ± 0·9	7·1 ± 1·3	2·8 ± 1·0	11·8 ± 0·6
IV + MB	—	—	6·0 ± 1·2	10·1 ± 1·0

[a] The errors are 95% confidence limits.

[b] MB, Methylene Blue ($5{\cdot}6 \times 10^{-7}$ mol per g polymer).

the blue dye. Other workers have reported extremely slow photofading of **III** in polyamide films[39] and low susceptibility to photo-oxidation.[10]

For **IV**, the relative fading rates given in Table 2 clearly show a quenching effect on the fading of **IV** by oxygen. This is consistent with the experimental results obtained with **I**(R = H) for which it was postulated that the hydrazone tautomer is able to sensitize the formation of singlet oxygen by energy transfer from the lowest $^3(\pi, \pi^*)$ state of the dye to ground state oxygen. However, whereas the hydrazone tautomer of **I**(R = H) was highly susceptible to attack by the singlet oxygen it had sensitized, **IV** appears to be resistant. Replacing the labile hydrogen atom of the hydrazone tautomer of **I**(R = H) with a methyl group apparently insulates the chromophore against the 'ene' reaction with singlet oxygen (see Scheme 1). Although a concerted 'ene' reaction is unlikely, **IV** can be degraded to a certain extent by singlet oxygen. This is apparent by the increased relative fading rate observed in air when **IV** was irradiated in the presence of Methylene Blue. The increased photoreactivity of **IV** under a nitrogen atmosphere relative to air indicates that **IV** is susceptible to photoreduction. The quinoid nature of **IV** could be responsible for this, as quinoids are known to be easily reduced.

4. CONCLUSIONS

It has been shown that the permanent photofading of 1-phenylazo-4-naphthol in cellulose acetate and cellulose triacetate is due to degradative attack by singlet oxygen on the hydrazone tautomer of the dye. As well as being susceptible to attack, the hydrazone tautomer appears to be the species responsible for sensitizing the formation of singlet oxygen.

Both the nature of the polymer concerned and the method of dye incorporation had an effect on the rate of dye fading. More rapid fading was observed in cellulose triacetate than in cellulose acetate. This was likely to be due to a longer singlet oxygen lifetime in the former polymer which has less —OH groups that are capable of deactivating singlet oxygen by energy transfer. Fading was also more rapid for disperse dyed films than for those dyed by casting from a common solvent. This was probably due to a greater accessibility of the dye to oxygen in the former case.

In solution, uniform fading rates of the azo and hydrazone tautomers of **I**(R = H) have been reported since the azo–hydrazone tautomeric interchange is considerably more rapid than the reaction of singlet oxygen with the hydrazone tautomer.[13] However, incorporating the dye in a polymer matrix inhibits free tautomeric interchange to a certain extent, and it is possible for the rate of degradation of the hydrazone tautomer to exceed the rate of azo → hydrazone conversion. Under the conditions employed in this study, the tautomeric equilibrium was not completely frozen within the polymers. Thus the concentration of the azo tautomer was reduced as a consequence of the dye temporarily existing in the hydrazone conformation. There are two possible routes leading to this temporary existence. First, free tautomeric interchange may occur to a certain extent. The second possibility depends on *trans* → *cis* isomerization of the azo tautomer. A considerable proportion of the *trans* azo tautomer of **I**(R = H) has been shown to be photochemically converted to the *cis* isomer.[28] Since the *cis* azo isomer is believed to revert to the *trans* via the hydrazone tautomer, the possibility exists for it to be degraded. The higher potential energy of the *cis* azo isomer relative to the *trans* isomer would make tautomeric conversion more likely in this instance. The relative rates of depletion of the azo hydrazone tautomers depend on the polymer concerned and the method used to incorporate the dye.

Examining the methylated derivatives **III** and **IV** confirmed many of the observations made on the tautomers of **I**(R = H). The azo compound **III** was quite resistant to attack by singlet oxygen. The hydrazone **IV** showed a preference for photoreduction, but its ability to sensitize singlet oxygen was indicated by a quenching effect on the reductive fading when oxygen was present.

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