Laser Flash Photolysis of Aromatic Azo-hydrazone Systems

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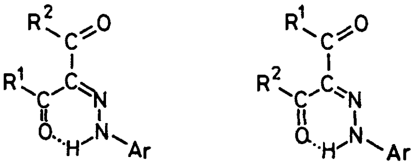
Laser flash photolysis using 347 nm excitation and pulse radiolysis have been used to study the transient species produced from solutions of a series of eight hydrazone compounds synthesised from substituted (R^1, R^2) 1,3-diones coupled to substituted (Ar) aromatic amines. Three classes of transient behaviour were found in hexane solution. Compound (8) gave a very short-lived transient ($t_{\frac{1}{2}}$ *ca.* 45 ns, $\lambda_{max.}$ 510 nm) which was identifed as a triplet species. The other three compounds from unsymmetrical dione derivatives gave short-lived transients ($t_{\frac{1}{2}}$ *ca.* 50—100 μs) in the spectral region 440—460 nm and long-lived transients ($t_{\frac{1}{2}}$ *ca.* 0.5—2.0 s) occurring at *ca.* 425 nm, whereas the four symmetrical derivatives ($R^1 = R^2$) gave only the short-lived transients in the region 450—470 nm. The lifetimes of the longer-lived transients were shown to be dependent on solvent polarity and added acid. It is proposed that the longer-lived transients are associated with isomerism about the C=N bond, induced by photoexcitation into the singlet excited state. Rate constants for quenching of various triplet species by three of the hydrazones were determined and shown to correlate with the triplet energy of the compounds being quenched. Assuming quenching occurred by electronic energy transfer the triplet energies of the hydrazones were estimated to lie in the range 150—190 kJ mol^{-1}. The photochemical breakdown products arising from extensive u.v. irradiation have been examined by chromatographic and spectroscopic techniques. It was shown that the compounds are relatively stable to irradiation above 330 nm.

THE compounds formed by reaction between arenediazonium salts and 1,3-dicarbonyl compounds like acetylacetone, benzoylacetone, and their derivatives have been shown to exist as intramolecularly hydrogen-bonded arylhydrazones rather than as the tautomeric azo-forms.[1] In addition, compounds formed using 1,3-diketones with different end-groups exist as two distinct stereoisomers (a) and (b).



(a) (1)-(9) (b)

The isolation of these isomers for a number of derivatives of 1-phenylbutane-1,3-dione has been reported recently.[2] Mitchell and Nonhebel found that the thermal interconversion of the isomers in deuteriochloroform to give an equilibrium mixture could be followed by i.r. and n.m.r. measurements, and the reaction was found to be susceptible to acid and base catalysis. Subsequently Courtot *et al.*[3] reported the changes in i.r., n.m.r., and u.v. characteristics of a similar series of compounds following displacement of the equilibrium position in solution by near-u.v. irradiation. We have also found[4] that the rate of interconversion of the uncatalysed system is enhanced by illumination with u.v. radiation.

It was therefore decided to examine in detail the photoreactions of this class of compound using both pulsed and continuous irradiation techniques.

The photochemistry of aromatic azo compounds has been reviewed by Griffiths,[5] the major reactions being *cis–trans* isomerisation, photocyclisation, and photoreduction; these reactions appear to proceed principally through excited singlet states. Despite considerable efforts[6] the triplet levels of azobenzene have not been observed by flash photolysis. However, thermal isomerisation of some *para*-donor–*para*-acceptor-substituted azobenzenes has been studied[7] by observing the relaxation to equilibrium following flash photolysis; sizeable solvent effects on isomerisation rates were observed. Laser flash photolysis has also been used to study the triplet states[8] and the *cis–trans* isomerisation[9] of nitrostilbene derivatives.

Isomerisation about the C=N bond is considerably faster than the equivalent processes with the azo or ethylene bond, and it was only with the availability of the flash photolysis technique that significant progress in studying such processes at room temperature became possible.[10] More recently studies of *cis–trans* (or *syn–anti*) photoisomerisation of 4-nitrophenylhydrazones of benzaldehydes[11] and pyridine-2-carbaldehyde[12] have suggested the involvement of singlet states in the direct photoisomerisation process, but triplet states are suggested as intermediates in the sensitised process.

Apart from the mechanism of tautomeric interconversion, our interest in the photoreactions of the arylhydrazones lies in their relationship to the commercially important yellow pigments of the arylamide class which are formed by coupling diazotised nitroanilines with the 1,3-diketone, acetoacetanilide. These pigments also exist in the hydrogen-bonded hydrazone form and their photochemical behaviour is of interest in relation to light stability (light fastness) studies. We have previously reported on the transient species derived from the pulse radiolysis and laser flash photolysis of anthraquinone dyes[13,14] and phthalocyanine pigments,[15] two other commercially important groups of colorants.

EXPERIMENTAL

The arylhydrazones were all prepared by coupling the appropriate diazonium salt with a 1,3-dicarbonyl compound. Details of m.p., purity, and i.r. and n.m.r. characteristics are reported elsewhere.[16] The u.v. absorption characteristics of the compounds studied here are listed in Table 1.

Transient species were produced and monitored by conventional flash photolysis (time resolution 20 µs) and laser flash photolysis (time resolution 25 ns) using for laser irradiation the frequency doubled ruby line at 347 nm (energies per pulse up to 400 mJ); details of the equipment have been given previously.[15] The pulse radiolysis experiments were carried out with a 9—12 MeV Vickers linear accelerator, using quartz cells of optical path 2.5 cm, as previously described by Keene.[17]

TABLE 1

Hydrazones of 1,3-diketones

Compound	R^1	R^2	Ar	$\lambda_{max.}$/nm (hexane)	$\lambda_{max.}$/nm (EtOH)
(1)	Me	Me	p-ClC_6H_4	365	365
(2)	Me	Me	p-$CH_3C_6H_4$	368	369
(3)	Me	Me	p-$CH_3OC_6H_4$	378	398
(4) *	Me	Ph	p-ClC_6H_4	368	365
(5) †	Me	Ph	p-ClC_6H_4	369	366
(6)	Me	Ph	p-$CH_3OC_6H_4$	368	400
(7)	Me	p-$NO_2C_6H_4$	Ph	369	367
(8)	Me	p-$NO_2C_6H_4$	p-$CH_3OC_6H_4$	312 (393) ‡	330 (410) ‡
(9)	Ph	Ph	p-ClC_6H_4	380	376

* Isomer (a). † Isomer (b). ‡ Figures in parentheses indicate a shoulder in the absorption band.

The solvents were all B.D.H. (either 'special for spectroscopy' or AnalaR) and were used as received. Argon (high purity), oxygen, and nitrous oxide were supplied by B. O. C.

The triplet energy (E_T) values were determined by energy transfer experiments [18] in which the enhanced rate of decay of the triplet of a donor molecule was measured in the presence of known concentrations of the hydrazone, acting as quencher.

Solutions of the above compounds were examined after continuous irradiation in a Hanovia 1 l photochemical reactor fitted with a medium pressure mercury arc. The photochemical breakdown products were analysed by preparative t.l.c. using silica gel plates. The eluant used to separate the products was toluene–ethyl acetate (2 : 1).

TABLE 2

Transient characteristics in hexane and ethanol solution

	Short-lived transients				Long-lived transient			
	In hexane		In ethanol		In hexane		In ethanol	
Compound	$\lambda_{max.}$/nm	Rate of decay $10^{-5}k/s^{-1}$	$\lambda_{max.}$/nm	Rate of decay $10^{-5}k/s^{-1}$	$\lambda_{max.}$/nm	Rate of decay k/s^{-1}	$\lambda_{max.}$/nm	Rate of decay k/s^{-1}
(1)	460	0.10	452	4.4				
(2)	455	0.10	470	4.4				
(3)	470	0.08	480	2.8				
(4)	455	0.12	455	1.4	421	1.4	436	1.7
(5)	455	0.12	*		421	1.4	*	
(6)	445	0.14	470	17.3	425	0.4	450	2.2
(7)	460	0.14	470	27.7	425	0.4	420	5.8
(9)	462	0.15	468	10.0				

* Isomer (5) is rapidly converted into (4) in a polar solvent.

RESULTS

Transient Species in Hexane.—Laser flash photolysis of the compounds studied gave three classes of behaviour: (i) compounds (1)—(3) and (9) produced single short-lived transients ($t_{\frac{1}{2}}$ *ca.* 50 µs) which were unaffected by the presence of oxygen; (ii) compounds (4)—(7) produced short-lived and long-lived ($t_{\frac{1}{2}}$ *ca.* 0.5—2 s) transients, both unaffected by oxygen; and (iii) compound (8) produced only a very short-lived transient ($t_{\frac{1}{2}}$ *ca.* 45 ns) which was quenched efficiently when oxygen was present in the solution. Figure 1 shows the typical transient difference spectra obtained for compound (6). The transients produced by laser-flash photolysis of 10^{-5}M solutions in hexane (Table 2) decay by first-order kinetics with the rate constants listed. At higher concentrations (*ca.* 10^{-3}M) the kinetics of decay of the short-lived species tended towards second-order behaviour.

Pulse radiolysis gave similar transient behaviour, although the lifetimes observed appeared to be dependent on the radiation dose. It was not possible to measure accurately the lifetimes of the long-lived transients on the pulse radiolysis apparatus.

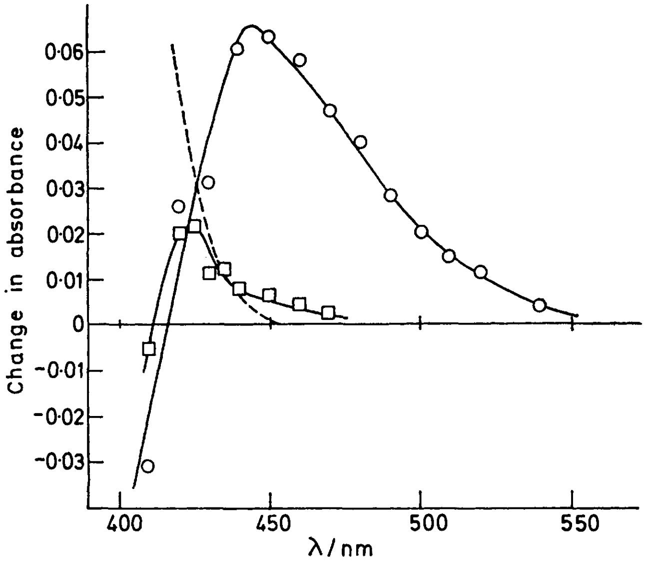


FIGURE 1 Difference spectra produced by laser-flash photolysis of compound (6) in hexane: — — — ground state absorption; ○ transient intermediate ($t_{\frac{1}{2}}$ *ca.* 50 µs); □ long-lived transient ($t_{\frac{1}{2}}$ *ca.* 2—3 s)

With the exception of compound (8), the lifetimes of the transients were unaffected by oxygen and nitrous oxide, and were not quenched by a triplet acceptor such as β-carotene. In addition the transients could not be produced by energy transfer from typical triplet sensitisers including biphenyl, 1,2-benzanthracene, and anthracene. However, the transient from compound (8) was quenched by oxygen and β-carotene with, in the latter case, the formation of the intense β-carotene triplet absorption ($\lambda_{max.}$ 520 nm, $t_{\frac{1}{2}}$ 5 µs). Confirmation that the transient from compound (8) was a triplet species was obtained by pulse radiolysis experiments when energy transfer from triplet biphenyl to compound (8) produced a transient with a spectrum identical to that obtained from laser flash photolysis (Figure 2).

Transient Species in Ethanol and Other Solvents.—Laser flash photolysis of the hydrazones in ethanol and other polar solvents gave transients with similar spectral characteristics to those observed in hexane. However, the relative yields of intermediates were substantially less than those obtained in hydrocarbon solvents, and the lifetimes were considerably shortened (Table 2). Bubbling the solutions with air, argon, and nitrous oxide had no effect, although saturation with oxygen did slightly lower the transient yields and further reduce the lifetime by a few microseconds. The influence of solvent polarity and viscosity on the lifetime of the short-lived transient of compound (4) was examined with the results shown in Table 3.

TABLE 3

The influence of solvent on the rate of decay of the short-lived transient of compounds (4) and (5)

Solvent	Transient decay rate constant $10^{-5}k/s^{-1}$
Hexane	0.11
Ethanol	1.4
Propan-2-ol	2.3
t-Butyl alcohol	6.9
Acetonitrile	6.9
Glycerol–ethanol (7 : 1)	1.7

The presence of trace amounts of acid added to both polar and non-polar solvents had no effect on the long-lived and the triplet transients, but dramatically shortened the lifetime of the short-lived transient. For example in hexane the lifetime was typically shortened from 50 μs to 2 μs and in ethanol from 5 μs to *ca.* 50 ns.

Energy Transfer Experiments.—As already indicated, addition of triplet quenchers had no effect on the hydrazone transients, with the exception of compound (8). However, all the hydrazones were able to quench other triplet species. For example, both anthracene and $Ru^{II}(bipy)_2Cl_2$ were excited into their triplet state by laser flash photolysis using 347 and 530 nm light respectively. On addition of the hydrazones at *ca.* 10^{-4}M concentration an enhanced rate of decay of the donor triplet was observed. However, we were unable to detect any sensitised triplet absorption over the range 300—1 000 nm for any of the hydrazones other than compound (8), despite using a wide range of triplet donors such as biphenyl, 1,2-benzanthracene, and duroquinone as well as anthracene and $Ru^{II}(bipy)_2Cl_2$.

By measuring the donor decay rate in the absence (k_1) and the presence (k_2) of known amounts of hydrazone acting as quencher (Q) we were able to measure the quenching rate constant (k_q) using relationship (1). The quenching

$$k_2 = k_1 + k_q\,[Q] \qquad (1)$$

constants for compounds (1), (4), (5), and (8) are listed in Table 4.

Plots of log k_q against the known triplet energy values (E_T) of the donor triplet species, were used [19] to obtain the triplet energy values of the hydrazones listed in Table 4.

Continuous Irradiation.—When solutions of the hydrazones in hexane and ethanol were subjected to irradiation from a medium pressure mercury lamp there was evidence that the compounds were slowly decomposed. For example for compounds (4) and (5) in hexane the absorption band at 370 nm decreased by 20% after 2—3 h irradiation with an appreciable increase in absorption below 340 nm.

However, this photodecomposition was eliminated if 330 nm ' cut-off ' filters were introduced to remove all the far-u.v. light. There was also no spectral change when the compounds were continually pulsed by the frequency doubled (347 nm, *E ca.* 300 mJ) ruby laser. These observations suggest that the hydrazone compounds are photochemically stable to light of wavelength 330 nm and above. Using the 240—280 nm region of the mercury arc emission and measuring the absolute intensity of radiation with the ferrioxalate actinometer, the quantum yield of photodecomposition of compounds (4) and (5) was estimated to be *ca.* 3 × 10^{-6}.

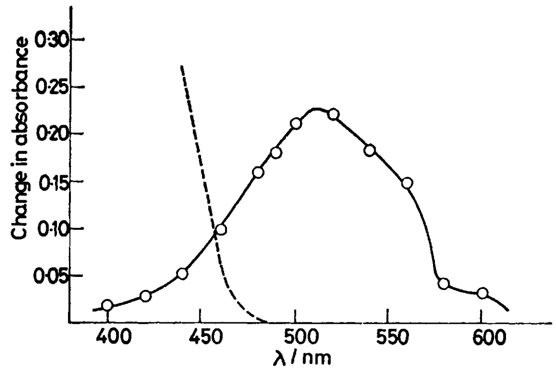


FIGURE 2 Triplet difference spectrum of compound (8) in hexane: --- ground state absorption; ○ triplet–triplet absorption

In a preliminary attempt to establish the nature of the photochemical breakdown products, a solution of compound (1) in alcohol was irradiated in the photochemical reactor for 12 h. The colour of the solution changed from a

TABLE 4

Rate constants for triplet energy transfer reactions, and estimated triplet energies for compounds (1), (4)—(5), and (8)

Triplet species being quenched	Triplet energy E_T/kJ mol^{-1}	k_q/dm^3 mol^{-1} s^{-1} Compound (1) in methanol	Compound (4)—(5) in hexane	Compound (8) in hexane
Naphthalene	254	5.3 × 10^9	1.7 × 10^{10}	6.0 × 10^9
Anthracene	171	2.3 × 10^9	2.1 × 10^9	4.8 × 10^8
Perylene	151	0.6 × 10^9	8.7 × 10^6	4.7 × 10^6
Chlorophyll b	131	0.4 × 10^9	10^6 (max)	10^6 (max)
Tetracene	123	0.2 × 10^9		
Chlorophyll a	117	0.08 × 10^9		
Estimated triplet energies (kJ mol^{-1})		150 ± 10	170 ± 10	190 ± 10

bright yellow to a brownish colour. The solution was evaporated to small volume and examined by t.l.c. using toluene–ethyl acetate (2 : 1) as the eluant. Three major bands were found, and under u.v. illumination another five minor products were observed.

Analysis by i.r. spectroscopy showed that one of the major bands was due to the original starting compound. Neither of the other two prominent bands showed the sharp band at 1 530 cm^{-1} characteristic of the hydrazone compounds; one was an aromatic derivative and the other aliphatic in nature. Both the photoproducts showed characteristic N–H stretch bands, and so it appeared that the major photoproducts resulted from cleavage of the $\rangle N-N\langle$ bond.

DISCUSSION

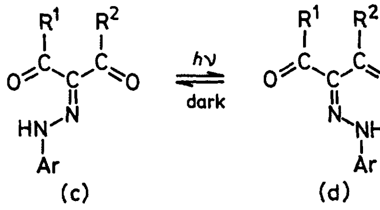
As already indicated, the transient species produced by laser flash photolysis and pulse radiolysis of compound (8), although short lived ($t_{\frac{1}{2}}$ *ca.* 41 ns) has all the characteristics associated with a triplet species, *viz.* (i) it decays by first-order kinetics; (ii) it is quenched by oxygen at the diffusion controlled rate; (iii) its formation is sensitised by triplet energy transfer from donor species; (iv) it is quenched by acceptors (*e.g.* β-carotene), with the sensitised formation of the acceptor triplet.

This behaviour is in contrast to all the other compounds studied which showed much longer-lived transients unaffected by oxygen and other triplet acceptors. However, the hydrazones do quench triplet donors at rates which enabled us to determine the triplet energy level of a number of the hydrazones, although no transients could be observed. The failure to observe transients in these experiments indicates that either the triplets have very weak absorption or the lifetimes are very short and they decay as rapidly as they are formed. Similar behaviour has been reported by Smith *et al.* for azomethine dyes [20] in which it is suggested that flexibility about the C=N bond provides a facile path for radiationless decay of the excited states of the dyes. The E_T values for the hydrazones (*ca.* 170 kJ mol^{-1}) show a small variation with substituent.

The above facts suggest that the hydrazone transients observed in hexane and alcoholic solvents are produced *via* the singlet excited state and that the triplet state is not involved. For the compounds derived from symmetrically substituted diketones (acetylacetone and dibenzoylmethane) only the short-lived transient intermediate is observed, whereas with the unsymmetrical benzoylacetone derivatives both short- and long-lived transients are produced.

The long-lived transients would appear to be associated with isomerisation about the photoexcited C=N bond, as in the Scheme. This, of course, represents the conversion of isomer (a) into (b), except we have not shown the hydrogen-bonded structure as undoubtedly this must be broken on photoexcitation to allow the rotation about the CN bond to occur. The lifetimes of the transients in hexane (0.5—2.0 s) are similar to those reported recently for the photoisomerisation of azomethine dyes derived from benzoylacetanilides [21] and lie in the range reported for the *cis–trans* isomerisation of benzylideneaniline and its derivatives.[10] Solvent effects on the decay rates are also similar to those reported for the azomethine dyes.[21]

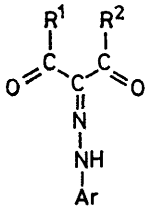
The absorption maxima of the long-lived transients are determined by the difference in the absorption curves of the (a) and (b) isomers. This was confirmed for the thermal isomerisation of compound (5), by using conventional spectrophotometry to record the difference spectrum between a catalysed and an uncatalysed solution of the compound in hexane. The difference spectrum developed a peak at 421 nm, identical in position to the transient produced by photoexcitation of the same compound. Courtot *et al.*[3] also reported difference spectra with peaks similarly displaced from the ground state λ_{max}.



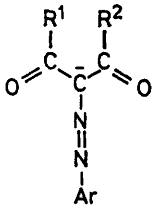
SCHEME

The absence of the long-lived transients from the symmetrically substituted derivatives is further evidence in support of the above assignments. However, both the symmetrical and the unsymmetrical derivatives give short-lived transients, which decay at the same rate as the long-lived transients grow in. As indicated previously, these transients are not triplets and therefore must be associated with some species intermediate between the excited singlet and the displaced *cis–trans* equilibrium. Many different structures could be written for such intermediates, although in the present situation we have to pay regard to the following observations: (i) the lifetimes of the intermediates are sensitive to solvent polarity implying that they have polar configurations; (ii) the isomers (4) and (5) give rise to transients in hexane with identical properties; (iii) the lifetime is sensitive to the presence of acid—this must in some way be associated with the observed acid-catalysis of the thermal interconversion.[2]

One possibility is that the short-lived intermediate is a species (e) with a linear configuration about the N–N bond, or even a carbanion intermediate (f) with an azo configuration. The lifetime of the latter would un-



(e)



(f)

doubtedly be influenced by added H^+ and be sensitive to solvent polarity. The spectrum of these transients is shifted to longer wavelengths than the long-lived transients which also suggests the formation of a more conjugated structure or even an ionised system. It is interesting to note [22] that the protonation of 1-(phenylazo)-2-naphthol causes a shift in the hydrazone $\rightleftharpoons$ azo equilibrium and is associated with a bathochromic shift of *ca.* 30 nm.

Several possible mechanisms have been considered by McCarthy [23] for geometrical isomerism at the C=N bond. The most favoured mechanisms include one involving a heterolytic rupture of the bond and passage through a polar transition state, whilst the other is a ' lateral shift ' mechanism in which a linear transition state is involved. This is said to resemble inversion in ammonia or trisubstituted amines in which nitrogen adopts linear *sp* bonds, the π bond remains intact, and the unshared pair occupies the perpendicular *p*-orbital on the nitrogen atom.

In the present study the lifetimes of the short-lived transients in hexane are little affected by substitution either in the dione or in the aromatic amine, although in ethanol solution compounds (6) and (7) show an order of magnitude decrease in lifetime. Compound (6) has an electron-donating group (OCH_3) in the aromatic amine, while compound (7) has a electron-withdrawing group (NO_2) in the aromatic ring of the substituted dione. Combination of both these substituent effects in compound (8) appears to prevent isomerisation about the C=N bond but leads instead to triplet formation. However, the ground state spectrum of compound (8) is quite unique indicating that the singlet-excited state of this compound is of different character from the others studied.

These preliminary studies of the influence of substituent on photoisomerisation about the C=N bond of the aromatic hydrazones suggest that such isomerisation is influenced by electron movement from the dione to the aromatic amine part. However, further studies of the influence of substitution are required before more definite conclusions about the mechanism of photoisomerism can be made. Certainly, the absence of triplet-sensitised photoisomerism is different behaviour from that reported for phenylhydrazones,[11,12] and the formation of a triplet species to the exclusion of photoisomerisation for compound (8) indicates that intersystem crossover to the triplet state is an alternative to photoisomerism as a decay route from the excited singlet state.

Although irradiation at 347 nm into the S_1 state readily induced the reversible photoisomerisation reported, the continuous irradiation studies indicated that excitation into higher singlet states was necessary to induce photodecomposition. We hope to extend our studies to the arylamide pigments derived from acetoacetanilide in which two hydrogen-bonded rings exist. It will be interesting to see what effect this has on photoisomerisation and photodecomposition.

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