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Photostability of substituted 4-diethylaminoazobenzenes

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Abstract

The stability to visible light of five 4-diethylaminoazobenzenes was investigated in different solvents under various experimental conditions, as well as in solid crystalline form and on dyed poly(ethyleneterephthalate). Though generally exhibiting relatively high photostability, all investigated dyes underwent photodegradation in acetone solution. Two different reaction paths were recognised in this solvent, depending on the nature and position of the substituting groups on the second aromatic ring, both involving the formation and subsequent fragmentation of organic free radicals, as suggested by the strong inhibiting effect of molecular oxygen on the photodegradation rate. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

When irradiated with visible or UV light, azobenzene compounds undergo both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. While in the parent azobenzene the low energy transition, being forbidden, exhibits a small molar extinction coefficient, a substantial hyperchromic effect is observed if an electron-releasing group, such as the diethylamino, is introduced in the 4-position of one aromatic ring, the low energy transition assuming in this case a highly allowed charge transfer character. Therefore, 4-diethylaminoazobenzene and its substituted derivatives are efficient azo dyes, which are widely used mainly for dyeing polyester fibres [1], also thanks to their outstanding stability. Indeed, *trans* → *cis* photoisomerisation around the azo double bond is by far the prevailing deactivation path of their electronically excited state, followed by thermal *cis* → *trans* isomerisation, which occurs at a different rate, depending on substituents [2,3]. Their main photodegradation path under UV irradiation is photoreduction of the azo group, yielding hydrazo derivatives and/or substituted anilines [3–7].

The photochemical behaviour under visible light irradiation of the five substituted diethylaminoazobenzene compounds **1a–e** has been investigated in the present work, both in solution and in the solid phase, as well as on dyed poly(ethyleneterephthalate) (PET) fibres. Their modes of photodecomposition have also been examined under the conditions in which they proved to be unstable, in order to

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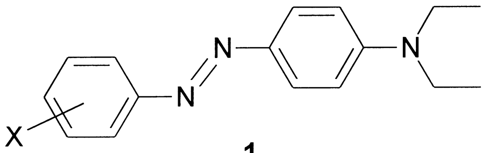

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X = H (a)
p-OCH_3 (b)
p-NO_2 (c)
p-COOH (d)
o-NO_2 (e)

provide a theoretical explanation of the phenomenon and hence a key to prediction of their stability.

2. Experimental

2.1. Materials

Dyes **1a–e** were obtained from ACNA and purified by flash column chromatography, employing *n*-hexane and ethyl acetate eluting mixtures, or acetic acid and ethyl acetate eluting mixtures, in the case of **1d**, followed by crystallisation from absolute ethanol.

Di-*n*-propylterephthalate was prepared with 70% yield by acid catalysed esterification of terephthalic acid by *n*-propanol and purified by standard procedures (m.p. = 26°C). Its structure was checked by ^{1}NMR and GC–MS analysis.

Thermofixed poly(ethyleneterephthalate) fibres (100.4 g m^{-2}) were dyed with **1a–c**. All solvents and other reagents were purchased from Aldrich and used as received. Oxygen (purity 99.998%) was purchased from SIAD, Italy; nitrogen (obtained from vaporisation of liquid nitrogen, purity 99.999%) was purchased from SIO, Italy.

2.2. Apparatus and methods

Irradiation was always performed through Pyrex glassware using a Rayonet RPR-100 reactor, equipped with F8T/D and F8T/CW 8W lamps (visible light) and an internal merry-go-round apparatus for the homogeneous exposure of the samples to light. Spectrophotometric analysis of dye solutions was carried out in a Hewlett Packard 8452A apparatus. Percentage photodegradation was evaluated as $(A_0-A_t)/A_0\times100$ (A = maximum absorbance at time $t=0$ or at time t).

Flat glasses (0.7 × 10 cm) were employed as supports for dye irradiation in solid crystalline form. Homogeneous layers of crystalline dyes were obtained through several depositions from methanol solutions, followed by evaporation of the solvent. Irradiation of such specimens was performed in sealed Pyrex vials, under nitrogen or oxygen atmosphere.

For PET dyeing, the dyes were dissolved in acetone and the polyester samples were immersed in these solutions in a programmable thermostated dyeing apparatus (Gavazzi, Italy), which was heated from 40 to 130°C at 2°C min^{-1}, held at this temperature for 1 h and then cooled back to 40°C at 1°C min^{-1}. The samples were subsequently washed with a standard soap solution for 1 h at 45°C and let dry overnight. Irradiation took place in sealed Pyrex vials, which had been saturated with nitrogen. Reflectance spectra of crystalline dye layers and of dyed polyester samples were recorded with a Perkin Elmer Lambda 19 UV/VIS/NIR spectrophotometer.

An LC-42 Bruker HPLC chromatograph, equipped with a Chrompack ChromSpher Si glass column (length 100 mm, internal diameter 3 mm), was employed for HPLC analyses, using a 5:1 *n*-hexane–ethyl acetate eluting mixture and a 1 ml min^{-1} flow rate. GC analyses were performed with a Dani 6500 gaschromatograph equipped with a Chrompack fused silica column and a flame ionisation detector, employing hydrogen as carrier gas. GC–MS analyses were performed with a Hewlett Packard HP 6890 Series GC equipped with a HP-5 MS column (length 30 m, internal diameter 0.32 mm) and a HP 5973 mass selective detector. ^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer, with TMS as internal standard.

3. Results and discussion

3.1. Effects of visible irradiation

The photostability of dyes **1a–e** was first tested in solution: *n*-hexane, acetone and methanol were chosen as non polar, polar and hydrogen bonding solvent, respectively. Solutions of the dyes in each

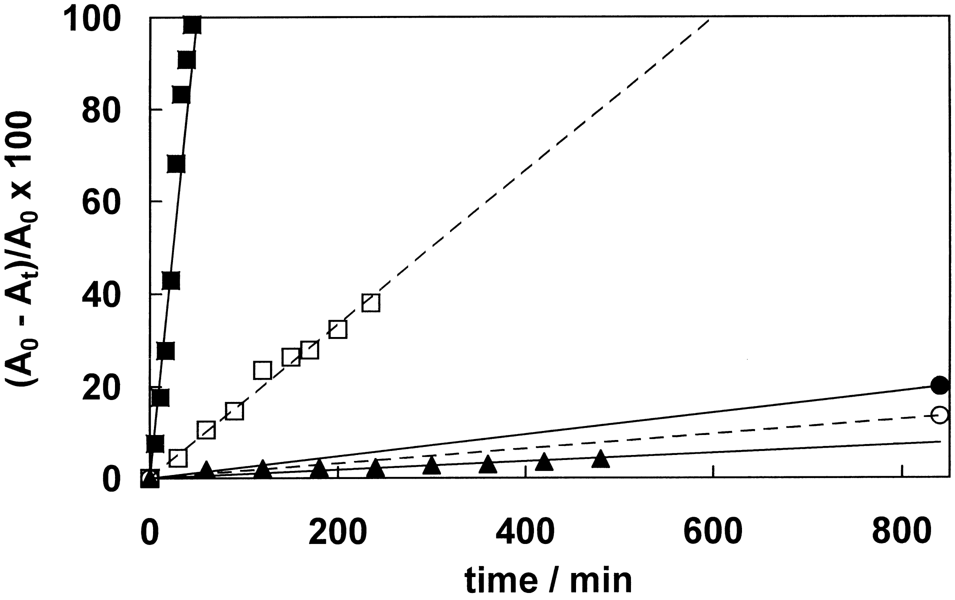


Fig. 1. Percentage photodegradation of dye **1c** in acetone solution (squares), in solid crystalline form (circles) and on dyed PET (triangles) under nitrogen (full symbols) or oxygen atmosphere (open symbols).

of the three solvents, exhibiting an initial maximum absorbance around 0.7, were irradiated with visible light in closed vials after either nitrogen or oxygen bubbling for 20 min, in order to highlight any effect due to the presence of molecular oxygen.

All compounds appeared unaltered after several hours of irradiation in *n*-hexane, both in the presence and in the absence of oxygen, while photodegradation was observed to occur in the two other solvents, at a much higher rate in the absence of oxygen and in acetone solution: maximum absorbance decreased by only 2–4% after 6 h irradiation in methanol solution under nitrogen atmosphere, while methanol solutions always appeared to be perfectly photostable under oxygen atmosphere. For all investigated dyes photodegradation in acetone solution occurred according to a zero-order process, after a more or less pronounced initial induction period. An example of the observed kinetic behaviour is shown in Fig. 1, while the complete set of kinetic data is reported in Table 1.

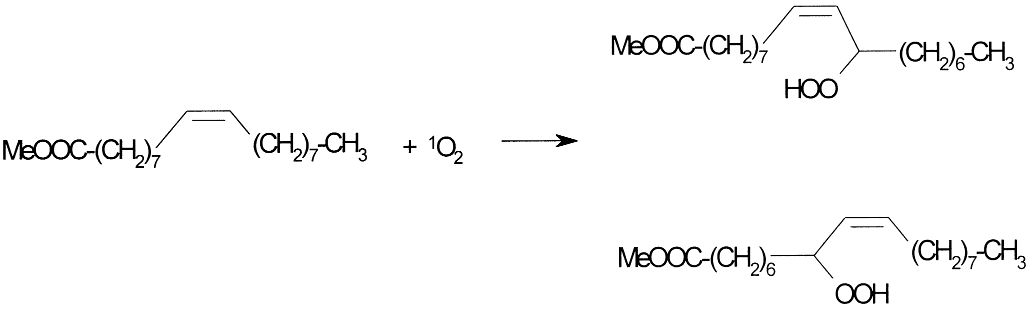
The inhibiting effect of oxygen might be explained by recalling that molecular oxygen could act as a quencher of the excited state of dyes [3,8]. Oxygen–dye interactions result in the formation of singlet oxygen, $^1O_2$, and in the return of the dye to its ground state. Indeed, the presence of singlet oxygen under our experimental conditions was confirmed by adding methyl oleate to the reaction mixture. This molecule efficiently traps $^1O_2$ [9a], yielding a couple of hydroperoxides, according to Eq. (1).

Table 1
Half-lives of photodegradation of dyes **1a–e** in acetone solution under oxygen or nitrogen atmosphere

Compound (X)	Under oxygen		Under nitrogen	
	10^5C^o M[a]	$t_{1/2}$ min	10^5C^o M[a]	$t_{1/2}$ min
1a (H)	6.0	90	6.0	70
1b (p-OCH$_3$)	4.1	90	7.3	12
1c (p-NO$_2$)	7.1	290	3.7	15
1d (p-COOH)	3.0	110	3.3	65
1e (o-NO$_2$)	1.4	70	1.3	70

[a] C° = intial concentrations.

As shown in Fig. 2, the presence of the two hydroperoxides in our reaction mixture after methyl oleate addition was detected by HPLC analysis and the same couple of hydroperoxides was obtained by irradiating a solution containing methyl oleate and bengal rose, which is a photosensitiser known [10] to give rise to $^1O_2$.



(1)

It is interesting to note that the dye-sensitised formation of singlet oxygen was questioned to occur under UV irradiation [11], where a radical pathway was instead proposed as the principal route of dye photofading.

3.2. Identification of photo products

Since photodegradation of all the investigated dyes was observed to occur in acetone at a much higher rate than in other solvents, the kinetic process of **1a–c** in this solvent was followed by GC and GC–MS analyses, in order to isolate the decomposition products and to identify them by NMR spectroscopy.

For all dyes, we verified that, both in the presence and in the absence of oxygen, the first step of the photodegradation process is the loss of one ethyl group from the *N*,*N*-diethylamino group. This reaction should be initiated by the photoinduced electron transfer from the azo dye to acetone and then proceed according to the reaction sequence shown in Scheme 1. The rate of formation of the de-ethylated product **2** was higher for compound **1b** ($X = OCH_3$, 21% yield after 30 min irradiation) and lower for compound **1c** ($X = NO_2$, 2% yield after 30 min irradiation), which is consistent with the above mechanism.

In the presence of oxygen, an alternative degradation path of the tertiary amine group could also be at work, involving singlet oxygen attack on the nitrogen atom, followed by hydrogen abstraction and formation of a peroxide species, finally also giving the de-alkylated amine group and a carbonyl compound [3,9b].

When irradiation was continued further, the amount of de-ethylated product **2** decreased and new products of lower mass appeared. These were isolated and identified as compounds **3b** and **3c**, deriving from **2b** and **2c**, respectively, which clearly proved to be originated from different fragmentation modes of the intermediate species **2**. Thus, the photodegradation process evolved according to two different reaction paths, depending on the electron availability of **2** and hence on its ease to give electron transfer.

In the case of the unsubstituted azo dye **1a** no products were formed in sufficient amount to allow their isolation and characterisation. The reaction mixture was thus directly analysed by GC–MS: no products similar to **3c** were detected, while a small amount of the unsubstituted analogue of **3b** was revealed.

3.3. Effect of 2-propanol addition

The photodecomposition of dyes **1a–e** was dramatically accelerated by the addition of a small quantity of 2-propanol, which notoriously is a good hydrogen donor and can be formed by disproportionation of the ketyl radical cation deriving from acetone (see Scheme 1). This suggests the involvement, in the steps of the mechanism following de-ethylation, of a reduction process leading to the formation of an unstable hydrazo intermediate [4–7]. The N–N single bond of this latter should then be easily broken in oxygen-inhibited radical reactions, in which acetone itself might play an active role.

It is worth mentioning that acetone was reported to have strong sensitising effects on the azo dyes degradation induced by irradiation at 253.7 nm [7,12], obviously involving the excited triplet state of acetone. This, however, should not occur under

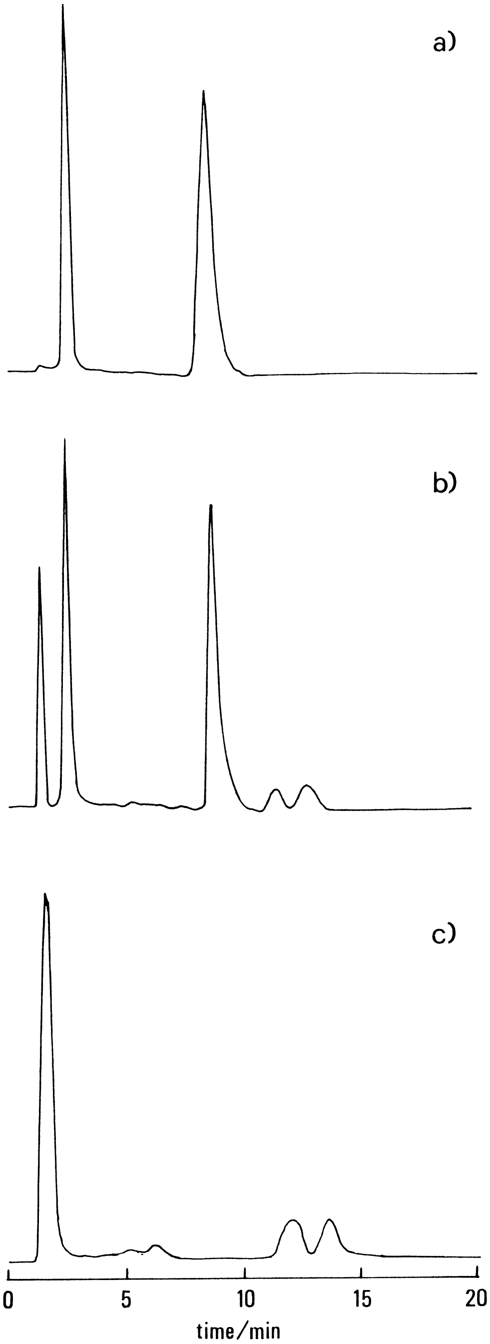


Fig. 2. HPLC traces of an acetone solution containing dye **1b** and methyl oleate (a) before and (b) after irradiation (20 h) under oxygen atmosphere; (c) HPLC trace of an acetone solution of methyl oleate and bengal rose after irradiation (8 h) under oxygen atmosphere. The signals due to the two hydroperoxides appear in the range 11–15 min.

our irradiation conditions, in which acetone should not undergo direct photoexcitation.

3.4. Irradiation of crystalline dyes

In order to eliminate solvent effects, the photostability of dyes **1a–e** to visible light was investigated also by irradiating them in solid crystalline form. The results of this investigation, reported in Table 2, confirm dye **1b**, carrying the electron releasing substituent –OCH_3, as the most photolabile dye of the series under study. Moreover, the inhibiting action of oxygen on photodegradation was clearly confirmed to occur also in the absence of solvent.

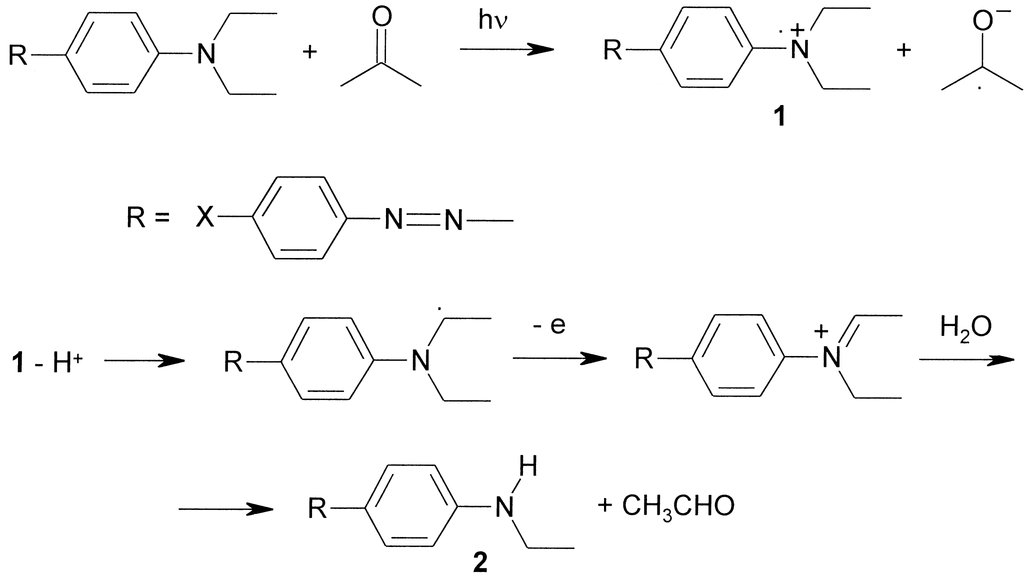
3.5. Effect of phthalates

Since this class of azo compounds is mainly used for dyeing polyester fibres, the effect of such ester group onto the photodegradation process was also investigated. As a preliminary approach, we added small quantities of di-*n*-butylterephthalate or di-*n*-propylterephthalate to the acetone solutions of dyes **1a–e**: no effect on the rate of photodecomposition was observed. On the other hand, di-*n*-butylterephthalate appeared to have a somewhat photostabilising effect on the dyes in methanol solution.

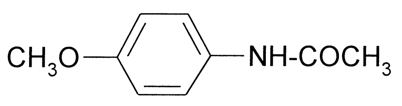
Finally, we also investigated the photostability under nitrogen atmosphere of poly(ethyleneterephthalate) fibres dyed with **1a–c**. In all cases the dyes resulted remarkably stable, with no significant variation in their absorption spectrum being noticed after up to 8 h-long irradiation (see for example Fig. 1). Thus, specific interactions of the investigated azo dyes with PET seem to have beneficial effects on their photostabilisation.

4. Conclusions

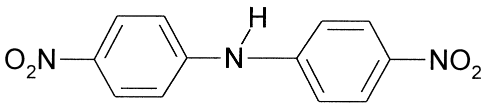
The peculiar behaviour of the investigated dyes, when irradiated with visible light in acetone solution, is evident from the overall outlook of the kinetic results obtained under different conditions (Fig. 1, for example). The present study thus leads to the following conclusions:



Scheme 1.



3b



3c

Table 2
Percentage photodegradation of dyes **1a–e** in solid crystalline form under oxygen or nitrogen atmosphere

Compound (*X*)	Irradiation time (h)	Percentage photodegradation	
		Under oxygen	Under nitrogen
1a (H)	12	4	9
1b (*p*-OCH_3)	16	38	58
1c (*p*-NO_2)	14	14	25
1d (*p*-COOH)	16	27	36
1e (*o*-NO_2)	18	5	9

1. The investigated azo dyes are stable or almost stable in *n*-hexane or methanol solution, while in acetone they undergo photodegradation according to two different reaction paths, depending on the nature and position of substituting groups. Such photodegradation paths involve organic free radicals, as suggested by the strong inhibiting effect of molecular oxygen.
2. Photodegradation occurs at a much lower rate if the dyes are illuminated in the solid crystalline state; the inhibiting action of oxygen is confirmed also in this case.
3. Dyed PET specimens exhibit high photostability, thanks to specific interactions of the dyes with such polymer substrates.

References

[1] Griffiths J. J Soc Dyers Colour 1972;88:106.
[2] Zollinger H. Color chemistry. Weinheim: VCH; 1987. p. 103.
[3] Griffiths J. In: Allen NS, editor. Developments in polymer photochemistry — 1. London: Applied Science; 1980.
[4] Irick Jr. J, Pacifici JG. Tetrahedron Lett. 1969:1303.
[5] Pacifici JG, Irick Jr J, Anderson CG. J Am Chem Soc 1969;91:5654.
[6] Flamigni L, Monti S. J Phys Chem 1985;89:3702.

[7] Albini A, Fasani E, Pietra S. J Chem Soc Perkin Trans 2 1983:1021

[8] Griffiths J, Hawkins C. J Chem Soc Perkin Trans 2 1977:747.

[9] Ranby B, Rabek JF. Singlet oxygen. Chichester: Wiley; 1978. (a) p. 21, 211; (b) p. 80.

[10] Arnone A, Assante G, Caronna T. Photochemistry 1988;27:1669.

[11] Albini A, Fasani E, Pietra S, Sulpizio A. J Chem Soc Perkin Trans 2 1984;10:1689.

[12] Chu W, Tsui S-M. Chemosphere 1999;39:1667.