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Photoreduction of electron-deficient azaarenes by di- and trialkylamines

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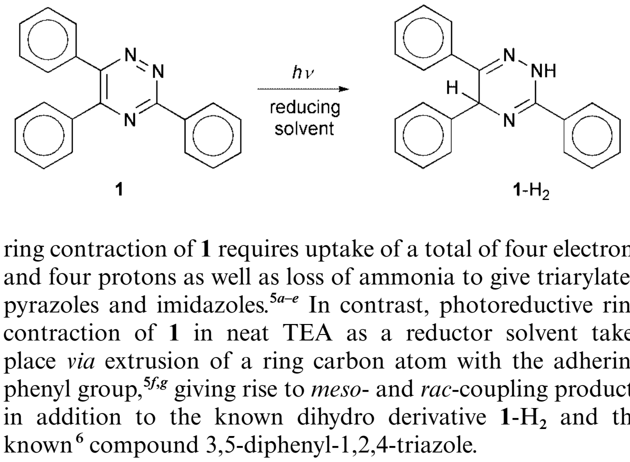
The photophysical and photochemical properties of several electron-deficient azaarenes were studied by pulsed (λ_{exc} = 308 nm) and steady-state photolysis. The triplet state characteristics of 3,5,6-triphenyl-1,2,4-triazine (**1**), 3-phenyl-1,2,4-benzotriazine (**2**), 3-phenyl-1,2,4-phenanthro[9,10-*e*]triazine (**3**) and tetraphenylpyrimidine (**4**) and, for comparison, of phenazine in several solvents are described. The quantum yield of triplet formation is substantial for **1**–**4** in solution at room temperature, whereas the fluorescence is negligible. Phosphorescence in glassy media at −196 °C and efficient formation of singlet molecular oxygen at 25 °C were detected. The triplet state of **1**–**3** is quenched by triethylamine (TEA) and other tertiary amines; the rate constant for quenching by TEA is $k_q = (0.9–1.5) \times 10^8\ M^{-1}\ s^{-1}$ in acetonitrile and slightly smaller in cyclohexane. Quenching the triplet state of **1**–**3** by 1,4-diazabicyclo[2.2.2]octane (DABCO) is more efficient and k_q is only slightly lower than the diffusion-controlled limit. The secondary transient of **1**–**3** in the presence of DABCO is ascribed to the radical anion, whereas with TEA or diethylamine (DEA) H-adduct radicals with maxima around 400 nm were observed. These radicals and the corresponding $Et_2N–{}^{\bullet}CHMe$ radical subsequently undergo a slow termination reaction yielding the corresponding dihydroarenes. The mechanisms of the two subsequent reduction reactions are discussed. The dihydroheterocycles are thermally converted back to the azaarenes on addition of oxygen.

Introduction

In comparison to the wealth of information available on the photoreactivity of carbocyclic arenes, less is known about the photoreactions of six-membered electron-poor azaarenes containing two or more nitrogen atoms.[1] Reports have, for example, appeared on photofragmentations of 1,2,4,5-tetrazines,[2a,b] nitrogen extrusion from fluorinated 1,2,3-triazines,[2c,d] on the photoarylation of halo-1,3,5-triazines,[2e] on isomerizations of various pyridazines[2f–h] and pyrazines,[2g] photodehalogenations[2i,j] and ring opening reactions of 4-aminopyrimidines,[2k,l] on pyrazine and pyrimidine photooxygenations,[2m] photosubstitution of pyrazines,[2n] quinoxaline and phenazines,[2o–q] and intramolecular cyclizations of a dipyrazinylethene[2r] and 2-styrylquinoxaline.[2s] Intramolecular hydrogen-abstraction following n,π* excitation has been observed for 4-alkylpyrimidines[3a] and 2-alkylpyrazines.[3b] Photoreductions by typical hydrogen atom donors have been reported for pyrazine and pyridazine,[4a] quinoxalines,[4b,c] phthalazine,[4d] and benzo[*c*]cinnoline;[4e,f] the latter compound has also been photoreduced by triethylamine (TEA).[4g]

Recently, interest has focused on photoreductions and photoreductive ring contractions of the 3,5,6-triaryl-1,2,4-triazine system,[5] brought about by photolysis of the parent 3,5,6-triphenyl-1,2,4-triazine (**1**)[5c–e] (or its 2,5-dihydro analogue **1a** in the form of its hydrohalogenide)[5a–e] in various alcohols. The product of photoreduction of **1** is always its 2,5-dihydro derivative (**1**-H_2). There is also indirect evidence for the formation of a 1,4-dihydrotriazine intermediate in one case.[5d] Photoreductive ring contraction of **1** requires uptake of a total of four electrons and four protons as well as loss of ammonia to give triarylated pyrazoles and imidazoles.[5a–e] In contrast, photoreductive ring contraction of **1** in neat TEA as a reductor solvent takes place *via* extrusion of a ring carbon atom with the adhering phenyl group,[5f,g] giving rise to *meso*- and *rac*-coupling products in addition to the known dihydro derivative **1**-H_2 and the known[6] compound 3,5-diphenyl-1,2,4-triazole.



It seemed desirable to get a deeper insight into the photophysical and photochemical properties of arylated 1,2,4-triazines and other electron-poor azaarenes with special emphasis on their light induced reactions with aliphatic amines. Thus, besides **1**, 3-phenyl-1,2,4-benzotriazine (**2**), 3-phenyl-1,2,4-phenanthro[9,10-*e*]triazine (**3**), tetraphenylpyrimidine (**4**) and phenazine (**5**)[7] were chosen for this study. Upon photolysis in oxygenated alcoholic or aqueous solution, **5** undergoes introduction of an oxy function at C-1.[2p]

The early literature on photoreduction of various classes of compounds including some electron-poor azaarenes by amines has been reviewed.[8] Interest is heavily concentrated on the

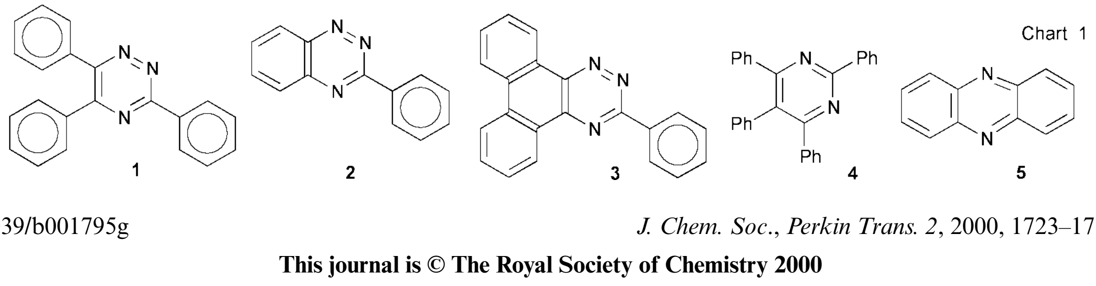


Chart 1

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action of amines on excited ketones[9–11] and aromatic hydrocarbons (especially stilbene),[12] and on functional group reductions or replacements.[13,14] Most work on ketone photoreduction has been centered on the interaction of excited benzophenone (BP) with *N*,*N*-dimethylaniline (DMA)[8,9a–c] or various other amines.[8,9d,e] When sterically hindered amines were used, a distinct dependence on the nature of the solvent in the partitioning between back electron transfer and proton transfer within the contact radical ion pair (CRIP) was noted.[9e] The reactions observed are generally interpreted as being initiated by electron transfer from the amine to the excited ketone (which is the mechanism of ketone triplet quenching in these cases) generating a CRIP, followed by proton transfer within the said pair to generate a radical pair.[8,9a–e] Quenching rate constants have become available for the interaction of $^3BP^*$ with several primary and tertiary amines.[8] The formation of ketyl radicals from BP and other aromatic ketones with TEA, which requires intrapair proton transfer, does not correlate, however, with the quenching rate constants,[9f,g] but depends on the nature of the lowest excited ketone triplet state (n,π*, π,π* or CT)[9g] and, if the nature of the amine is varied, on structural factors in the reductant.[9f] In this context it seems noteworthy that fluorenone (low lying π,π* triplet), while unreactive towards alkanes, alcohols and ethers, is readily reduced by tertiary alkyl- or aralkylamines.[9h] For further literature with TEA,[10–19] see below.

Materials and methods

The azaarenes used were prepared by literature procedures:[5a,20] 3,5,6-triphenyl-1,2,4-triazine (**1**), mp 145–147 °C (lit.[20a] mp 145–146 °C); 3-phenyl-1,2,4-benzotriazine (**2**), mp 124 °C (lit.[20b] 122–123 °C); 3-phenyl-1,2,4-phenanthro[9,10-*e*]triazine (**3**), mp 186 °C (lit.[5a] 187 °C); 2,4,5,6-tetraphenylpyrimidine (**4**), mp 190–191 °C (lit.[20c] 191–192 °C). Phenazine (**5**) was available as a commercial sample. The amines were purified by distillation: TEA, diethylamine (DEA), tripropylamine (TPA) or used as purchased: tributylamine (TBA) and 1,4-diazabicyclo[2.2.2]-octane (DABCO). The solvents (Merck) were of the purest spectroscopic quality. The molar absorption coefficient at the maximum of **1**, **2** and **3** is $\varepsilon_{262} = 5.1 \times 10^4$, $\varepsilon_{258} = 3.7 \times 10^4$ and $\varepsilon_{275} = 2.9 \times 10^4$ M^{-1} cm^{-1}, respectively. The absorbance of neat TEA at 308 nm is *ca.* 1 in a 1 cm cell, and for low concentrations (<10 M) this has only a minor effect on the excitation of the triazines. The absorption spectra were monitored on spectrophotometers (Perkin-Elmer, 554 and HP, 8453) and the emission spectra on a spectrofluorimeter (Perkin-Elmer, LS-5). A second longer-lived phosphorescence band of **1** with $\tau_p > 50$ ms and a broad band (460–560 nm) is probably due to an impurity since, unlike the shorter-lived phosphorescence, the excitation spectrum does not contain the band at longer wavelengths, *i.e.* above 350 nm.

An excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns and energy <100 mJ) and a Nd laser (J.K. Lasers, pulse width: 15 ns and energy: <30 mJ) were used for excitation at 308 and 354 nm, respectively.[21] Unless otherwise indicated $\lambda_{exc} = 308$ nm was used, except for **5** where $\lambda_{exc} = 354$ nm. The absorption and phosphorescence signals were measured with two digitizers (Tektronix 7912AD and 390AD). Typically, absorbances of 2 were used for $\lambda_{exc} = 308$ nm. The increase in absorbance at the triplet absorption maximum (λ_{TT}), at the end of the pulse, for optically matched conditions is almost linear with the incident laser intensity (I_L). The slope is taken as the relative quantum yield for triplet population (changes in the T–T absorption coefficient, due to variation of the solvent, are assumed to be negligible). The first half-life ($t_{1/2}$ after subtraction of a constant part in most cases) was found to depend strongly on the amount of traces of oxygen and the presented values refer to those after vigorous bubbling by argon. Note that this coloured product formation can even be slightly enhanced by the analyzing light (on an even longer time scale). This, however, was prevented by appropriate filters.

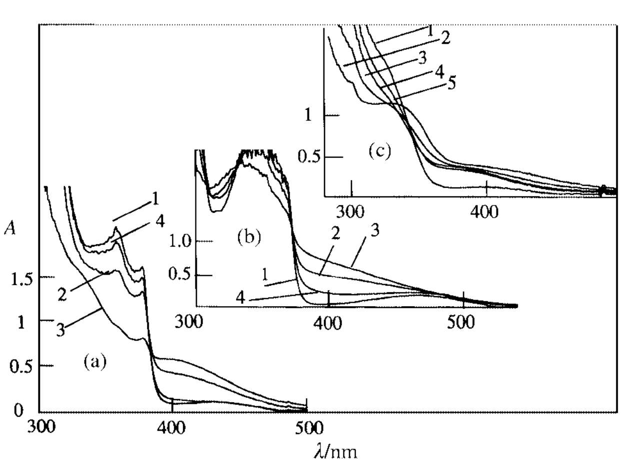


Fig. 1 Absorption spectra in argon-saturated cyclohexane in the presence of TEA (0.01, 0.03 and 0.1 M, respectively) of (a) **3**, (b) **2** and (c) **1**; prior to (curve 1) and after excitation by 308 nm (2 and 3 for a,b refer to 10 and 20 pulses, respectively) and subsequent purging with oxygen (4; c: 3,4,5: 1 min interval).

Phosphorescence of singlet molecular oxygen at 1269 nm was detected after the pulse using a cooled Ge detector (North Coast, EO 817FP), silicon and interference filters and an amplifier (Comlinear, CLC-103) as described elsewhere.[22] The signal, which can be overlapped by fluorescence and/or scatter, was extrapolated to the end of the 20 ns pulse (I_Δ). The observed lifetime is $\tau_\Delta = 22$–25, 24–28 and 60–75 µs in cyclohexane, toluene and acetonitrile, respectively. At a fixed laser intensity I_Δ was found to show a linear dependence on the absorbed energy, being proportional to $(1–10^{-A})$ and on I_L with a curvature at higher intensities; the slope of the latter plot is denoted by q_Δ. The quantum yield of formation of $O_2(^1\Delta_g)$ in toluene was obtained from q_Δ values using optically matched solutions ($A_{308} = 0.8$) and 2-acetonaphthone as reference $\Phi_\Delta^{ref} = 0.84$.[23] For the values in other oxygen-saturated solvents a correction has to be applied using the rate constant k_r for radiative deactivation of $O_2(^1\Delta_g)$ relative to that in benzene (k_r°): $\Phi_\Delta = \Phi_\Delta^{ref} \times q_\Delta/q_\Delta^{ref} \times k_r^\circ/k_r$. The k_r/k_r° ratios taken from the literature are 0.96 and 0.30 in toluene and acetonitrile, respectively.[24] Based on separate measurements with the reference $k_r^\circ/k_r = 0.6$ in cyclohexane rather than 0.44 was used.

For photoconversion the 308 nm pulse or the 366 nm line of a 1000 W Xe–Hg lamp combined with a monochromator were used. The concentration was adjusted such that the absorbance (in a 1 cm cell) was 1–3 at λ_{irr}. The conversion was carried out after vigorous bubbling by argon prior to and during irradiation. The effect of converting the azaarene dihydro forms thermally back on addition of oxygen was found to occur within a few seconds or minutes for all cases. The measurements (unless otherwise specified) refer to 25 ± 2 °C.

Results

Photoconversion

Fluorescence is negligible for **1**–**4** in solution at room temperature, but photoconversion can lead to an emission. Upon flashing, with 308 nm laser pulses, **3** in argon-saturated cyclohexane (Fig. 1a) or acetonitrile in the presence of TEA (0.01 M), the absorption at 280–380 nm decreases and a new band with a maximum at 400 nm is formed. In addition, a structured fluorescence band with a main maximum at 390 nm appears (not shown), its intensity increases with the irradiation time. Thus, the fluorescence originates from the photoproduct absorbing at 300–400 nm. The conversion is efficient, but this photoproduct is only stable if traces of oxygen are excluded. A green

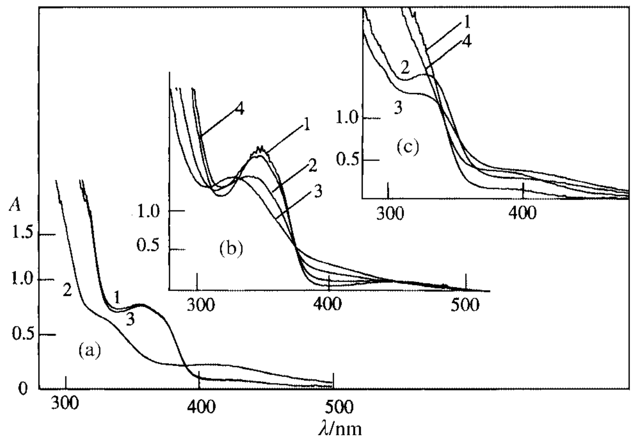


Fig. 2 Absorption spectra in argon-saturated acetonitrile in the presence of TEA (1 M) of (a) **3**, (b) **2** and (c) **1**; prior to (curve 1) and after excitation at 308 nm (2 and 3 for b,c refer to 10 and 20 pulses, respectively) and subsequent purging with oxygen (4; a: 3).

emission with a maximum at 510 nm for the photoproduct of **3** is tentatively attributed to phosphorescence.

UV excitation of **2** and TEA (0.03 M) in argon-saturated cyclohexane (Fig. 1b) and acetonitrile leads to a new band with absorption maxima at 320 and 400 nm. For **1** and TEA (0.1 M) in cyclohexane (Fig. 1c) and acetonitrile corresponding effects were observed. In these cases, a maximum photoconversion was achieved under careful exclusion of oxygen and the photoproduct, which is observed above 280 nm, converts thermally back on addition of oxygen. This is reminiscent of the photoreduction of **5** in benzene by TEA, in which it has been reported that 5,10-dihydrophenazine immediately reverts back to **5** upon exposure to the atmosphere.[7a]

Essentially the same spectral changes and efficiency were found for **1**–**3** and TEA (Fig. 2) or DEA at high concentrations (1 M). In fact, the increase in absorption at longer wavelengths, as a measure of the relative quantum yield of photoconversion, increases in acetonitrile with [TEA] or [DEA] in the 0–0.1 M range and remains then almost constant up to concentrations of 1 M or more. Efficient back-conversion, when the solutions were afterwards saturated by oxygen, demonstrates the reversibility of the systems, at least to a major extent.

Virtually the same photoconversion was achieved for **1**–**3** in TEA upon irradiation at 366 nm, where the dihydro compounds (later generally termed AH_2 as dihydro derivatives of an acceptor A) as major products of **1** in DEA and TEA and **3** in DEA have been isolated.[25] The absolute quantum yield of conversion of **1** is 0.10 in cyclohexane in the presence of 0.7 M TEA and 0.17 in neat TEA. Photoconversion for **1**–**3** in cyclohexane with [TEA] (0.3 M) at $\lambda_{irr} = 436$ nm and efficient back-conversion, when the solutions were afterwards saturated by oxygen, indicates that photoreduction also occurs upon irradiation into the long wavelength band of the azaarenes.

The triplet state of 3,5,6-triphenyl-1,2,4-triazine (1)

The T–T absorption spectrum of **1** shows a maximum at 400 nm and levels off at 700 nm. The initial spectrum in argon-saturated acetonitrile is not changed on addition of DABCO at low concentration (3 mM, see Fig. 3c). The formation of the triplet state occurs within the pulse width of 20 ns ($\lambda_{exc} = 308$ nm), the decay in the absence of an amine is first-order and the lifetime is $\tau_T = 0.7$ µs. The triplet state is quenched by oxygen, the rate constant for triplet quenching is $k_{ox} = 3 \times 10^9$ M^{-1} s^{-1}. In cyclohexane and ethanol the features of the triplet state are similar (Table 1) and no secondary transient appears.

The triplet nature of the observed transient is also confirmed by the result that the T–T absorption spectrum in ethanol at low temperatures, *e.g.* at −150 °C, is very similar to that at 24 °C. The temperature dependence of the reciprocal triplet lifetime is shown in Fig. 4. This illustrates a fast relaxation in fluid ethanol and a much longer value in the rigid matrix. At −150 °C the decay is mixed order with $t_{1/2} \approx 30$ µs. Phosphorescence in ethanol at −196 °C was detected in low quantum yield ($\Phi_p = 0.01$) with a phosphorescence lifetime of $\tau_p \approx 2$ ms and a maximum at 520 nm (Table 2), the triplet energy is $E_T \approx 240$ kJ mol^{-1}.

Table 1 T–T absorption maxima of the azaarenes **1**–**5**, triplet lifetime and rate constant for quenching by oxygen[a]

Azaarene	Solvent	λ_{TT}[b]/nm	τ_T/µs	10^{-9} k_{ox}[c]/ M^{-1} s^{-1}
1	Cyclohexane	400	0.8	2
	Ethanol	410	0.5	3
	Acetonitrile	410	0.7	3
2	Cyclohexane	$\underline{330}$,420	3	2
	Ethanol	$\underline{330}$,420	3	
	Acetonitrile	$\underline{330}$,420	3	2
3	Cyclohexane	$\underline{340}$,430	10	1
	Ethanol	$\underline{340}$,420	12	2
	Acetonitrile	$\underline{335}$,420	10	1
4	Cyclohexane	440	20	3
	TEA	440	20[d]	
	Ethanol	440	10	3
	Acetonitrile	440	10	3
5	Cyclohexane	440	8	3
	Acetonitrile	440	5–8	2

[a] In argon-saturated solution, $\lambda_{exc} = 308$ nm. [b] Main band underlined. [c] Using air- and oxygen-saturated solution. [d] At low pulse intensity.

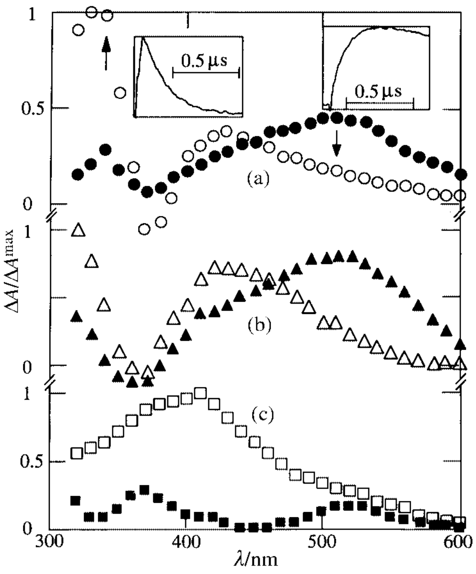


Fig. 3 Transient absorption spectra in argon-saturated acetonitrile in the presence of DABCO (3 mM) at 30 ns (open symbols) and 1 µs (full symbols) after the 308 nm pulse for (a) **3**, (b) **2** and (c) **1**; insets: kinetics for **1** at 340 nm (left) and 520 nm (right).

On addition of DABCO to **1** in argon-saturated acetonitrile at room temperature the triplet lifetime is reduced and the first-order rate constant (k_{obs}) shows a linear dependence on the DABCO concentration. The slope of this plot is $k_q \approx 3 \times 10^9$ M^{-1} s^{-1}; *i.e.* triplet quenching by DABCO is only slightly below the diffusion-controlled limit. A remaining weak transient with a first half-life of $t_{1/2} < 5$ µs in the 470–540 nm range was detected (Fig. 3c), which should be assigned to the radical anion of the azaarene (see Discussion).

The presence of TEA in cyclohexane (Fig. 5a) or acetonitrile (Fig. 5b) gives rise to a longer lived transient with a maximum at 370 nm after quenching of the triplet state. The k_{obs} value depends linearly on [TEA], the rate constant for triplet quench-

Table 2 Phosphorescence maxima of the azaarenes **1**–**4**, quantum yield and lifetime[a]

Azaarene	Solvent[b]	λ_{max}/nm	Φ_p	τ_p/ms
1	MCH	522	0.01	
	Ethanol	518	0.01	2 (<1)[c]
2	MCH	500	<0.001	
	Ethanol	500,525	<0.001	1
3	MCH	533,566,593	0.06	
	Ethanol	540,566,594	0.05	5 (2.5)
4	MCH	463,488	0.1	
	Ethanol	464,489	0.2	500 (>200)

[a] At −196 °C, λ_{irr} = 290 nm. [b] MCH is methylcyclohexane. [c] Values in parentheses refer to absorption at −160 °C, λ_{exc} = 308 nm.

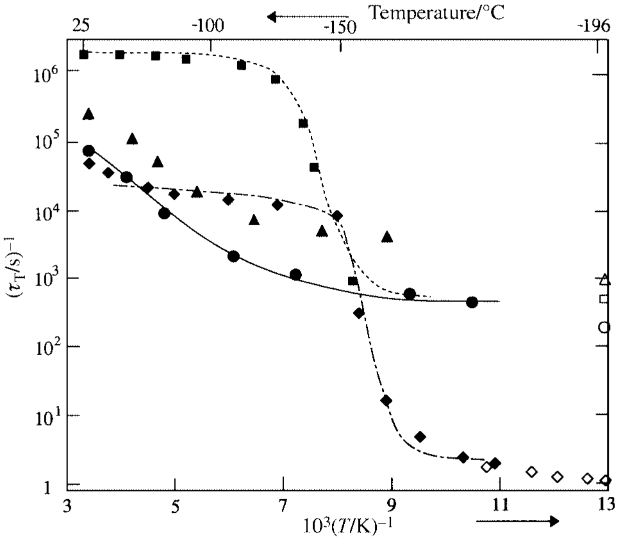


Fig. 4 Semilogarithmic plot of $1/\tau_T$ (full symbols) *vs.* $1/T$ for **1** (squares), **2** (triangles), **3** (circles) and **4** (diamonds) in argon-saturated ethanol; open symbols refer to τ_p.

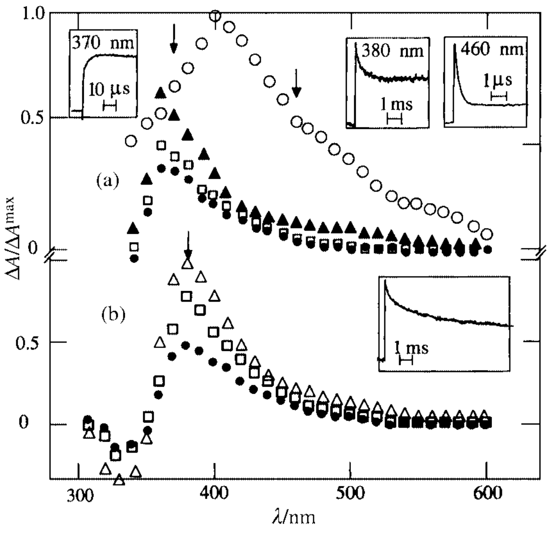


Fig. 5 Transient absorption spectra of **1** under argon (a) in cyclohexane in the presence of TEA (0.1 M) at 30 ns (○), 10 μs (▲), 1 ms (□) and 0.1 s (●) after the 308 nm pulse and (b) in acetonitrile and TEA (1 M) at 1 μs (△), 1 ms (□) and 1 s (●); insets: decay kinetics (a) at 370, 380 and 460 nm (from left to right) and (b) at 390 nm.

ing (slope in Fig. 6) is $k_q = 9 \times 10^7$ M^{-1} s^{-1} in acetonitrile and 3×10^7 M^{-1} s^{-1} in cyclohexane. The half-concentrations, *i.e.* the [TEA] values for 50% of triplet quenching, were calculated (using the τ_T and k_q values) to be $[TEA]_{1/2}$ = 42 and 16 mM in cyclohexane and acetonitrile, respectively. The remaining absorption contains essentially two parts which have only slightly different spectra (Fig. 5). The relative absorption increase in acetonitrile at 380 nm after triplet quenching, *e.g.* at 10 μs, *vs.* log [TEA] shows a characteristic sigmoidal behavior, approaching a maximum value (Fig. 7). The [TEA] value of *ca.* 20 mM, at which the curve is 50% of the maximum, is close to the above $[TEA]_{1/2}$.

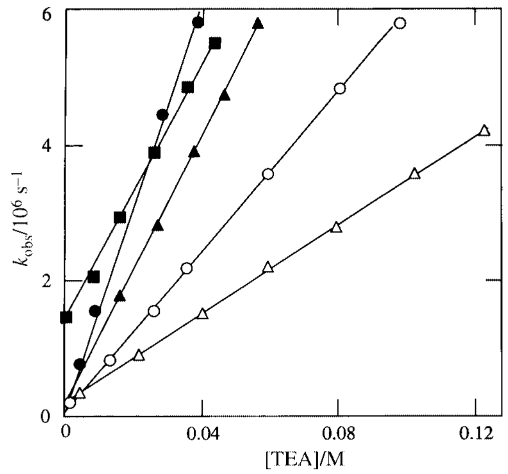


Fig. 6 Rate constant for triplet decay as a function of [TEA] for **1** (squares), **2** (triangles) and **3** (circles) in cyclohexane (open symbols) and acetonitrile (full symbols).

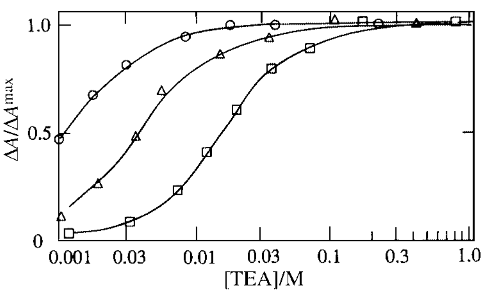


Fig. 7 Relative absorption increase at 400 nm at 100 μs after the pulse *vs.* [TEA] for **1** (squares), **2** (triangles) and **3** (circles) in acetonitrile.

The triplet state of 3-phenyl-1,2,4-benzotriazine (2)

The T–T absorption spectrum of **2** in cyclohexane or acetonitrile with maxima at 330 and 420 nm and a weak bleaching at 370 nm and the rate constant for quenching by oxygen are similar to those of **3**, but the triplet lifetime is longer (Table 1). The temperature dependence of the reciprocal triplet lifetime, as shown in Fig. 4, supports the triplet assignment. Phosphorescence of **2** in glassy ethanol at −196 °C shows $E_T \approx 240$ kJ mol^{-1} and $\tau_p \approx 1$ ms. The rather short-lived transient ($t_{1/2} \approx 3$ μs) in the presence of DABCO at room temperature (Fig. 3b) is assigned to a radical anion of **2**. Note that the photoreaction causes a build-up at 480–600 nm since the ε value of this species is larger than that of the triplet precursor. The build-up kinetics are first-order, the rate constant increases linearly with [DABCO] and $k_q = 1.5 \times 10^{10}$ M^{-1} s^{-1} was measured from the slope.

The rate constants for triplet quenching by TEA in cyclohexane and acetonitrile are $k_q = 3 \times 10^7$ and 1×10^8 M^{-1} s^{-1}, respectively (Table 3). The $[TEA]_{1/2}$ values are 10 and 3 mM, respectively. The secondary transient in the presence of TEA has a minimum around 350 nm, one maximum below and a more easily accessible one at 380–400 nm in cyclohexane (Fig. 8a) and acetonitrile (Fig. 8b). On addition of water (5 M) to acetonitrile the k_q value becomes three times smaller. The relative absorption increase in acetonitrile at 400 nm after triplet quenching *vs.* log [TEA] also shows sigmoidal behavior (Fig. 7). The [TEA] value at which the curve is 50% of the maximum is similar to the above $[TEA]_{1/2}$ of 3 mM.

Table 3 Rate constant k_q ($\times 10^7$ M^{-1} s^{-1}) for triplet quenching of the azaarenes **1**–**5** by electron donors[a]

Donor	Solvent	1	2	3	4	5[b]
DABCO	Acetonitrile	300	1500	800	<0.2	
	Acetonitrile[c]		200			
TEA	Cyclohexane	3	3	6		0.2
	Acetonitrile	9	10	15	<0.002	2
	Acetonitrile[c]		3	4		
DEA	Acetonitrile	7	12	14		
TPA	Cyclohexane	2	3	1.5		<0.6
	Acetonitrile	10	8	9	<0.01	1
TBA	Cyclohexane	2	3			0.3
	Acetonitrile	12	8			2

[a] In argon-saturated solution, λ_{exc} = 308 nm. [b] Using λ_{exc} = 354 nm. [c] Plus water (5 M).

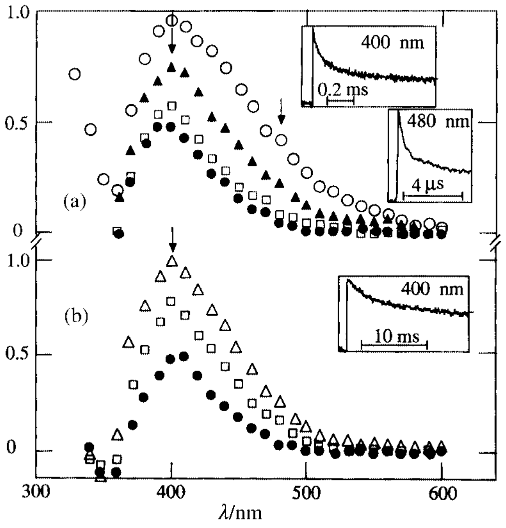


Fig. 8 Transient absorption spectra of **2** under argon (a) in cyclohexane in the presence of TEA (0.03 M) at 30 ns (○), 10 µs (▲), 1 ms (□) and 0.1 s (●) after the 308 nm pulse and (b) in acetonitrile and TEA (1 M) at 1 µs (△), 1 ms (□) and 1 s (●); insets: decay kinetics (a) at 400 nm (upper) and 480 nm (lower) and (b) at 400 nm.

The triplet state of 3-phenyl-1,2,4-phenanthro[9,10-*e*]triazine (3)

Apart from a bleaching at 370 nm the T–T absorption spectrum of **3** extends from 320 nm to 700 nm with λ_{TT} = 335 nm and a weaker band in the visible range. The triplet lifetime (essentially first-order decay at low laser intensity) is $\tau_T \approx 8$ µs in argon-saturated acetonitrile and $k_{ox} = 1 \times 10^9$ M^{-1} s^{-1}. The properties of the triplet state of **1** in cyclohexane and ethanol are similar (Table 1). From energy transfer of the triplet state of naphthalene a value of $\varepsilon_{420} = 5 \times 10^3$ M^{-1} cm^{-1} was estimated for the triplet state of **3** using $\varepsilon_{415} = 3.0 \times 10^4$ M^{-1} cm^{-1} for naphthalene.[26] The significantly longer triplet lifetime at ambient temperatures (Fig. 4) is probably due to a more rigid structure of the azaarene with respect to **1**. The triplet nature of the observed transient is further confirmed by the result that the absorption spectrum of **3** in argon-saturated ethanol at −170 °C (the lifetime is *ca.* 2.5 ms) is very similar to that at 24 °C. The phosphorescence spectrum of **3** in ethanol at −196 °C has two peaks at 540 and 566 nm, the triplet energy is $E_T \approx 226$ kJ mol^{-1}. This main spectrum has $\tau_p \approx 5$ ms and its excitation spectrum coincides with that of the absorption.

The k_{obs} value, measured at 330 nm, depends linearly on [TEA] (Fig. 6) or the concentration of the other amines examined. The subseqent short-lived transient ($t_{1/2} \approx 3$ µs) in the presence of DABCO (Fig. 3a) is similar to that in the case of **2**. The $[TEA]_{1/2}$ values of **3** are 1.7 and 0.6 mM in cyclohexane and acetonitrile, respectively. The relative absorption increase in acetonitrile at 400 nm after triplet quenching *vs.* log [TEA] shows the 50% value at the smallest [TEA] of <1 mM (Fig. 7).

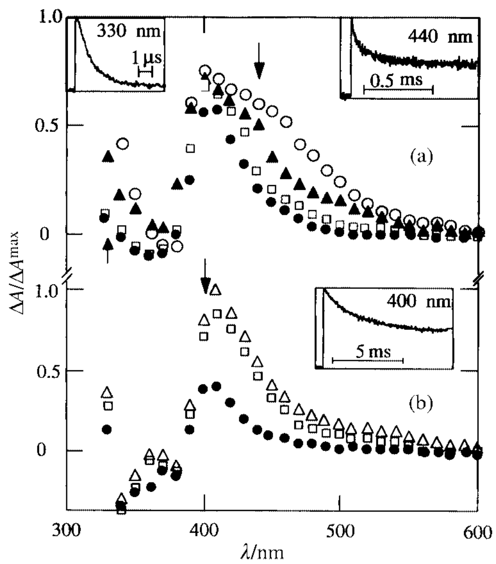


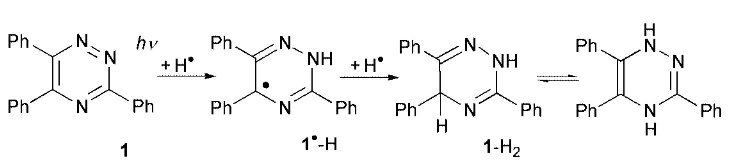
Fig. 9 Transient absorption spectra of **3** under argon (a) in cyclohexane in the presence of TEA (0.01 M) at 30 ns (○), 10 µs (▲), 1 ms (□) and 0.1 s (●) after the 308 nm pulse and (b) in acetonitrile and TEA (1 M) at 1 µs (△), 1 ms (□) and 1 s (●); insets: decay kinetics (a) at 330 nm (left) and 440 nm (right) and (b) at 400 nm.

The resulting longer lived transient has a λ_{max} at 410 nm (Fig. 9).

Secondary reactions

The remaining transient absorption spectra of the **1**–TEA system in cyclohexane (Fig. 5a) and acetonitrile (Fig. 5b) reveal mainly two parts which are sensitive towards oxygen: one is a longer lived intermediate ($HA^•$) which is converted into a permanent species (AH_2) with absorption above 350 nm and bleaching below (if the concentration is low enough). This conversion follows mainly a second-order decay law. The species subsequent to **1** shows almost the same maximum, but the long-wavelength band is steeper. Owing to its constant amplitude (extending to >1 s) this species is assigned to the dihydro compound **1**-H_2 and its precursor is therefore assigned to an H-adduct radical **1**$^•$–H. From theoretical considerations, **1**-H_2 prefers the 2,5-dihydro tautomeric structure.[5h]

The first half-life of $HA^•$ after subtraction of the constant part is $t_{1/2} \approx 0.5$ ms and becomes longer at lower laser intensity (I_L). Consistent with the second-order law $t_{1/2}$ increased by a factor of 2–3 when the I_L was decreased fourfold. In aqueous acetonitrile (<5 M water), apart from a smaller k_q value, no significant changes were observed. For high TEA concentrations (>1 M) triplet quenching could only partly be observed (on a 10–100 ns time scale), but the spectra of the two observable components (Fig. 5b) are essentially the same as at low concentrations. The permanent component in Fig. 5, *i.e.* absorption above 350 nm and the bleaching below, is consistent



1 **1**•-H **1**-H$_2$

Table 4 Properties of the resulting secondary transient HA• obtained from the azaarenes **1**–**3** and **5**[a]

Azaarene	Donor	λ_{max}/nm Cyclohexane	 Acetonitrile	$t_{1/2}$/ms Acetonitrile
1	TEA	370	370	>0.3
	DEA	370	370	>0.3
	TPA	370		>0.2
	TBA	380	370	>0.1
	DABCO		360,520	<0.005
2	TEA	<400	370	>0.5
	DEA	<400	380	>0.3
	DABCO		520	≤0.003
3	TEA	400	410	>0.2
	DEA	400	410	>0.2
	DABCO		510	≤0.003
5[b]	TEA	380	375	>0.2

[a] In argon-saturated solution, using [DABCO] = 0.5–2 mM and 0.05–0.2 M for the other amines; λ_{exc} = 308 nm. [b] Using λ_{exc} = 354 nm.

with the steady-state spectra (Figs. 1c and 2c). To further test for the nature of the longer lived transient and the permanent component TEA was replaced by DEA, TPA or TBA. The results are similar to those with TEA (Tables 3 and 4).

The decay of the transients for the **2**–TEA system in cyclohexane and acetonitrile also follows a second-order law under argon (after subtraction of the constant part) and $t_{1/2}$ is in the 0.2–2 ms range under our conditions. The two species showing the same maximum (Figs. 8a and 8b) are likewise assigned to an H-adduct radical of **2** and the respective dihydro compound. The results with DEA are analogous to those with TEA (Tables 3 and 4). The permanent bleaching component between 340–360 nm and the remaining absorption above are consistent with the steady-state spectra in Figs. 1b and 2b.

Essentially the same spectral and kinetic features were found for the **3**–TEA system in cyclohexane and acetonitrile (Figs. 9a and 9b, respectively). Similarly to **2**, the spectrum shows the permanent bleaching component between 330 and 380 nm; the wavelengths for $\Delta A = 0$ and the maximum coincide with the isosbestic point and the largest change in the steady-state spectra, respectively (Figs. 1a or 2a). The results are analogous when TEA is replaced by DEA (Tables 3 and 4).

Three major subsequent steps, triplet quenching, formation of an H-adduct radical and of the respective dihydro compound, were distinguished in all cases (Fig. 10). Note that in some cases, *e.g.* for **1** in cyclohexane (inset in Fig. 5a) or acetonitrile, a third component is indicated by an increase in absorption at 360–400 nm. It could be registered just after triplet quenching in the 2–10 μs range and is tentatively assigned to the H-adduct radical.

The triplet state of tetraphenylpyrimidine (4)

The T–T absorption spectrum of **4** in cyclohexane (Fig. 11a) or acetonitrile extends from 300–700 nm with a maximum at λ_{TT} = 440 nm. The decay is essentially first-order with a lifetime of $\tau_T \geq 10$ μs under argon (and a faster component at higher pulse intensity) and $k_{ox} = 3 \times 10^9$ M^{-1} s^{-1} (Table 1). The triplet nature of the observed transient is confirmed by energy transfer to β-carotene in cyclohexane. Addition of β-carotene reduces the triplet lifetime and generates the triplet state of β-carotene with λ_{TT} = 515 nm (Fig. 11b). This is in agreement with other examples in the literature.[26] For 90% energy conversion a molar absorption coefficient of $\varepsilon_{440} = 2 \times 10^4$ M^{-1} cm^{-1} was obtained

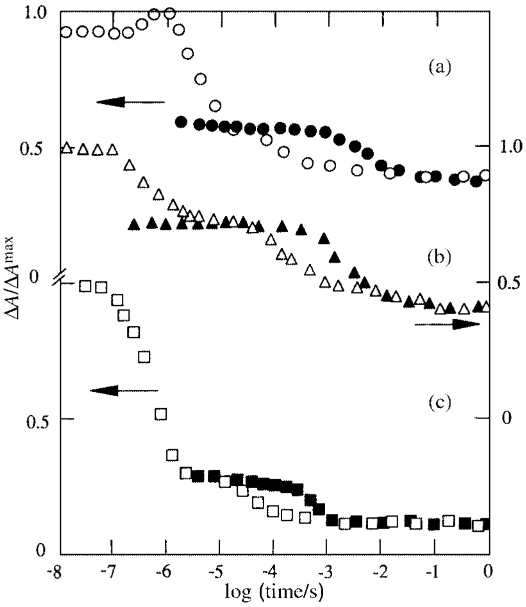


Fig. 10 Semilogarithmic plots of the relative transient absorption *vs.* time for (a) **3**, (b) **2** and (c) **1** in the presence of TEA under argon in cyclohexane (open symbols) and acetonitrile (full symbols); same [TEA] as in Figs. 9, 8 and 5, respectively.

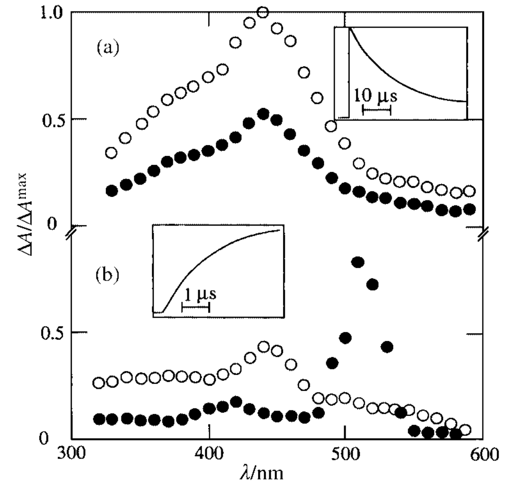


Fig. 11 T–T absorption spectra of **4** in argon-saturated cyclohexane (a) in the absence and (b) in the presence of β-carotene (<0.5 mM) (a) at 30 ns (○) and 10 μs (●) after the 308 nm pulse and (b) at 30 ns (○) and 2 μs (●); insets: (a) decay kinetics at 440 nm and (b) build-up at 510 nm.

using 2.0 × 10^5 M^{-1} cm^{-1} for that of the triplet state of β-carotene.[26] The quantum yield of population of the triplet state (Φ_T) of **4** was obtained by using optically matched solutions and benzophenone in acetonitrile ($\varepsilon_{520} = 6 \times 10^3$ M^{-1} cm^{-1}) as reference, $\Phi_T = 0.8$. Addition of TEA in acetonitrile (and even neat TEA) has no pronounced effect on the above triplet properties under the conditions of laser excitation. The rate constant for triplet quenching by TEA is smaller than 2 × 10^4 M^{-1} s^{-1} and also no marked effect of triplet quenching by DABCO was observed, $k_q < 2 \times 10^6$ M^{-1} s^{-1} (Table 3).

The reciprocal triplet lifetime decreases with decreasing temperature, approaching a value of ≤5 s^{-1} at −170 °C (Fig. 4). The T–T absorption spectrum in glassy ethanol has a maximum at λ_{TT} = 515 nm. Close inspection at −140 °C shows two components whereby the decrease at 515 nm corresponds to the

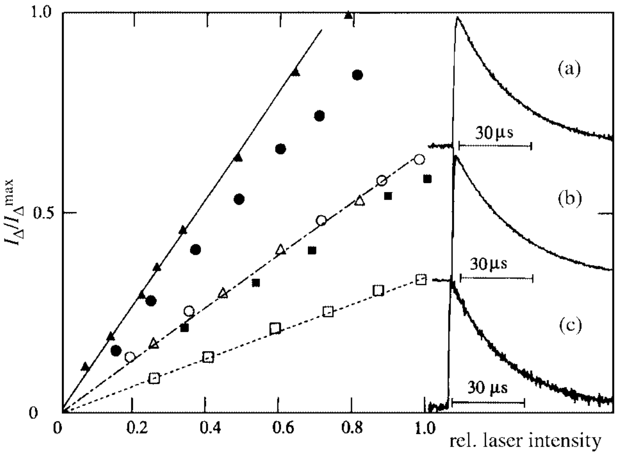


Fig. 12 Signal of $O_2(^1\Delta_g)$, extrapolated to the pulse end, as a function of the laser intensity for **1** (squares), **2** (triangles) and **3** (circles) in air-saturated cyclohexane (open symbols) and toluene (full symbols); insets: signals of (a) **3**, (b) **2**, and (c) **1** in air-saturated toluene.

increase at 440 nm. This indicates the involvement of two close-lying triplet states. Phosphorescence was detected in glassy ethanol with maxima at 468 and 495 nm. From the onset a triplet energy of $E_T = 266$ kJ mol^{-1} is obtained. The phosphorescence lifetime at −196 °C is *ca.* 0.5 s (Table 2) indicating that emission and absorption refer to the same triplet state.

Photoprocesses of phenazine (5)

Compound **5** was reported to undergo photoreduction to 5,10-dihydrophenazine *via* its $^1(n,\pi)^*$ state.[7a,b] T–T absorption with build-up rates of 7×10^{10} s^{-1} in isooctane and 5×10^{10} s^{-1} in methanol[7c] as well as O_2-enhanced intersystem crossing[7d] have been observed. The T–T absorption spectrum has $\lambda_{TT} = 440$ nm, the triplet decay under argon has a main first-order component at low laser intensity ($\lambda_{exc} = 354$ nm), the limiting triplet lifetime is *ca.* 30 μs and $k_{ox} = (2–3) \times 10^9$ M^{-1} s^{-1} (Table 1). $\Phi_T = 0.85$ in benzene, albeit much lower values of 0.21 in MCH[7d] and 0.30 in trifluoroethanol[7b] have also been reported. The absorption coefficient of the triplet state is $\varepsilon_{356} = 3.8 \times 10^4$ M^{-1} cm^{-1} or $\varepsilon_{440} = 1.5 \times 10^4$ M^{-1} cm^{-1} (in MCH).[7b] Also with **5** k_{obs} is a linear function of the amine concentration and for triplet quenching by TEA $k_q \approx 2 \times 10^6$ and $\approx 2 \times 10^7$ M^{-1} s^{-1} in cyclohexane and acetonitrile, respectively (Table 3). A bleaching at 340–350 nm was observed in the presence of TEA (under argon) and essentially one secondary transient with a sharp peak at 380 nm and a broad band around 520 nm. Its ε value is $\varepsilon_{380} = 1.1 \times 10^4$ M^{-1} cm^{-1}, using conditions of quantatitive conversion and $\varepsilon_{440} = 1.5 \times 10^4$ M^{-1} cm^{-1} for the triplet state. The results with TBA and TPA are similar to those with TEA (Table 3). The secondary transient is assigned to the hydrophenazine radical and the photoproduct to 5,10-dihydrophenazine. The latter is based on findings for the reduction of **5** in benzene by TEA.[7a]

Electrochemistry

The reduction potential (E_{red}) of **2**, **3**, **1** and **4** in acetonitrile (*vs.* ferrocene) was determined to change from −1.57 to −1.70, −1.90 and −2.37 V, respectively. This is in agreement with the rate constant for triplet quenching (Table 3). The reason for the very small k_q values in the case of **4** is the high reduction potential rather than a low triplet energy since this level is *ca.* 20 kJ mol^{-1} above that of **1** (Table 2).

Singlet molecular oxygen

The quenching of the triplet state of **1**, **2**, **3** and **4** by oxygen is accompanied by the formation of singlet molecular oxygen, $O_2(^1\Delta_g)$ (inset in Fig. 12). The $O_2(^1\Delta_g)$ signal in the presence of oxygen appears after the pulse and the decay is first-order. The lifetime (τ_Δ) is characteristic for each solvent, *e.g.* 30 μs in benzene and toluene. The signal (I_Δ), which was extrapolated to the end of the 20 ns pulse, exhibits a linear dependence on the laser intensity (Fig. 12). The quantum yield (Φ_Δ) was obtained from the slope of Fig. 12 using the correction for a given solvent (see Experimental). Φ_Δ is rather large for **1**–**4** and the solvent dependence is relatively small (Table 5). Virtually no change in τ_Δ on going from an aerated to oxygen-saturated solution is in agreement with k_{ox} and the triplet lifetime (Table 1). Note that the fraction of triplet state which is intercepted by oxygen is larger than 94% (typically 99%), based on the triplet lifetimes of *ca.* 30 ns and >3 μs in oxygen- and argon-saturated solution, respectively.

Table 5 Quantum yield Φ_Δ of singlet molecular oxygen formation with the azaarenes **1**–**4**[a]

Azaarene	**1**	**2**	**3**	**4**
Cyclohexane	0.3	0.6	0.5	0.65
Toluene	0.3	0.7	0.6	0.7
Acetonitrile	0.3 (0.3)[b]	0.8 (0.8)	0.8 (0.8)	0.8 (0.9)

[a] In oxygen-saturated solution, $\lambda_{exc} = 308$ nm. [b] Values in parentheses refer to air-saturated solution.

Discussion

Triplet state properties

Under the conditions employed in this study, the photoreactions of **1**–**3** with amines originate from the triplet state, which is characterized in cyclohexane and acetonitrile at room temperature and in ethanol at low temperatures. Formation of singlet molecular oxygen from excited azaarenes was observed. The quantum yield of $O_2(^1\Delta_g)$ formation (Φ_Δ) was determined in several solvents and is taken as a minimal value for the quantum yield of triplet formation. The photoreduction of **5** is also initiated *via* the observed triplet state.

The triplet nature of the transient which was observed for **1**–**4** in non-polar and polar solvents after the laser pulse is established by various measurements, including quenching measurements by oxygen (Table 1) and energy transfer from the triplet state of **4** to β-carotene or from triplet naphthalene to **3**. Moreover, the T–T absorption spectra in fluid and glassy ethanol are practically identical (except for the special case of **4**). The triplet lifetime approaches the phosphorescence lifetime at very low temperatures (Fig. 4 and Table 2). Why is the lifetime of the observed triplet state of **1** unusually short at room temperature? The similarity of the results in argon-saturated cyclohexane and acetonitrile indicates an internal rearrangement rather than a reaction with the solvent. The similarity of the τ_T values (Table 1) excludes photoreduction by ethanol[8] as a significant process for **1**–**4**. The quantum yield of population of the triplet state is probably close to unity. This is supported by efficient formation of singlet molecular oxygen; the quantum yield is $\Phi_\Delta = 0.3–0.8$ for **1**–**4** (Table 5).

Quenching of the triplet state

A dynamic photoprocess in the presence of an amine as electron donor (D) can, in principle, be initiated by reaction with an azaarene molecule as acceptor (A) in the excited singlet [reaction (3)] or triplet state [reaction (4)].

$$A \xrightarrow{h\nu} {}^1A^* \qquad (1)$$

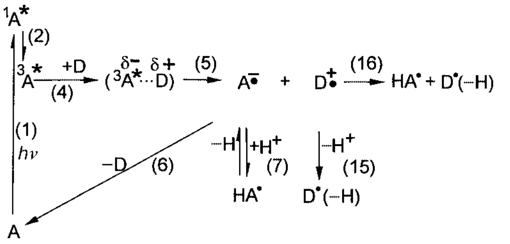
$$ {}^1A^* \longrightarrow {}^3A^* \qquad (2)$$

$$ {}^1A^* + D \longrightarrow {}^1A^* \cdots D \longrightarrow A^{\cdot -} + D^{\cdot +}$$
$$\text{(or hydrogen abstraction)} \qquad (3)$$

$$ {}^3A^* + D \longrightarrow {}^3A^* \cdots D \qquad (4)$$

Here, $^1A^* \cdots D$ and $^3A^* \cdots D$ are the collision complexes leading to photoreduction, $A^{\bullet -}$ is the radical anion of the azaarene and $D^{\bullet +}$ the radical cation of the amine.

The question arises as to the initial reactive state. Quenching of diaza-aromatic compounds by amines can involve n,π singlet states.[8] However, no fluorescence could be detected for **1**, **2**, **3** and **4** in cyclohexane or acetonitrile (see Results). The singlet reaction (3) does not occur, at least for **1**–**3**, and the results in the presence of the amines examined are therefore interpreted by quenching of the triplet state, reaction (4). The primary reactions are illustrated in Scheme 1.



Scheme 1

Electron transfer from DABCO

A characteristic intermediate with a rather short half-life and no transient on the ms time scale was observed (Fig. 3 and Table 3). This transient is assigned to the radical anion of the azaarene, formed by electron transfer from DABCO to the triplet state of **1**–**3** [reaction (5)].

$$^3A^* \cdots D \longrightarrow A^{\bullet -} + D^{\bullet +} \qquad (5)$$

For **3** (Fig. 3a), where the relative signal is larger than for **1** (Fig. 3c), the observed species could also be due to the radical anion of the phenanthrene moiety. The radical cation of DABCO has $\lambda_{max} = 450$ nm and a very low ε value[27] which is much smaller than that of the triplet precursor. From electron transfer studies with other systems it is known that $D^{\bullet +}$, $A^{\bullet -}$ and the radical $HA^{\bullet}$ are longer lived species. However, their intermediacy can be limited by several reactions; one is electron back transfer (6) which should be favored in the absence of water.

$$A^{\bullet -} + D^{\bullet +} \longrightarrow A + D \qquad (6)$$

Alternatively, the transient could be $HA^{\bullet}$, the conjugate acid.

$$A^{\bullet -} + H^+ \rightleftharpoons HA^{\bullet} \qquad (7)$$

This, however, can be excluded owing to significant kinetic and spectroscopic differences of the secondary transient in the cases of the other amines examined. It should be mentioned that the electron adduct of heterocycles, *e.g.* quinoxaline or acridine, in aqueous solution, when observed by pulse radiolysis, is present on the right hand side of equilibrium (7).[28]

Reactivity of the triplet state

The rate constant for triplet quenching by TEA is below the diffusion-controlled limit, as expected from the free energy changes using the Rehm–Weller relationship [eqn. (8)].[29]

$$\Delta G = E_{ox} - E^*_{red} - E_c \qquad (8)$$

Here, E_{ox} is the oxidation potential of the amine, E^*_{red} the reduction potential of the triplet state of the acceptor and E_c the Coulombic term accounting for ion pairing (0.06 V in acetonitrile). Using the phosphorescence data the E_T values of **1**–**4** are estimated to be 240, 240, 226 and 266 kJ mol^{-1}, respectively. With E^*_{red} values of 0.65, 0.93, 0.6 and 0.40 V for **1**–**4**, respectively, and the oxidation potential of TEA (0.78 V *vs.* SCE in acetonitrile) it follows that the ΔG value is negative (−0.15 V) for **2**, close to zero for **3** and **1** and significantly positive (0.38 V) for **4**. For **1**–**3** in acetonitrile $k_q = 1 \times 10^8$ M^{-1} s^{-1} or below (Table 3). The smaller k_q values in cyclohexane are also expected from the larger E_c value.

For the case of DABCO with $E_{ox} = 0.57$ V the ΔG values of **1**–**3** are (more) negative and therefore the k_q values with DABCO are much larger and close to the diffusion-controlled limit for **2**. The result that for the **4**–DABCO system k_q is $< 2 \times 10^6$ M^{-1} s^{-1} is somewhat surprising since the calculated ΔG value is 0.17 V. Note that the E_{red} values, when given *vs.* SCE, are *ca.* 0.3 V more negative and thus the ΔG values should be even smaller.

Photoreduction by amines

A number of ns and ps flash photolysis studies aimed at characterizing transients in the photoreduction of ketones by amines have been carried out.[9b,10] From solvent effects on the ps dynamics of BP photoreduction by DMA and *N*,*N*-diethylaniline it was concluded[10a] that rapid electron transfer generating a solvent separated ion pair (SSIP) was followed by formation of a CRIP by diffusion and that, depending on the dielectric properties of the medium, an equilibrium between the CRIP and the ketyl radical is established. Proton transfer thus occurs within the CRIP and is exothermal, thus there are no problems with back proton transfer within the time span of the experiment.[10e] Efficient proton transfer is shown to be dependent on distance and might require reorientation of the radical ions within the complex or CRIP.[10e] Other authors,[9f] however, point out that the processes observed in the aforementioned studies may be too complex due to the high amine concentrations used.

Studies on the photoreduction of BP by various reductants, among them *tert*-butylamine, 2-aminobutane, cyclohexylamine, TEA and DABCO, show that quenching without radical formation occurs only with DABCO. Triplet quenching rate constants are high for amines (~10^8–10^9 M^{-1} s^{-1}).[10c] Such rate constants for quenching by DMA, TEA, dibutylamine and *tert*-butylamine have also become available for triplet thioxanthone[10d] and for three 1,4-naphthoquinones (near diffusion controlled for TEA and DMA).[10g] Time resolved spectroscopy of the photoreduction of benzil by TEA is complicated due to H-transfer from the α-aminoalkyl radicals to ground state benzil.[10h,i]

A few reports on the conjugate photoaddition of the α-C–H bond of tertiary amines to cyclohexenones (*via* consecutive electron and proton transfers to generate α-aminoalkyl radicals) giving β-substituted cyclohexanones[11a–c] and the analogous diastereoselective addition of *N*-alkylated pyrrolidines to photoexcited (5*R*)-5-menthyloxyfuran-2(5*H*)-one[11d,e] have appeared and show promising utility in synthesis.

Another focus has been on the photoaddition of aliphatic amines to hydrocarbons such as benzene,[12a] and of secondary amines to 1-phenylpropene[12b] including an analogous intramolecular addition. Most effort has been put into the investigation of the action of tertiary aliphatic amines including DABCO on (*E*)-stilbene in polar solvents,[12c–h] including a Hammett correlation for various π-conjugating substituents R in Me_2NCH_2R[12e] and the direct observation (by ^{1}H-CIDNP) of *N*,*N*-diethylvinylamine formed from TEA.[12f]

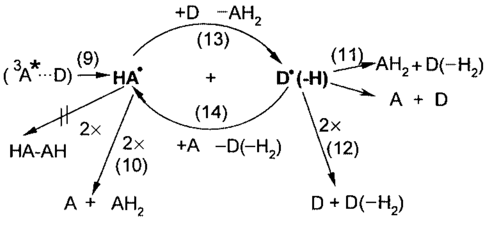
Triplet excited monochloroarenes[14a] and singlet excited 9-chloro- and 9,10-dichloroanthracene[14b] undergo dechlorination under the influence of amines, and one CN group in 1,2- and 1,4-dicyanobenzene is replaced by aminoalkyls derived from tertiary amines.[14c] In the presence of TEA, one CN group in 9,10-dicyanoanthracene is replaced by the solvent acetonitrile.[14d] It should be pointed out that one aspect of photoreduction of excited substrates may be the intended and preparatively useful *N*-dealkylation (mostly *N*-demethylation) of tertiary amines.[15]

Special attention has been given to the characterization of aminylium radical cations formed in the electron transfer step. A series of tertiary amines containing one to four nitrogen atoms (mostly in caged structures) have been investigated by cyclic voltammetry.[16a] Aminylium cation radicals are strong protic acids (for *N*,*N*-dimethylanilinium the pK_a of the α-CH is 27 units lower than that of the corresponding neutral).[16b] CIDNP studies in the system naphthalene–TEA in protic solvents revealed that the α-protons of the TEA cation radical are exchanged with the α-protons of neutral TEA and that back electron transfer takes place to some extent in the caged pair.[16c] The radical ion pairs derived from TEA and various triplet sensitizers may be differentiated from the pairs of neutral radicals (after proton transfer) by their ^{1}H-spin polarizations.[16d] Deprotonation of electrochemically generated methyldi(*p*-anisyl)aminium ions has also been investigated.[16e] Cases of α-C–C fission competing with α-deprotonation are also known.[16f]

To undergo efficient proton transfer the aminylium α-C–H bond has to be aligned parallel with the axis of the nonbonding orbital on nitrogen[9f,17] and the absolute rate constants for the reaction of ^{3}BP* with various primary, secondary and tertiary amines fulfilling this condition to a larger or smaller extent, have been determined.[17] α-Aminoalkyl radicals have also been obtained by pulse radiolysis[18a–c] and are generally regarded as strongly reducing species.[18b,c] They tend to undergo fragmentation or net hydrogen transfer to form vinylamines.[5f,g,10h,i,12f,17,18d,e] Estimates of radical stabilization by the amine donor are between 42 and 84 kJ mol^{-1}.[18f]

Electron *versus* hydrogen transfer in the presence of alkylamines

For the 9-chloroanthracene–TEA system in acetonitrile no electron back transfer, involving a second-order decay of $A^{\bullet -}$, has been observed.[14b] For the 1,4-naphthoquinone–TEA system in aqueous acetonitrile reactions (4) and (5) have been reported.[10g] The suggested secondary reactions in the cases of **1**–**3** with alkylamines are illustrated in Scheme 2. The triplet reaction of **1**–**3** with TEA leads to neutral radicals after hydrogen abstraction [reaction (9)].



Scheme 2

$$^3A^* \cdots Et_3N \longrightarrow HA^\bullet + Et_2N\text{–}^\bullet CHMe \qquad (9)$$

This overall reaction may be regarded as electron plus proton transfer reactions rather than as one step.

The termination reactions in the case of azaarenes eventually yield the dihydroproduct AH_2 as the only spectroscopically observable "stable" photoproduct. One possibility is reaction (10).

$$HA^\bullet + HA^\bullet \longrightarrow AH_2 + A \qquad (10)$$

This is different to several non-heterocycles, where photodimers could be detected.[12f] For the cases of **1**–**3** no indication for dimers (HA–AH) was found. Alternatively, $HA^\bullet$ could react with the $Et_2N^\bullet CHMe$ radical, by combination, formation of the initial reactants (A and Et_3N) or *via* a second overall hydrogen abstraction (electron transfer followed by proton transfer) to form AH_2 and diethylvinylamine [reaction (11)].

$$HA^\bullet + Et_2N\text{–}^\bullet CHMe \longrightarrow AH_2 + Et_2NCH{=}CH_2 \qquad (11)$$

Both reactions (10) and (11) are consistent with a second-order law for the decay kinetics, but the amount of dihydroproduct per triplet azaarene which is formed *via* reaction (11) is twice that formed *via* reaction (10). Which process is dominant remains an open question as yet. The results do not reveal a major difference between TEA and DEA. For the case of DEA, $Et_2N\text{–}^\bullet CHMe$ has to be replaced by the $EtHN\text{–}^\bullet CHMe$ radical and diethylvinylamine by *N*-ethyliminoethane. The third radical termination process (12) is not accessible by our spectroscopic analysis.

$$Et_2N\text{–}^\bullet CHMe + Et_2N\text{–}^\bullet CHMe \longrightarrow Et_3N + Et_2NCH{=}CH_2 \qquad (12)$$

The decay kinetics of $HA^\bullet$ could also follow a first-order law by reaction with the amine itself.

$$HA^\bullet + Et_3N \longrightarrow AH_2 + Et_2N\text{–}^\bullet CHMe \qquad (13)$$

However, for alkylamines at high concentration there is no clear indication for this reaction, even in neat TEA. A first-order law in formation of $HA^\bullet$ can be described by reaction (14).

$$Et_2N\text{–}^\bullet CHMe + A \longrightarrow HA^\bullet + Et_2NCH{=}CH_2 \qquad (14)$$

The increase in absorption just after triplet quenching for **1** (inset in Fig. 5a) may be related to this radical transfer. Interestingly, there is no indication for excitation of a possible ground state complex (see Figs. 1 and 2).

If the radical cation of TEA were formed *via* electron transfer (5), its intermediacy could be limited by the deprotonation reaction (15).

$$Et_3N^{\bullet +} \longrightarrow Et_2N\text{–}^\bullet CHMe + H^+ \qquad (15)$$

$Et_3N^{\bullet +}$ in aqueous solution was reported to have a lifetime of 3 μs.[19b] The subsequent step besides reaction (6) should be reaction (16).

$$A^{\bullet -} + Et_3N^{\bullet +} \longrightarrow HA^\bullet + Et_2N\text{–}^\bullet CHMe \qquad (16)$$

This reaction can only be a minor process, if it occurs at all, since otherwise the characteristic band of $A^{\bullet -}$ around 520 nm should have been observed. At high amine concentrations a reaction of $Et_3N^{\bullet +}$ with ground state TEA yielding $(Et_3N)_2^{\bullet +}$ has been considered.[12g] For excitation of **1**–**3** at >300 nm reactions (15) and (16) as major processes can be excluded (see above).

In principle, photoreductions by amines may also be brought about by production of solvated electrons, *e.g.* by 254 nm irradiation of TEA in acetonitrile. Solvated electrons (e^-_{sol}) are also produced in the laser flash induced sensitization of methionine by 1,5-sulfonatoanthraquinone ions in water.[19a] Recently a photoionization method using two-pulse/two-colour laser flash irradiation *via* sequential absorption/electron transfer/absorption became available; 4-carboxybenzophenone was used as a sensitizer for TEA (donor) in water at pH 12.[19b] If photoionization of TEA occurs as the initial photoprocess, then the radical cation of the amine and the solvated electrons are formed [reaction (17)].

$$D \xrightarrow{h\nu} D^{\bullet +} + e^-_{sol} \qquad (17)$$

While e^-_{sol} is rapidly scavenged (the rate constant with MeCN is 3.7×10^7 M^{-1} s^{-1}),[30] e^-_{sol} is detectable (usually on a 0.02–10 μs time scale) in alcohols. For TEA (1 M) in ethanol, however, no transient around 600–700 nm was observed after the 308 nm pulse and only a weak e^-_{sol} signal was observed for TEA (1 M) in ethanol–water (1 : 1) under high-intensity conditions. Therefore, under steady-state and even with the usual laser pulse experiments, reaction (17) can be excluded for the applied conditions.

Finally, a hydrogen abstraction reaction from the solvent (RH) can be considered.

$$HA^{\bullet} + RH \longrightarrow AH_2 + R^{\bullet} \qquad (18)$$

Reaction (18) is rather unlikely since similar kinetics were found in cyclohexane and the rather inert acetonitrile. Nevertheless, for **3** or **2** in the presence of propan-2-ol at high concentrations (>5 M) formation of $HA^{\bullet}$ and AH_2 was observed in low yield, which is due to a low k_q value.

Mechanistic considerations

The secondary transient of **5** in the presence of TEA is assigned to the hydrophenazine radical and the photoproduct to 5,10-dihydrophenazine.[7,8] Upon pulsed or continuous irradiation in the presence of TEA or DEA the products absorbing at wavelengths longer than 280 nm are assigned to the AH_2-type products 3,5,6-triphenyl-2,5-dihydro-1,2,4-triazine, 3-phenyl-1,4-dihydro-1,2,4-benzotriazine and 3-phenyl-1,4-dihydro-1,2,4-phenanthrotriazine for **1**, **2** and **3** respectively.

For **1**–**3** in argon-saturated cyclohexane and acetonitrile in the presence of TEA the only observable species at times longer than a few milliseconds is AH_2 (Figs. 5, 8–10), which is also suggested to be formed at low amine concentrations, *e.g.* <0.1 M (Fig. 1), at high concentrations, *e.g.* 1 M (Fig. 2) or neat TEA or DEA. In each case, the triplet state, which is populated with substantial yield, is quenched by the amine due to reactions (4) and (9) rather than *via* reaction (5). Based on time-resolved spectra, we assign the major intermediate to the radical $HA^{\bullet}$ (rather than to the radical anion).

In the simplified reaction sequence (Scheme 2) one could expect that for lower amine concentrations AH_2 is formed *via* second-order processes involving $HA^{\bullet}$, whatever the sequence could be, reaction (10) or (11). Also in reaction (11) both $HA^{\bullet}$ and $Et_2N{-}^{\bullet}CH{-}Me$ should lead to a linear dependence of $1/t_{1/2}$ on the laser intensity, which was (essentially) observed in the decay kinetics. It should be mentioned that in neat TEA or DEA a significant part of the exciting 20 ns light pulse is absorbed by the H-adduct radical because of the k_q values in the range of 10^8 M^{-1} s^{-1} (Table 3). The analysis of our results was therefore restricted to [TEA] <1 M.

It should be recalled that oxygen interferes at several stages of the reaction sequence. An obvious competition is triplet quenching, which however, has in air-saturated solution with 1 M TEA virtually no chance (<2%) due to the k_{ox} (Table 1) and k_q (Table 3) values and the much lower O_2 concentration. Other very sensitive reactions of oxygen are those with $HA^{\bullet}$ and $Et_2N{-}^{\bullet}CHMe$, thereby preventing formation of AH_2 at all. When the photoproduct is already formed, oxygen causes the reversion (19),[31] as illustrated in Fig. 2. The details, however, are not known.

$$AH_2 + {}^1\!/_2O_2 \longrightarrow A + H_2O \qquad (19)$$

Conclusion

The photoreduction of **1**–**3** by amines examined involves the lowest triplet state of the azaarenes. In contrast, the triplet state of **4** is not reactive at all. Electron transfer to the triplet state of **1**–**3**, followed by proton transfer within the collision complex, is efficient in forming the H-adduct radical(s) as the observed transient. This species, at least under conditions of pulsed excitation, reacts slowly, either bimolecularly or with the amine-derived radical, to produce the dihydro-products. For the azaarene–TEA system we have shown that the first and second photoreduction steps occur in substantial yield over a large [TEA] range, as long as oxygen is carefully excluded. Owing to similarities in k_q and differences in τ_T, the half-concentration for **3** of *ca.* 1 mM is tenfold smaller than that for **1**. Thus, for synthetic applications of **1**–**3** no major problems are expected and the overall quantum yield of photoreduction should be almost constant, when the TEA or DEA concentrations are varied over a large range.

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