theless, the data can be tested against the predictions. Since the values of r are quite consistent, the predicted values of n are computed from the two models based on the average value of r, 0.2045. From the first-order model, $n = 1.12$; from the diffusion model, $n = 1.09$. Ignoring experimental error, the fit is definitely better for the diffusion model, for which the predicted n lies between the two experimental values. For the first-order model, the predicted n is greater than either experimental value. While these results favor the diffusion model slightly, they carry little weight because the spread in experimental values of n is twice the difference between the calculated values.

To bring the experiment into the range $r = 0.85$ would require a 30-fold increase in $D\tau_r$, other parameters held constant. Any significant increase in D seems out of the question. Thus, one must seek ways to slow rotation without slowing diffusion in a compensating fashion.

However, this kind of test is not restricted to experiments with chiral radical pairs. For any other process which is first-order in radical pairs and which leads to new radical pairs which collapse to distinguishable products, similar equations apply. What is needed is a process with a first-order rate constant in the range 10^9–10^{10} sec^{-1}. Molecular rotation is a little too fast to serve this purpose well.

Finally, we note that the treatment above is closely related to the problem of the scavenging of secondary geminate recombination. If scavenging occurs with a pseudo-first-order rate constant $2k_s[S]$,[4,8] where k_s is the "long-time" second-order rate constant for the reaction between S and R·, then the fraction A of radical pairs which are not scavenged is given by eq 26. This is the exact form corresponding to the approximate (truncated series) integration given earlier by Noyes.[4,8]

$$A = \int_0^\infty h(t)\, e^{-2k_s[S]t}\mathrm{d}t = b e^{-2(2ak_s[S])^{1/2}} \qquad (26)$$

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$$\int_0^\infty e^{-a/t} e^{-kt} t^{-3/2}\mathrm{d}t = (\pi/a)^{1/2} e^{-2(ak)^{1/2}}$$

The substitution $t = x^{-2}$ reduces the integral above to $2\int_0^\infty e^{-ax^2} e^{-k/x^2}\mathrm{d}x$, which is found in standard tables such as M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions", Dover Publications, New York, N.Y., 1973, p 302, integral 7.4.3. The author is grateful to R. C. Morrison, O. Day, and J. M. Deutch for demonstrating, on separate occasions, the utility of this substitution in connection with integrals containing $t^{-3/2}\mathrm{d}t$.
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Chemistry of the Triplet State of Diazines in Solution Studied by Laser Spectroscopy

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Abstract: Optical excitation at 265 nm of diazines in aqueous and organic solvents was carried out using single pulses of ~15-nsec duration from a frequency quadrupled neodymium glass laser. The technique of kinetic absorption spectrophotometry was used to observe and study the short-lived transient species formed at room temperature. Pyrazine, pyrimidine, pyridazine, quinoxaline, and phthalazine were studied in water, isopropyl alcohol, acetonitrile, and cyclohexane. The transient absorption spectra of these diazines were determined in the wavelength region 230–900 nm. These are assigned, primarily, to triplet states. Their lifetimes in water at 25° are 4.5, 1.4, 29.4, and 21.2 μsec for pyrazine (Pz), pyrimidine (Pm), quinoxaline (Qx), and phthalazine (Pl), respectively. In organic solvents, the triplet lifetimes are generally reduced. The observed triplet states of Pz and Pm are suggested to be (n,π^*) in character and are effectively quenched by H atom donors; e.g., $k_q \sim 10^8$ M^{-1} sec^{-1} by isopropyl alcohol. The triplet states of Qx and Pl are predominantly (π,π^*) in character and are quenched relatively slowly, $k_q \leq 10^4$ M^{-1} sec^{-1}, by H atom donors. The spectra of the azyl radicals produced from these diazines have been identified. For example, in water the ·PzH and ·PzH$_2^+$ radicals are observed. The rate constants for quenching of the triplet states of diazines by O$_2$, H$^+$, OH$^-$ ions and by inorganic ions of CTTS character were determined. These and other results are discussed.

It is the "lone-pair" electrons of aromatic nitrogen heterocyclic molecules which usually determine the nature of the radiative and radiationless paths for deactivation of the excited states of these compounds, as well as the photochemical properties of heteromolecules. The electronic absorption spectra and the (n,π^*) and (π,π^*) nature of the excited singlet and triplet states of diazabenzenes, as well as diazanaphthalenes, have been studied in great detail.[2-11] These molecules exhibit a weak fluorescence but are found to show strong phosphorescence. The diazabenzenes are re-

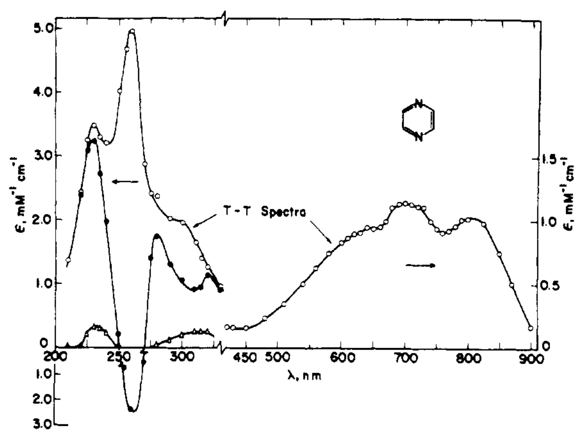


Figure 1. Absorption spectra of the transient species produced on optical excitation at 265 nm of pyrazine (10^{-4} *M*) in water at pH 5.4, 25°. Optical density was read at 20 nsec (symbol ● at λ <420 nm and symbol ○ at λ >420 nm) and at 15 μsec (△) after the pulse. Depletion of ground state pyrazine was corrected for (symbol ○ at λ <360 nm) based on the assumption of complete quenching of the triplet by isopropyl alcohol (see text for details). At λ >380 nm, solutions contained N_2O (1 atm) to scavenge the optically produced e_{aq}^- (see text).

ported to have allowed $^1(n,\pi^*)$ states as the lowest singlet excited states and $^3(n,\pi^*)$ as the lowest triplet states. The diazanaphthalenes have $^3(\pi,\pi^*)$ as the lowest triplet states, and their lowest singlet excited states are $^1(n,\pi^*)$.

The chemistry of $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states of aromatic carbonyl compounds in solutions has been studied in great detail and is reasonably well understood (see, e.g., ref 2, 3, and 12). The $^3(n,\pi^*)$ states of these compounds are quenched by H atom donors (e.g., isopropyl alcohol, hexane) with quenching rates $k_q \leq 10^6$ M^{-1} sec^{-1}, while the $^3(\pi,\pi^*)$ states are longer-lived and relatively unreactive toward H atom donors, $k_q \ll 10^4$ M^{-1} sec^{-1}.

Pyrazine, pyrimidine, pyridazine, and quinoxaline exhibit[2] a lowest energy (n,π^*) singlet-triplet separation which is approximately twice that of the corresponding S_1-T_1 (n,π^*) transitions of many aromatic carbonyl compounds. This difference has been attributed primarily to weaker charge transfer characteristics in (n,π^*) transitions of diaza aromatic molecules, as compared to aromatic carbonyl compounds where the oxygen is more electronegative. These differences have not been examined or tested in so far as they may affect the chemistry of the triplet state of diazines. Indeed, no precise mechanistic information is available on the chemistry of $^3(n,\pi^*)$, $^3(\pi,\pi^*)$, and $^1(n,\pi^*)$ states of diaza derivatives of benzene and naphthalene in solution.

Presented below is a laser photolysis study of the nature, lifetime, and reactions of the triplet states of pyrazine, pyrimidine, pyridazine, quinoxaline, and phthalazine in polar and nonpolar solvents at room temperature. Preliminary results on pyrazine have been published.[13]

Experimental Section

A frequency quadrupled neodymium glass laser (Holobeam, N.J.) was used. Single pulses of ~15-nsec duration and ~20-25 mJ at 265 nm were employed. Kinetic absorption spectrophotometry was used to monitor the transient species produced on optical excitation. The monitoring light from a 250-W Xenon lamp crossed the optical cell at 90° to the laser beam. The light output from the lamp was boosted for a period of ~1 msec and an increase of ~400-500 times at ~250 nm was obtained. The optical cell was jacketted and the temperature maintained at 25°. Transient signals from the photomultiplier were digitized and analyzed using an on-line Biomation 8100 waveform digitizer and a Hewlett-Packard 9830A calculator. Further experimental details are available elsewhere.[14a]

The solutions were prepared from highly purified "Millipore" water or dry Spectrograde organic solvents from Eastman Chemicals and Matheson Coleman and Bell. The diazines used were obtained from Aldrich, Calbiochem, and Eastman Chemicals and were the best research grade available. Pyrazine was an Aldrich Gold Label product and quinoxaline was resublimed under vacuum just before use. Solutions were either degassed by bubbling Matheson research grade argon or saturated with Gold Label oxygen. Fresh solutions were used for each pulse. Photolysis by the monitoring light was minimized by using a synchronized shutter (open for ~5-10 msec) and appropriate cutoff filters.

Aqueous solutions were buffered using ~1.0 m*M* tetraborate, boric acid, or 0.2 m*M* phosphates, as well as perchloric acid and potassium hydroxide. Other chemicals and reagents were obtained from Baker and Adamson and Mallinckrodt.

The absorption spectra of the diazines in the appropriate solvents were recorded and used to correct the measured absorbances for ground state depletion.

The quantum yield of triplet state formation was measured for some systems. This was based on the anthracene actinometer, using solutions of the same absorbance at 265 nm as employed for the diazines. The anthracene actinometry was performed in cyclohexane and the triplet-triplet absorption monitored (using narrow slits on the monochromator) at 428 nm. The ϕ_{ISC} was taken as 0.75 and ϵ_{428} 64,700 M^{-1} cm^{-1} (see ref 14b).

Results and Discussion

Pyrazine. Optical excitation of pyrazine at 265 nm in an oxygen-free (argon saturated) aqueous solution at pH 5.4 gave rise to a short-lived absorption extending from ~210 to 900 nm, see Figure 1. A strong depletion of the ground-state of pyrazine was observed in the wavelength range 250-270 nm. Pyrazine ($pK_a = 0.65$) has absorption bands in water at pH 6.0 at 261, 268, and 303 nm with extinction coefficients of 5.9×10^3, 4.3×10^3, and 8.5×10^2 M^{-1} cm^{-1}, respectively.

In the visible region, part of the transient absorption was found to be that of the hydrated electron with the characteristic λ_{max} ~720 nm, indicating that photoexcitation of pyrazine in water leads to electron ejection. The small yield of e_{aq}^- was formed within the 15-nsec duration of the laser pulse. The ionization potential[15] of pyrazine is ~9.3 eV. The formation of e_{aq}^- may occur via a biphotonic process from the triplet or singlet excited states or from a higher-lying excited state. Due to experimental limitations, no attempt was made to establish the nature of the precursor leading to the photoionization of pyrazine.

The part of the spectrum in the visible region shown in Figure 1 was obtained on excitation of pyrazine in the presence of N_2O (1 atm), a known scavenger of e_{aq}^-:

$$e_{aq}^- + N_2O \longrightarrow N_2 + OH + OH^- \qquad (1)$$

$k_1 = 8.7 \times 10^9$ M^{-1} sec^{-1} (ref 16). This reaction competes with $k(e_{aq}^- + \text{pyrazine}) = 2.1 \times 10^{10}$ M^{-1} sec^{-1} (ref. 17). The lifetime of the short-lived transient absorption (Figure 1) was not affected by the presence of 1 atm (2.2×10^{-2} *M*) of N_2O. The OH radicals produced in reaction 1 can add to pyrazine to form an intermediate which absorbs[17] rather weakly in the far-uv region.

The transient species shown in Figure 1 was found to decay at all wavelengths by first-order kinetics with $k = 2.2 \times 10^5$ sec^{-1} in 1.3×10^{-4} *M* pyrazine at pH 7.1 (see Table I). It is assigned (see below for arguments in support of this assignment) to the triplet-triplet (n,π^*) absorption spectrum of pyrazine in water. Since it is produced within the 15 nsec duration of the laser pulse, it follows that the lifetime of the $^1(n,\pi^*)$ excited state is much shorter. A weak residual transient absorption was found after the decay of the triplet and is shown in Figure 1.

Laser photolysis of 1.3×10^{-4} *M* pyrazine in oxygen-free acetonitrile produced a similar transient optical absorption which decayed with $k = 7.2 \times 10^4$ sec^{-1}. It is interesting to

Table I. Lifetimes of Triplet States of Diazines in Solution at 25°

Diazine	Concentration, M	Solvent	pH	k, sec^{-1}	τ
Pyrazine		Water	7.1	$2.2 \times 10^{5\,a}$	4.5 μsec
	1.3×10^{-4}	Acetonitrile		7.2×10^{4}	13.9 μsec
	1.3×10^{-4}	Cyclohexane		$\sim 3.0 \times 10^{7}$	33.3 nsec
Pyrimidine		Water	7.1	$7.1 \times 10^{5\,a}$	1.4 μsec
Quinoxaline		Water	7.1	$3.4 \times 10^{4\,a,c}$	29.4 μsec
	1.1×10^{-4}	Cyclohexane^{b}		6.0×10^{4}	16.7 μsec
	1.1×10^{-4}	Isopropyl alcohol		1.7×10^{5}	5.9 μsec
Phthalazine	3.3×10^{-4}	Water	7.1	4.7×10^{4}	21.3 μsec
	3.3×10^{-4}	Isopropyl alcohol		2.6×10^{5}	3.8 μsec

^{a} Value extrapolated to "zero" concentration of diazine. ^{b} 2.0×10^{-4} M quinoxaline. ^{c} Some second-order component observed.

Table II. Rate Constants for Quenching of Triplet States of Diazines in Water at 25°

Diazine	Triplet state	pH	Quencher	k_q,^{a} M^{-1} sec^{-1}
Pyrazine	^{3}(n, π*)	7.1	Pyrazine	5.8×10^{8}
		7.1	O_2	3.2×10^{9}
		3–4	H_3O^+	1.6×10^{10}
		12–13	OH^-	3.2×10^{8}
		6.4	*tert*-Butyl alcohol	6.7×10^{6}
		6.4	Methyl alcohol	2.7×10^{7}
		6.4	Isopropyl alcohol	1.3×10^{8}
			Cyclohexane	$\sim 3.3 \times 10^{6\,b}$
Pyrimidine	^{3}(n, π*)	7.0	Pyrimidine	1.5×10^{8}
		7.0	O_2	4.6×10^{9}
		3–4	H_3O^+	7.7×10^{9}
		12–13	OH^-	1.3×10^{8}
		7.0	Isopropyl alcohol	8.6×10^{7}
		7.0	KBr	$\sim 7.0 \times 10^{9}$
Quinoxaline	^{3}(π, π*)	7.0	Quinoxaline	6.9×10^{7}
		7.0	O_2	1.4×10^{9}
			Isopropyl alcohol	$\leqslant 1.4 \times 10^{4\,b}$
		2–3	H_3O^+	9.7×10^{8}
		1–3	OH^-	2.6×10^{5}
		7.0	KI	$\leqslant 2.0 \times 10^{5}$
		7.0	KCNS	$< 5.0 \times 10^{4}$
Phthalazine	^{3}(π, π*)	7.1	O_2	1.4×10^{9}
			Isopropyl alcohol	$\leqslant 2.0 \times 10^{4\,b}$

^{a} Obtained from k (sec^{-1}) vs. [quencher] plots; values to ±15%. ^{b} Estimated from "neat" solutions.

note that ^{3}Pz decays more slowly in a polar aprotic solvent such as acetonitrile than in water. On optical excitation of pyrazine in cyclohexane the T-T absorption decayed much faster, with $k \sim 3.0 \times 10^7$ sec^{-1}. As described below, the ^{3}(n,π*) pyrazine is quenched effectively by H atom donors such as cyclohexane and this accounts for the apparent fast decay of the triplet state.

Quenching and Chemistry of ^{3}(n,π*) Pyrazine. The short-lived species assigned to the T-T (n,π*) absorption spectrum of pyrazine in water (Figure 1) was rapidly quenched by oxygen with $k_q = 3.2 \times 10^9$ M^{-1} sec^{-1} (see Table II). Self-quenching of ^{3}Pz by ground-state pyrazine was also observed, $k_q = 5.8 \times 10^8$ M^{-1} sec^{-1}. Based on this result, the decay of ^{3}Pz in water at "infinite" dilution was found to be $k = 2.2 \times 10^5$ sec^{-1} at pH 7.1. In slightly acidic aqueous solution, pH 3-4, the triplet-triplet absorption decayed rapidly and a quenching rate constant by H_3O^+ of 1.6×10^{10} M^{-1} sec^{-1} was derived. In alkaline solutions, ^{3}Pz was also quenched by OH^- ions with $k_q = 3.2 \times 10^8$ M^{-1} sec^{-1} (see more below). It should be noted that in the presence of H_3O^+ or OH^- the *initial* quantum yield for formation of ^{3}Pz remained the same, only its lifetime was affected.

In the presence of good H atom donors, such as aliphatic alcohols, cyclohexane, cyclopentane, etc., the pyrazine triplet is effectively quenched with rate constants $\sim 10^6$–10^8 M^{-1} sec^{-1} (see Table II). New transient absorptions were observed following the quenching of ^{3}Pz by H atom donors—with the rate of formation of the new species equal to the rate of decay of the T-T absorption. These observations support the ^{3}(n,π*) assignment given previously.[5]

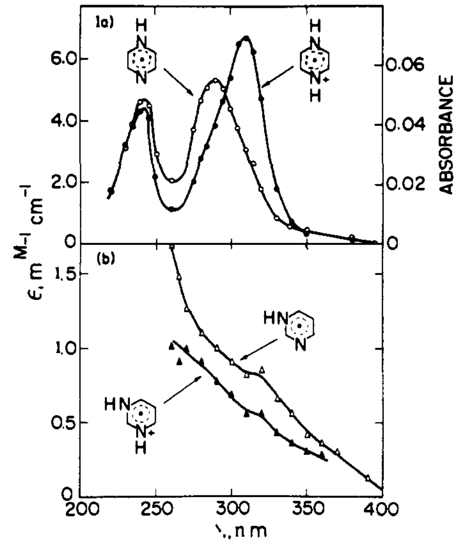
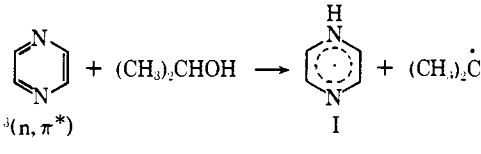
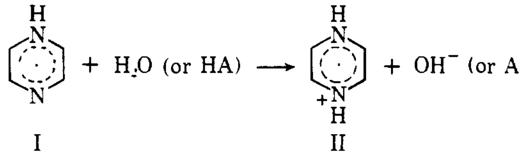


Figure 2. Absorption spectra of the radicals produced in water by quenching of the triplet states of diazines by H atom donors: (a) pyrazine (10^{-4} M, pH 7.1) by isopropyl alcohol (2.0 M), optical density read at 30 nsec, ○, and 1.0 μsec, ●, after the laser pulse; (b) pyrimidine (2.5 mM, pH 5.4) by isopropyl alcohol (1.0 M), optical density read at 100 nsec, ○, and 15 μsec, ●, after the pulse.

In 2.0 M isopropyl alcohol at pH 7.1, the ^{3}Pz has essentially decayed within the 15-nsec laser pulse. The transient species (I) observed has maxima at ~290 and ~242 nm; see Figure 2a. Species I decays and, at ~1 μsec after the laser pulse, species II is observed with λ_{max} at ~310 and ~242 nm, Figure 2a. The transient absorptions of species I and II have recently been observed[17] in the pulse radiolysis of pyrazine in water. These were produced from the one-electron reduction of pyrazine by hydrated electrons, e_{aq}^-. Based on the assignment given[17] for these species, the chemical reaction of ^{3}(n,π*) pyrazine is suggested to be as follows:



^{3}(n, π*) + $(CH_3)_2CHOH \longrightarrow$ I + $(CH_3)_2\dot{C}OH$ (2)



I + H_2O (or HA) $\longrightarrow$ II + OH^- (or A^-) (3)

Species I is the neutral monohydropyrazyl radical ·PzH and species II the dihydrocation radical $\cdot PzH_2^+$. The pK_a for eq 4 was found[17] to be 10.6 ± 0.1.

$$\cdot PzH_2^+ \rightleftharpoons \cdot PzH + H^+ \tag{4}$$

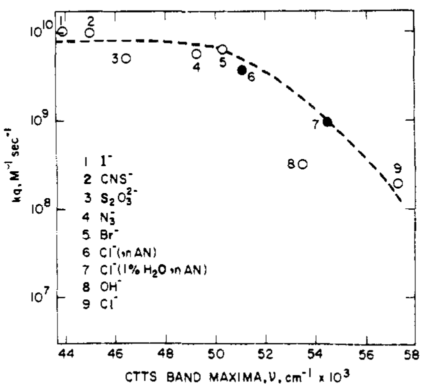


Figure 3. Correlation between the quenching rate of the pyrazine triplet state (1.0×10^{-4} *M*, pH 7.1) by inorganic ions in water and the CTTS absorption band maxima of the ions (see text).

Table III. Quenching of $^3(n, \pi^*)$ Pyrazine by Inorganic Ions in Aqueous Solution[a]

Inorganic ion	CTTS band maxima ν, cm^{-1} × 10^{-3}	k_q,[f] M^{-1} sec^{-1}
KI	43.9	1.0×10^{10}
KCNS	45.0	9.7×10^9
$Na_2S_2O_3$	46.5	5.0×10^9
KN_3	49.3	5.9×10^9
KBr	50.3	6.7×10^9
$(CH_3)_4NCl$[b]	51.1	3.8×10^9
LiCl[c]	54.5	1.0×10^9
KOH[d]	53.5	3.2×10^8
KCl	57.1	1.9×10^8
Na_2SO_4	57.1	$\leq 5.0 \times 10^5$
KH_2PO_4[e]		6.9×10^8
KNO_2		6.4×10^9

[a] Argon-saturated solutions containing 10^{-4} *M* pyrazine at pH 7.1. [b] In neat acetonitrile. [c] 1% water in acetonitrile. [d] pH 11–13. [e] pH 5.4. [f] Values to ±15%.

The rate of formation of $\cdot PzH_2^+$ from the decay of $\cdot PzH$ in solutions containing 0.5 *M* *i*-PrOH and 10^{-4} *M* pyrazine at pH 7.1 (no buffer added) was monitored at 290 and 310 nm, and a $k \sim 7.0 \times 10^6$ sec^{-1} was observed. Assuming that the protonation of $\cdot PzH$ is by water, $k_3 \sim 1.3 \times 10^5$ M^{-1} sec^{-1} can be derived.

The acetone ketyl radicals produced in reaction 2 do not react with pyrazine to form $\cdot PzH$ (or $\cdot PzH_2^+$), since the kinetic potentials for such a reaction are not favorable.[17,18]

Based on the extinction coefficients derived by pulse radiolysis[17] for the $\cdot PzH$ and $\cdot PzH_2^+$ radicals, and assuming that the quenching of $^3(n,\pi^*)$ pyrazine by isopropyl alcohol produced stoichiometric equivalents of the radicals, the T-T absorption spectrum shown in Figure 1 was corrected for depletion of ground state pyrazine. In addition, it was possible to determine the extinction coefficient of ^3Pz: for the absorption maxima at 230, ~260, ~295, ~640, 700, and 810 nm the ϵ values are 3.5×10^3, 4.9×10^3, 2.0×10^3, 9.4×10^2, 1.1×10^3, and 1.0×10^3 M^{-1} cm^{-1}, respectively.

The quantum yield for intersystem crossing (ϕ_{ISC}) was derived based on the anthracene actinometer (see Experimental Section). A $\phi_{ISC} = 0.87 \pm 0.1$ was obtained for pyrazine in water at 25°. A $\phi_{ISC} = 0.33$ has been reported[5] in *n*-hexane at 25°, using the cis-trans isomerization method for measuring ϕ_{ISC}. This low yield of triplets is most probably due to partial quenching of ^3Pz by *n*-hexane, which can be estimated based on the ratio of rate constants of k_q and *k* (energy transfer to isomerization) and the concentration of isomer used. It was not realized[5] at the time that $^3(n,\pi^*)$ pyrazine can be quenched by H atom donors.

On laser photolysis of pyrazine in neat cyclohexane, immediately following the decay of the T-T absorption a transient absorption spectrum was observed which can be assigned to the superimposition of the spectrum of $\cdot PzH$ and that of the cyclohexyl radical $C_6H_{11}\cdot$ previously reported.[19]

$$^3(n,\pi^*)Pz + C_6H_{12} \longrightarrow \cdot PzH + C_6H_{11}\cdot \qquad (5)$$

One may argue, with justification, that the formation of radicals on optical excitation of Pz in H atom donating solvents may be due, in part, to the quenching of the $^1(n,\pi^*)$ state. The strong absorption of ^3Pz in the 240-290-nm region prevents an accurate assessment of the yield of $\cdot PzH$ formed from $^1(n,\pi^*)$ within the laser pulse (~15 nsec). However, a small "growing in" of the absorption due to $\cdot PzH$, at a rate corresponding to the decay of ^3Pz, can be observed at 280 nm. This indicates that a substantial amount of $\cdot PzH$ is formed via quenching of ^3Pz. In dilute aqueous solutions of quenchers, the short lifetime of ^1Pz prevents significant formation of $\cdot PzH$ from $^1(n,\pi^*)$, but this argument cannot be used in more concentrated solutions.

Quenching by Inorganic Ions. Because of the charge transfer character of the triplet (n,π^*) states of aromatic nitrogen heterocyclic molecules, efficient quenching by electron donor compounds could be expected. Table III shows the quenching rates of $^3(n,\pi^*)$ pyrazine by a number of inorganic ions. These ions were chosen on the basis of their known ability to photoionize. The electronic spectra[21] of these ions in polar solvents have been assigned as charge-transfer-to-solvent, CTTS. The k_1 values given in Table III have been plotted against the CTTS band maxima[21,22] of these ions; see Figure 3.

The dependence of k_q upon ν_{max} of the CTTS electronic transitions of the inorganic ions would appear to suggest that the quenching of the triplet state of pyrazine occurs via an electron transfer type of interaction with the quencher, and not via an energy transfer mechanism. Weller and coworkers[23] have provided ample evidence for charge-transfer interactions leading to the quenching of singlet excited states. However, our results and another study[24a] appear to be the first correlation indicating a charge-transfer mechanism for the quenching of triplet states in fluid solution.

The CTTS maxima of $H_2PO_4^-$ and NO_2^- ions are not known. The quenching of ^3Pz by $H_2PO_4^-$ is probably via a proton transfer mechanism, similar to H_3O^+, but with a lower quenching rate constant. Quenching by KNO_2 is considered to occur via an energy transfer mechanism (as compared to a charge transfer mechanism) since the triplet level of NO_2^- was found[24a] to be 53 ± 2 kcal/mol. This E_T level is lower than that of ^3Pz, 76 kcal/mol.[2,3] The low quenching rate by SO_4^{2-} ions may, in part, be due to the double negative charge on the ion.

Subsequent to the quenching of ^3Pz by M^- ions, very weak absorptions are observed at the wavelengths corresponding to the absorption maxima of the inorganic radicals, e.g., for $I_2\cdot^-$ at 385 nm, for $S_2O_3\cdot^-$ at 375 nm, for $(CNS)_2\cdot^-$ at 485 nm, and for $Br_2\cdot^-$ at 365 nm. Based on the known[24b] extinction coefficients of these radicals, one can say that if they are formed via reaction 6 then the efficiency of this reaction is ≤5%.

$$^3Pz + M^- \xrightarrow{H_2O} \cdot PzH + M\cdot + OH^- \qquad (6)$$

Pyrimidine. Optical excitation at 265 nm of pyrimidine (1.0×10^{-3} M) in water at pH 7.1 produced a broad short-lived absorption spectrum with a prominent band at $\lambda < 260$ nm; see Figure 4. This spectrum is suggested to be the $^3(n,\pi^*)$ T-T absorption of pyrimidine (Pm). Its lifetime ($k = 7.1 \times 10^5$ sec^{-1}) at "infinite dilution" is appreciably shorter than that of ^3Pz. No formation of e_{aq}^-, and hence

Table IV. Quantum Yields and Extinction Coefficients of Triplet States of Diazines in Water at 25°

Diazine	ϕ_{ISC}	λ, nm	ε,[a] M^{-1} cm^{-1}
Pyrazine	0.87 ± 0.1	~260	4.9 × 10^3
		700	1.1 × 10^3
Pyrimidine	1.0 ± 0.2	260	~3.0 × 10^3
		600	5.3 × 10^2
Pyridazine	⩽0.02[b]		
Quinoxaline	⩾0.67	270	⩽14.9 × 10^3
		413	⩽7.4 × 10^3
		432	⩽7.2 × 10^3
		660	⩽1.4 × 10^3

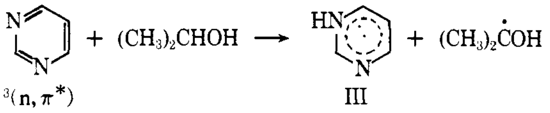
[a] See text for method used to derive these values. [b] In neat isopropyl alcohol.

no photoionization of pyrimidine in water, could be observed. The ionization potential of pyrimidine is reported[15] to be 9.5 eV. Following the decay of ^{3}Pm, a very weak transient spectrum was seen (Figure 4).

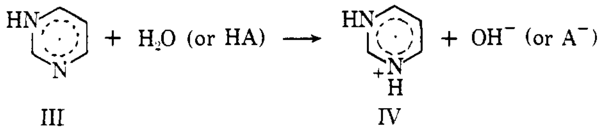
Based on the anthracene actinometer, a $\phi_{ISC} = 1.0 \pm 0.2$ was found for pyrimidine in water at 25°. A $\phi_{ISC} = 0.12$ was reported[5] in *n*-hexane at 25°, determined using the cis-trans isomerization method.[20] This value may be too low for the same reasons given above for pyrazine.

Quenching and Chemistry of ^{3}(n,π*) Pyrimidine. Oxygen quenches ^{3}Pm with $k_q = 4.6 \times 10^9$ M^{-1} sec^{-1}. Ground state pyrimidine also quenches ^{3}Pm with $k_q = 1.5 \times 10^8$ M^{-1} sec^{-1}. Just as was found for ^{3}Pz, H_3O^+ and OH^- ions quench ^{3}Pm but with a somewhat lower rate (see Table II).

In the presence of isopropyl alcohol, the ^{3}(n,π*) Pm is quenched with $k_q = 8.6 \times 10^7$ M^{-1} sec^{-1} and a new transient absorption is observed (see Figure 2b). The relatively weak and poorly defined transient spectrum observed changes with time, as shown. These spectra, however, are quite similar to those observed[17] by pulse radiolysis from the reaction of e_{aq}^- with pyrimidine. Based on this comparison, the quenching of ^{3}(n,π*) pyrimidine by H atom donors is suggested to be as follows:



(7)



(8)

The pK_a for equilibrium 9 was found[17] to be 7.6 ± 0.1. The acetone ketyl radicals produced in reaction 7 do not

$$\cdot PmH_2^+ \rightleftharpoons \cdot PmH + H^+ \qquad (9)$$

react with pyrimidine[17,18] by an electron transfer mechanism. Based on the extinction coefficients of the $\cdot PmH_2^+$ and ·PmH radicals derived from pulse radiolysis work,[17] and assuming stoichiometric conversion of ^{3}Pm to these radicals, an ϵ_{260} ~3 × 10^3 M^{-1} cm^{-1} was derived for the T-T absorption of pyrimidine in water. Unlike the observations described above for ^{3}Pz, no "growing in" of ·PmH could be observed in the region 260-300 nm. However, this is understandable when one compares the extinction coefficients of ^{3}Pm and ·PmH in this wavelength region.

Pyridazine. An extremely weak absorption was observed, under our experimental conditions, on optical excitation of 5 mM pyridazine (Pd) in water. In neat isopropyl alcohol, the transient absorption was also too weak to examine. Based on the extinction coefficients derived from pulse radiolysis[17] for the ·PdH radical, an estimated value of $\phi_{ISC} \leq 0.02$ was derived.

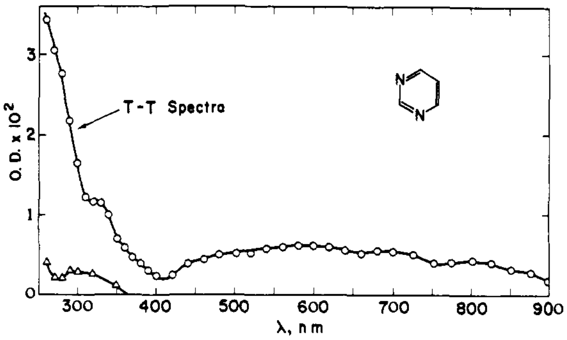


Figure 4. Absorption spectra of the transient species produced on optical excitation at 265 nm of pyrimidine (10×10^{-3} M, pH 7.1, 25°) in water (and in presence of 1 atm of N_2O and 1.0 M *t*-BuOH). Optical density was measured at 30 nsec, ○, and ~2 μsec, △, after the laser pulse. T-T spectrum was corrected for depletion of ground state pyrimidine (see text).

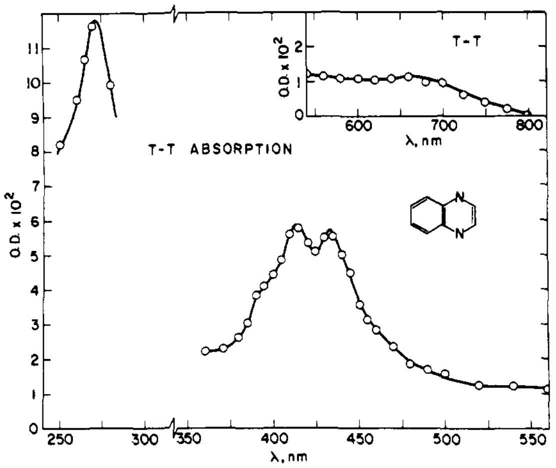


Figure 5. Absorption spectrum of the triplet state of quinoxaline (1.1×10^{-3} M, pH 7.1, 25°) in water. Optical density was read at 30 nsec after the pulse and was not corrected for depletion of ground state quinoxaline.

It is interesting to note that the fluorescence of (n,π*) singlet excited pyridazine has been observed[8] in various solvents, but no phosphorescence has been reported.[2,3,5] However, a $\phi_{ISC} = 0.2$ in *n*-hexane at 25° was reported[5] using the cis-trans isomerization method.[20] No explanation for this difference can be offered. The ϕ_F at 25° is reported[5] to be 3×10^{-4} in water and 2×10^{-4} in isooctane.

Quinoxaline. Optical excitation at 265 nm of quinoxaline (1.1×10^{-3} M) in water at pH 7.1 produced a strongly absorbing transient species with maxima at ~270, 413, 432, and ~660 nm, see Figure 5. This transient absorption decayed with $k = 3.4 \times 10^4$ sec^{-1} (in 1.1×10^{-4} M quinoxaline); see Table I. This spectrum is assigned to the (π,π*) triplet-triplet absorption spectrum of quinoxaline in water, as previously suggested[4,7,25-28] in glassy media. The T-T absorption maximum of quinoxaline was reported to have a one band maximum at 417 nm in an EPA glass[7] and at 425 nm in an alcohol-pentane glass.[26] The resolved double bands in the 410-430-nm region, as well as the bands in the far-uv and the visible regions (Figure 5) have apparently not been observed.

A very similar T-T spectrum was observed on excitation of quinoxaline in neat isopropyl alcohol (see Figure 6). In 1.1×10^{-4} M solutions it decays with $k = 1.8 \times 10^5$ sec^{-1}.

Quenching and Chemistry of ^{3}(π,π*) Quinoxaline. The ^{3}Qx in water is quenched by oxygen with $k_q = 1.4 \times 10^9$ M^{-1} sec^{-1}, and by ground-state quinoxaline with $k_q = 6.9 \times 10^7$ M^{-1} sec^{-1}. The quenching by H_3O^+ and OH^- ions, Table II, is much slower than was observed for ^{3}(n,π*) Pz

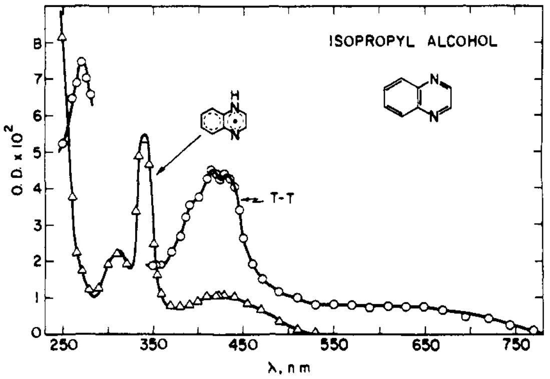
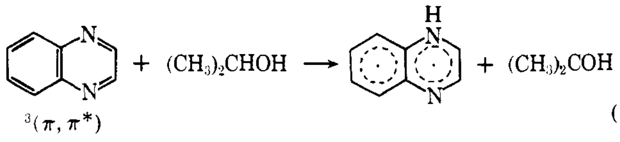


Figure 6. Absorption spectra of the transient species produced on optical excitation at 265 nm of quinoxaline (6.0×10^{-4} M) in neat isopropyl alcohol. Optical density of triplet was measured at 30 nsec after the pulse and optical density of radical at ~20 μsec after the pulse. The radical spectrum was corrected for depletion of ground state quinoxaline (see text).

and ^{3}(n,π*) Pm, while the quenching by oxygen and by the ground-state of the parent molecule is of the same order of magnitude for all these diazines. These results are in agreement with the (π,π*) character of ^{3}Qx.

In neat isopropyl alcohol, ^{3}Qx decays faster than in water, Table I. The decay of ^{3}Qx in *i*-PrOH was monitored at 413 nm ($k = 1.8 \times 10^5$ sec^{-1}), and the simultaneous formation of a strong new transient absorption was monitored at 340 nm ($k = 1.7 \times 10^5$ sec^{-1}). From these data, $k_q \leq 1.4 \times 10^4$ M^{-1} sec^{-1} can be derived for quenching of ^{3}Qx by *i*-PrOH. The new transient is assigned to the quinoxalinyl radical, Figure 6, based on the known[17] absorption spectrum for this radical.

The absorption maxima at ~435 and ~340 nm for the radical (Figure 6) correspond to that of the neutral radical ·QxH previously identified,[17] with extinction coefficients 1.6×10^3 and 8.8×10^3 M^{-1} cm^{-1}, respectively. The following mechanism is suggested:



(10)

The ·QxH can be protonated, and a pK_a = 8.8 ± 0.1 has been found[17] for equilibrium 11

$$\cdot\mathrm{QxH_2}^+ \rightleftharpoons \cdot\mathrm{QxH} + \mathrm{H}^+ \qquad (11)$$

The acetone ketyl radical can react with quinoxaline, with $k_{12} = 1.6 \times 10^8$ M^{-1} sec^{-1} (ref 17)

$$(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + \mathrm{Qx} \longrightarrow \cdot\mathrm{QxH} + \mathrm{CH_3COCH_3} \qquad (12)$$

The formation of a strong radical absorption due to ·QxH at a rate identical with that of the decay of ^{3}Qx is a significant observation. It demonstrates, for the first time, that quenching of the ^{3}(π,π*) state of aza aromatics by H atom donors leads to the formation of azyl radicals. A comparison of the absorbance at 340 nm before and after the decay of ^{3}Qx indicates that ≥85% of ·QxH radicals are formed from ^{3}Qx. It should be noted that it is not, of course, possible to exclude some chemistry from the ^{1}(n,π*) state of quinoxaline.

In a manner identical with that employed for ^{3}Pz and ^{3}Pm, it is possible to determine the extinction coefficient of ^{3}Qx, based on the known[17] ε of ·QxH. Because of the relatively slow rate of quenching by *i*-PrOH, it is possible that ^{3}Qx is also decaying by other pathways which do not lead to the formation of ·QxH. The ε obtained can, therefore, only be considered as an upper limit. The value thus obtained in *i*-PrOH solution is $\epsilon_{413} \leq 7400$ M^{-1} cm^{-1}. This can be compared with previously determined values of 8.1×10^3 M^{-1} cm^{-1} at 425 nm[26] and 2.5×10^3 M^{-1} cm^{-1} at 410 nm.[25]

If the extinction coefficient of ^{3}Qx in water is assumed to be the same as that in *i*-PrOH, then the ϕ_{ISC} of quinoxaline in water at 25° can be derived. This was determined vs. the anthracene actinometer, and a value of $\phi_{\mathrm{ISC}} \geq 0.67$ was derived (see Table IV). This value is to be compared[26] with 0.18 in rigid alcohol glasses at 77 K and 0.27 in hydrocarbon glasses at 77 K.

The quenching rate of ^{3}(π,π*) quinoxaline by inorganic ions in aqueous solutions is very low, $k_q < 10^5$ M^{-1} sec^{-1} (see Table II), whereas ^{3}(n,π*) Pz and Pm exhibited high quenching rates. These results show that the (n,π*) or (π,π*) nature of the excited states of diazines can be inferred from the quenching rates of the excited states of these molecules by H atom donors and by inorganic ions having CTTS character.

Phthalazine. A few experiments have been carried out with this compound. Previous[29-31] phosphorescence results on phthalazine indicated properties akin to either (π,π*) or (n,π*) triplet states. A recent[30] reassignment for the phthalazine triplet indicates (π,π*) character with some (n,π*) character.

The T-T absorption of phthalazine (3.3×10^{-4} M) was found to decay with $k = 4.7 \times 10^4$ sec^{-1} in water at pH 7.1. In neat isopropyl alcohol, the triplet decays with $k = 2.6 \times 10^5$ sec^{-1} indicating a relatively low quenching rate by this H atom donor ($k_q \leq 2.0 \times 10^4$ M^{-1} sec^{-1}). This is in keeping with a strong ^{3}(π,π*) character in this solvent. In water, triplet phthalazine is quenched by oxygen with $k_q = 1.4 \times 10^9$ M^{-1} sec^{-1}.

A very recent[32] flash photolysis work on phthalazine in ethanol at room temperature concluded that the lowest triplet state is of (n,π*) character. This was based on the observation of the transient spectrum of the phthalazinyl radical, in addition to the T-T spectrum. The formation of the radical could be due, however, to either (a) the quenching of the ^{3}(π,π*) by ethanol, as mentioned above for *i*-PrOH, with a relatively low quenching rate constant, and/or (b) to the quenching of ^{1}(n,π*) excited state by the H atom donor. The rate constant for this reaction is not known, but would have to be $\geq 10^8$ M^{-1} sec^{-1} in view of the short lifetime of the singlet excited state. The quenching of a higher excited singlet state of phthalazine[33] by alcohols and other H atom donating solvents cannot be eliminated.

Conclusions

The triplet-triplet absorption spectra and lifetimes of (n,π*) and (π,π*) states of diazines have been determined. In water as solvent, the lifetimes of the ^{3}(n,π*) states of pyrazine and pyrimidine are found to be shorter (by about one order of magnitude) than the lifetimes of the ^{3}(π,π*) states of quinoxaline and phthalazine. The ^{3}(n,π*) states are strongly quenched by H atom donors with the formation of azyl and donor radicals, while the ^{3}(π,π*) diazines react relatively very slowly with H atom donors.

Another possible probe to distinguish between ^{3}(n,π*) and ^{3}(π,π*) states of diazines is the rate of quenching by certain inorganic ions which exhibit CTTS character. The ^{3}(n,π*) states are effectively quenched ($k_q \sim 10^{10}$ M^{-1} sec^{-1}) while ^{3}(π,π*) states are quenched with relatively low rates ($k < 10^5$ M^{-1} sec^{-1}) by these ions.

The quenching of ^{3}(n,π*) states of diazines by H atom donors is considerably more efficient than the corresponding reaction with ^{3}(n,π*) states of aromatic carbonyl compounds.[2,12] From the limited data available, it would appear that the rates of quenching of ^{3}(π,π*) states of diazines and carbonyl compounds by H atom donors may be of the same order.

The chemistry of the triplet state of *sym*-triazine has been studied[34] and was found to be similar to that of the diazabenzenes examined in this work.

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Photoelectron Spectroscopy and Quantum Chemical Analysis of Some *N*-Nitrosamines

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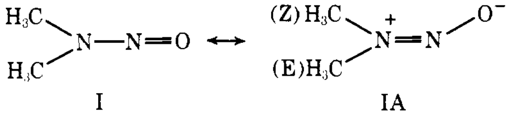
Abstract: Photoelectron (PES) and electronic absorption spectra of a series of *N*-nitrosamines have been obtained and compared with the results of CNDO/2 and CNDO/S calculations; all observable PES and electronic absorption bands have been assigned. The highest occupied molecular orbital is a π orbital, and the subjacent occupied orbital is an n orbital localized on the nitroso oxygen. Bond orders, charge densities, and dipole moments determined by the calculations are presented and discussed. The calculated π charge densities indicate that the amino nitrogen is electron deficient; however, the calculated total charge densities indicate that amino nitrogen is slightly electron rich. Barriers to syn-anti isomerization of dimethylnitrosamine by means of both rotation around the N-N bond and inversion at the nitroso nitrogen have been calculated by means of the CNDO/2 method. The inversional barrier is four times greater than the rotational barrier. The calculated rotational barrier, 18.2 kcal/mol, has the same magnitude as that of the experimentally determined barrier, 23 kcal/mol. Conformational analyses of methylphenylnitrosamine and of diisopropylnitrosamine have been made by means of the CNDO/2 method and have been compared with the analyses of previous investigations.

Introduction

The NMR spectrum of dimethylnitrosamine (I) consists of two singlets.[1] The nonequivalence of the two methyl groups is postulated to be the result of partial double bond character between the two nitrogen atoms; one methyl group is syn (*Z*) and the other is anti (*E*) to the nitroso oxygen.[1,2,3] NMR coalescence studies have given the energy of activation for reorientation of the methyl groups in dimethylnitrosamine (I) to be 23 kcal/mol.[1] The observation of two separate methyl resonances implied a planar or nearly planar configuration for all atoms but hydrogens in dimethylnitrosamine.



I IA

X-Ray diffraction studies[4] on dimethylnitrosaminecopper(II) chloride $(CH_3)_2N\text{-}NOCuCl_2$ and electron diffraction studies on dimethylnitrosamine[5,6] have indicated that the C_2N_2O atoms in both compounds lie in a single plane. A comparison of the bond lengths of gaseous dimethylnitrosamine and of the copper(II) chloride complex reveals that both have the same C-N bond length but the N-N and N-O bond lengths in the complexed molecule are shorter by 0.08 and 0.02 Å, respectively,[6] than the corresponding bond lengths in the gaseous one. The greater shortening of the N-N bond distance in the complex indicates that complexation increases the N-N bond order more than it increases the N-O bond order.

In order to establish the energetic ordering of the molecular orbitals we have studied the photoelectron spectra of some *N*-nitrosamines. Quantum chemical calculations of the CNDO/2 and CNDO/S type have been performed to obtain orbital energies and transition energies of com-