The Photochemistry of Azo Dyes. Photoisomerisation *versus* Photoreduction from 4-Diethylaminoazobenzene and 4-Diethylamino-4'-methoxyazobenzene

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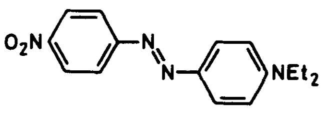
4-Diethylaminoazobenzene (2) and 4-diethylamino-4'-methoxyazobenzene (3) undergo geometrical isomerization with a quantum yield of almost unity by irradiation in the visible region, and, with lower efficiency, by irradiation at a shorter wavelength or sensitization both with high and low energy hydrocarbons. These dyes are also photoreduced, this time however only by irradiation at $\lambda \leqslant 313$ nm and with low quantum yield (10^{-4}—4×10^{-2}). Photoreduction also takes place by energy transfer from high energy sensitizers as well as by radical initiation by ketones. It is concluded that the lowest singlet and triplet states of these azobenzene derivatives, which are reasonable models for commercially useful monoazo-dyes, are only capable of geometrical isomerization, whereas hydrogen abstraction takes place from the high-lying triplet state of both the *trans*- and *cis*-configuration of these dyes.

While the photochemistry of azobenzene has been extensively investigated, less attention has been given to its derivatives, particularly azo-dyes despite the great commercial importance of these compounds.

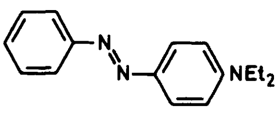
Two photoprocesses have been recognized, *viz.* *trans–cis* isomerization and reduction. The former process has been reported to take place in solution[1,2] as well as in solid matrices,† but the efficiency of the photoisomerisation is not known. The *cis*-form is generally unstable and the rate of the thermal back isomerisation is strongly dependent on the solvent polarity for dyes with push–pull substituents, such as 4-diethylamino-4'-nitroazobenzene (1) ($k_{c\text{-}t}$ 7×10^{-3} s^{-1} in hexane, 4.4×10^{2} s^{-1} in dimethyl sulphoxide), while it is lower and less solvent-dependent in the other cases (for 4-diethylamino-4'-aminoazobenzene, $k_{c\text{-}t}$ 3×10^{-3} s^{-1} in benzene and 9×10^{-3} s^{-1} in dimethyl sulphoxide).[1]

As for photoreduction, which is generally considered to be important in the fading of azo-dyes in practice,[5,6] the only quantitative data available are those concerning compound (1).[7] We recently showed that the photoreactivity of this dye in different solvents is remarkably wavelength-dependent, the irradiation in the first absorption band producing no irreversible effect, while decomposition with a quantum yield as high as some hundredths is obtained by irradiation at shorter wavelength.[8] This decomposition is due to the reduction to the corresponding hydrazo-derivative and to anilines. Furthermore it was shown that the reduction can be promoted by triplet energy transfer, and that it proceeds from high-lying triplet state(s) of the *trans*-form of the dye.[8]

The lack of quantitative information on the photochemistry of azo-dyes made it desirable to study both isomerization and reduction of a simple azo-dye. However, in the case of compound (1), the rapid thermal isomerisation of the photochemically generate *cis*-form precludes, at least for steady state measurements, comparison of the efficiencies of the two reactions. We found that 4-diethylaminoazobenzene (2) and 4-diethylamino-4'-methoxyazobenzene (3) are better models, as the *cis*-isomer is sufficiently stable, at least in apolar solvents [$k_{c\text{-}t}$ 5.5×10^{-4} s^{-1} for (2) and 6×10^{-4} s^{-1} for (3) in cyclohexane].



(1)



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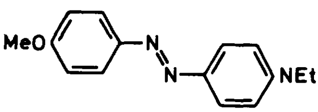

(3)

Results and Discussion

The irradiation of the azobenzene derivatives (2) and (3) with Pyrex-filtered light results in *trans–cis* isomerisation, both in aerated and in degassed solutions. The photochromic equilibrium allows a significant population of the *cis*-form to build up in apolar solvents, while the phenomenon is weaker in alcohols due to the higher rate of the thermal *cis–trans* back conversion. The spectral modification observed is a decrease in the visible band [$\lambda_{max.}$ 407 nm in cyclohexane for both (2) and (3)] with the appearance of a new, less intensive maximum at shorter wavelength. This corresponds to the spectrum attributed to the *cis*-form in similar cases.[1] When discontinuing the irradiation a complete return of the original spectrum takes place after some hours in the dark.

In order to determine the quantum yield of the *trans–cis* isomerisation, it has been assumed, as in analogous cases,[1] that the *cis*-form has practically zero absorbance at the maximum of the *trans*-form. Therefore the values reported in Table 1 have to be considered minimum values. The measurements were carried out at different wavelengths, and it transpired that the quantum yield for the irradiation in the first absorption band (charge-transfer character) is not far from one, while by irradiation at the high energy limit of this band (366 nm) or at shorter wavelengths the efficiency is uniformly lower. No oxygen quenching is observed, somewhat higher quantum yields being measured even in aerated solutions.

The geometrical isomerisation can be sensitized (see Table 2) and both high and low energy hydrocarbon sensitizers are

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† Reversible photochromism of azo-dyes adsorbed on films[3] as well as chemically linked to polymer chains has been reported.[4]

Table 1. Quantum yields for the *trans–cis* isomerization ($\Phi_{c\text{-}t}$) of dyes (2) and (3) by direct irradiation in cyclohexane

Dye	Conditions	λ_{irr}/nm 254	313	366	434
(2)	*a*	0.38	0.30	0.29	0.70
	b	0.23	0.25	0.21	0.72
(3)	*a*	0.37	0.25	0.28	0.93
	b	0.34	0.31	0.27	0.84

[a] Air-saturated solvent. [b] Degassed solvent.

equally effective. The methoxy-group of compound (3) appears to have a negligible effect on the isomerization, approximately equal quantum yields result from the same conditions for both compounds.

As opposed to the case for Pyrex-filtered irradiation, the use of a low pressure mercury arc causes, besides *trans–cis* isomerization, irreversible disappearance of the starting material. Thus, after the rapid back isomerisation of the *cis*-form a permanent variation of the spectrum is observed, and no further change takes place either in the dark or when readmitting air. Therefore, contrary to the case of the dye (1) and of azobenzene itself, the hydrazo-derivative (4), which would be reoxidized by air, is not the end product of the irreversible reaction in the case of (2) and (3). G.c.–m.s. examination showed that the main product of this reaction are the amines (5a and b), respectively, obtained in a yield higher than 50%, and *NN*-diethyl-*p*-phenylenediamine (6).

These products arise from further reaction of the hydrazyl radical formed in the primary hydrogen abstraction. Indeed, the same degradation can be effected with higher efficiency by radical initiation, as shown by the acetone-sensitized experiments (Table 2, *cf.* refs. 8 and 9). Furthermore, the solvent dependence is that expected for such a process, as is the extremely efficient oxygen quenching of the reaction.* The chemical evolution of the hydrazyl radical differs from that found in the case of (1) in that the hydrazo-derivatives (4a and b) expected from (2) and (3) are unstable and undergo quick disproportionation to the starting material and to the amines (5a and b) and (6).†

Table 2. Quantum yields for photoreduction and photoisomerization of dyes (2) and (3) in sensitized conditions (λ_{irr} 254 nm)

Solvent	Sensitizer (molarity)	(2) Φ_{red}	(2) $\Phi_{t\text{-}c}$	(3) Φ_{red}	(3) $\Phi_{t\text{-}c}$
Methanol	Benzene (2×10^{-2})	1×10^{-2}		6.5×10^{-3}	
	Fluorene (1.2×10^{-3})	2.2×10^{-3}		1×10^{-3}	
	Naphthalene (1.2×10^{-3})	2.2×10^{-3}		1.5×10^{-3}	
	Anthracene (1.2×10^{-3})	$\leqslant 2 \times 10^{-5}$		$\leqslant 2 \times 10^{-5}$	
	Acetone (1.17)	9×10^{-2}		6×10^{-2}	
Cyclohexane	Benzene (2×10^{-2})	3×10^{-3}	0.20	6×10^{-3}	0.17
	Anthracene (1.2×10^{-3})	$\leqslant 2 \times 10^{-5}$	0.16	$\leqslant 2 \times 10^{-5}$	0.17

Table 3. Quantum yields for the photoreduction (Φ_{red}) of dyes (2) and (3) by direct irradiation in degassed solvent

Dye	Solvent	λ_{irr}/nm 254	313	366	434
(2)	Methanol	1.6×10^{-2}	8×10^{-4}	$\leqslant 2 \times 10^{-5}$	$\leqslant 2 \times 10^{-5}$
	Cyclohexane	5×10^{-3}	1×10^{-4}	$\leqslant 2 \times 10^{-5}$	$\leqslant 2 \times 10^{-5}$
(3)	Methanol	8×10^{-3}	1.3×10^{-3}	$\leqslant 2 \times 10^{-5}$	$\leqslant 2 \times 10^{-5}$
	Cyclohexane	4×10^{-2}	3.5×10^{-3}	$\leqslant 2 \times 10^{-5}$	$\leqslant 2 \times 10^{-5}$

As for the excited states involved, Tables 2 and 3 show that the photoreduction of compounds (2) and (3) has similar characteristics to the analogous reactions of compound (1) (*cf.* ref. 8), such as a strong wavelength effect on the quantum yield by direct irradiation, the possibility of sensitizing the reaction with hydrocarbons with $E_T \geqslant 60$ kcal mol^{-1}, and the efficient oxygen quenching.

The results presented here develop and clarify those obtained from the photochemical studies on compound (1), allowing conclusions of general validity to be reached for the photochemical behaviour of this type of azo-dyes, an appropriate model for commercially used monoazo-dyes. To be understood, the photochemistry of these dyes requires consideration not only of the lowest singlet and triplet states, but also of high lying states, sufficiently different in energy and character to have the time to play a significant role before being converted into S_1 and T_1. Scheme 2 gives a reasonable picture of the different reactivities.

The lowest excited singlet state undergoes highly efficient geometric isomerisation and thus only minimal intersystem crossing. No trace of hydrogen abstraction is detected. Thus, the chemical behaviour of this state does not differ qualitatively from the corresponding state of azobenzene, although the former corresponds to a highly allowed charge transfer transition and the latter to a forbidden n–π^* transition.

Also analogous to the azobenzene case is the sharp decrease in the isomerization quantum yield on decreasing the irradiation wavelength, which could be related, as has been shown for azobenzene itself,[11] to a change in the isomerization mechanism. As opposed to the case of the low-lying charge transfer state, the π–π^* singlet states corresponding to the weak benzenoid absorptions at shorter wavelength undergo efficient intersystem crossing to high-lying triplets. Indeed irradiation of the short wavelength bands has an effect similar to indirect photolysis with high energy sensitizers. The efficiency of internal conversion to S_1 is limited to at most 0.4, as shown by the low isomerization quantum yield.

Analogously to the lowest excited singlet, the lowest triplet state undergoes geometric isomerization as the only chemical reaction. As shown by the sensitization experiments, the efficiency of the triplet isomerization is $\geqslant 0.2$ and, as it can be

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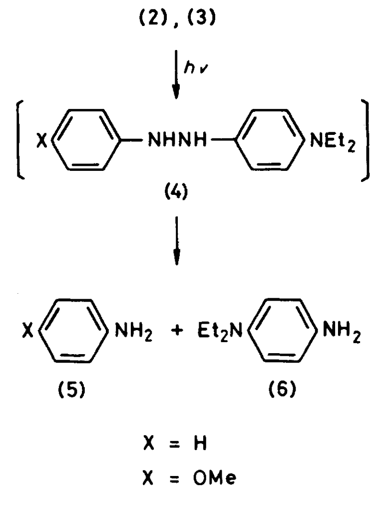
* As the excited states of (1) and other azo dyes are too short-lived to be intercepted by oxygen,[10] the quenching has rather to be attributed to the reaction of oxygen with the hydrazyl radicals.

† Another possibility is that the amines (5) and (6) arise from direct cleavage of the hydrazyl radical.



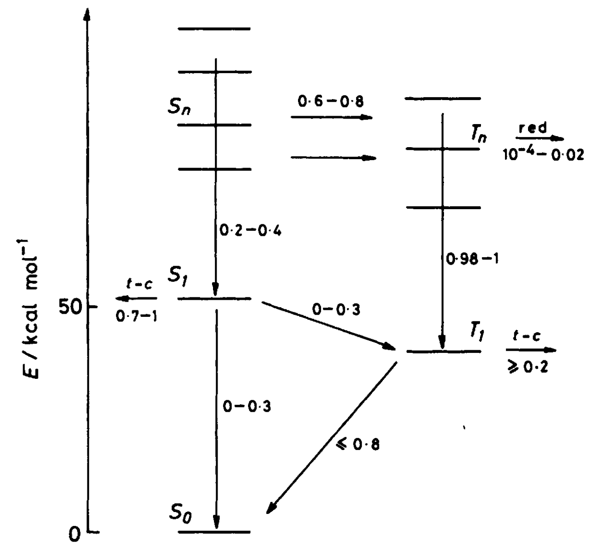
Scheme 1.

presumed that the energy transfer is efficient, not far from 0.2. Thus, it is significantly lower than that from the charge transfer singlet.

High-lying triplets (π–π^*) reached by intersystem crossing from S_n or energy transfer have some, although low, probability of abstracting hydrogen from the solvent, but the overwhelming process is the conversion to T_1, which is unreactive towards hydrogen abstraction. The low quantum yield of this reaction is not surprising in view of the short lifetime of the states involved [$\tau_{T_n} \leqslant \tau_{T_1} < 10^{-9}$ s, assuming that (2) and (3) do not differ much from compound (1)].[10] The fact that hydrogen abstraction is observed at all means that the rate of this process is very high and suggests a particular character for these states, such as mixing with a high lying n–π^* state. On the other hand, even $\pi\pi^*$ triplets of alkenes are good hydrogen abstractors.

The situation discussed above for the *trans*-form of these dyes is probably paralleled by the case of the *cis*-form. In fact irradiation at long wavelength causes no reduction even when a large amount of the *cis*-form has accumulated. However, in this case also hydrogen abstraction is observed from high lying triplets, which are reached by irradiation at short wavelength. The reduction quantum yield for the dye (3) is higher in cyclohexane than in the better hydrogen donor methanol, contrary to other cases.[8] Apparently this is due to the reduction of the *cis*-form which has accumulated in cyclohexane, and is more efficiently reduced than the *trans*-form. The involvement of high-lying triplets in this case also is confirmed by the fact that high-energy sensitizers promote both reduction and isomerization, while the low energy ones promote only the latter (see Table 2). Notice that for azobenzene only high-lying triplets of the *cis*-form have been reported to undergo hydrogen abstraction.[12]

In conclusion despite the great difference in the visible spectrum which makes them useful as dyes, monoazo-dyes have photochemistry qualitatively similar to that of the parent molecule azobenzene.* Of the two photoreactions, geometrical isomerization is very efficient, but is compensated for by the high rate of the thermal back conversion, so that photochromism is rare, except under very strong illumination, whereas the only irreversible photoreaction, *i.e.* reduction, is an inefficient process involving high-lying triplets not attained in practice, and moreover proceeds *via* radicals easily quenched by O_2. On the other hand, this light fastness is well known and is a necessity for practically useful dyes.



Scheme 2. Excited states of simple *trans*-monoazo dyes, such as compounds (1)—(3), with the efficiencies of reduction (red) and geometrical isomerisation (*t–c*) (the location of T_n is tentative, for T_1 see ref. 7)

Experimental

Materials.—Compounds (2) and (3) were prepared by standard methods and purified by column chromatography on alumina with toluene as eluant followed by recrystallization of the key fraction from toluene. The sensitizers were also of commercial origin and were purified by repeated crystallization, checking their purity by t.l.c. Spectroscopic grade solvents were used without further purification.

Photolysis Procedure.—Solutions (5×10^{-5}M) of either (2) or (3) were irradiated as follows.

(a) Solutions in a preparative reactor (300 ml) were irradiated by means of a low pressure mercury arc (Hanau TNN 15) after de-aeration by boiling and cooling under argon. The reaction was quenched at *ca.* 10% conversion and the concentrated photolysate examined by t.l.c. (silica gel), g.l.c. (OV 17 3% on a 2 m Gaschrom Q column), g.c.–m.s. (Du Pont 492-B spectrometer) with comparison with authentic samples of compounds (5a and b) and (6).

(b) Quantitative irradiation took place in spectrophotometric cuvettes (1 cm optical path) for air-saturated solutions or for solutions degassed by four or five freeze–degass–thaw cycles to *ca.* 5×10^{-6} Torr. The 313, 366, and 434 nm wavelengths were isolated from the collimated beam of a high pressure mercury arc (Osram 200 W/4) by means of interferential filters ($\Delta\lambda_{1/2}$ 9—12 nm). The light intensity was measured by ferrioxalate actinometry. The flux rate was 3.3 (at 254 nm), 2 (313), and 4.4 (434) $\times 10^{-7}$ einstein min^{-1} on a 3 cm^2 area. The bleaching of the dye was followed by absorbance spectroscopy (Cary 219 spectrophotometer). In the sensitized experiments the concentration was adjusted so that the light was completely adsorbed by the sensitizer. Reported values are the average of at least three separated determinations. In the case of the geometrical *trans–cis* isomerization the extent of the transformation was calculated by extrapolating the thermal *cis–trans* back conversion to zero time. It was noticed that the back conversion takes place somewhat irregularly, although

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* Compare with the work of Arnaud and Lemaire,[12–14] Bortolus and Monti,[15,16] and Rau.[11]

not to such an extent as to seriously affect the measurements. This phenomenon, which has already been reported in the case of azobenzene,[17] is due to a catalytic effect of the vessel walls and is attenuated but not eliminated by repeated washing of the cuvettes or ultrasonic cleaning.

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