Formal Hydride Transfer Mechanism for Photoreduction of 3-Phenylquinoxalin-2-ones by Amines. Association of 3-Phenylquinoxalin-2-one with Aliphatic Amines

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The photophysical and photochemical behavior of 1-methyl-3-phenylquinoxalin-2-one (MeNQ) and 3-phenylquinoxalin-2-one (HNQ) in the presence of amines is reported. While HNQ fluorescence shows an auxochromic effect and a bathochromic shift with added amines, explained by association of HNQ with amine in the ground state and emission from both excited species HNQ* and [HNQ−amine]*, both MeNQ and HNQ are photoreduced efficiently on irradiation in the presence of amines, leading to the semireduced quinoxalin-2-ones, $MeNQH^-$ and $HNQH^-$, respectively, via an electron−proton−electron transfer, with unit quantum yields at high amine concentrations. The semireduced quinoxalin-2-ones $XNQH^-$ (X = H, Me) revert almost quantitatively to the parent XNQ in a dark thermal reaction with an activation free energy for $MeNQH^-$ of 17.4 and 25.9 kcal/mol in acetonitrile and benzene, respectively. Kinetic and spectroscopic (UV and NMR) evidence supports the proposed reaction mechanism for the reversible photoreduction.

Introduction

Quinoxalin-2-ones and their derivatives have been studied extensively during the past two decades and are synthetic precursors of antihypertensives and analgesics.[1,2] Other derivatives have been prepared to evaluate their anticancer activity in vitro[3] and as neurotransmitter antagonists.[4,5]

Many studies are focusing on the use of quinoxalin-2-one derivatives as fluorophores for trace analyses of carboxylic acids, alcohols, and amines in high-performance liquid chromatography.[6−10] Quinoxalin-2-ones bound to azacrown ethers have also been used as fluoroionophores to sense alkali metal ions.[11,12]

Quinoxalin-2-ones and related oxazin-2-ones undergo efficient [2 + 2] cycloadditions with alkenes to give tricyclic azetidines.[13−15] Dye-sensitized oxygenation of tetrahydro derivatives produces the epidioxygenated quinoxalin-2-ones,[16] and the photoreduction of quinoxalin-2-ones by amines is an efficient process. Irradiation of substituted 3-phenylquinoxalin-2-ones in the presence of amines gives the corresponding dihydro-quinoxalin-2-ones, while irradiation of 3-alkyl-substituted quinoxalin-2-ones gives the reductive dimers. A mechanism analogous to the photoreduction of ketone triplets by amines has been invoked to explain product formation.[17]

In the photoreduction of many chromophores by electron donors, excited-state quenching by electron transfer from the reductant leads to transient ion-radical pairs, but as a result of back electron transfer, there are no permanent chemical changes.[18] For some compounds, electron-transfer quenching generates basic radical anions that are easily protonated and semireduced free radicals accumulate.[19,20] Disproportionation of the radical can generate, among other compounds, stable or metastable products of two-electron reduction or dihydro compounds. This type of photoreaction has been reported for ketones, quinone derivatives, and thioindigo dyes.[19−21]

It is generally accepted that for some donor−acceptor pairs, excited-state quenching proceeds via sequential transfer of a single electron, SET, followed by proton and

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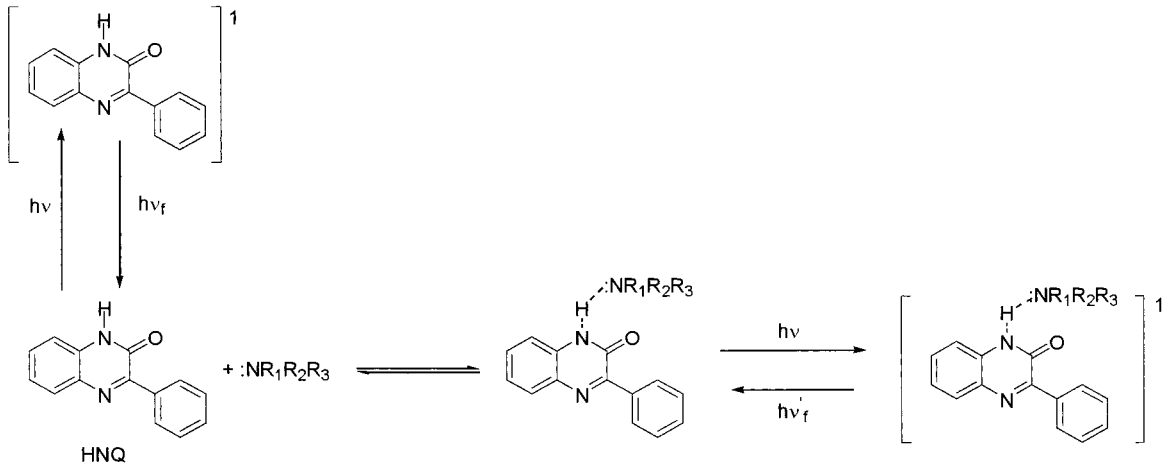
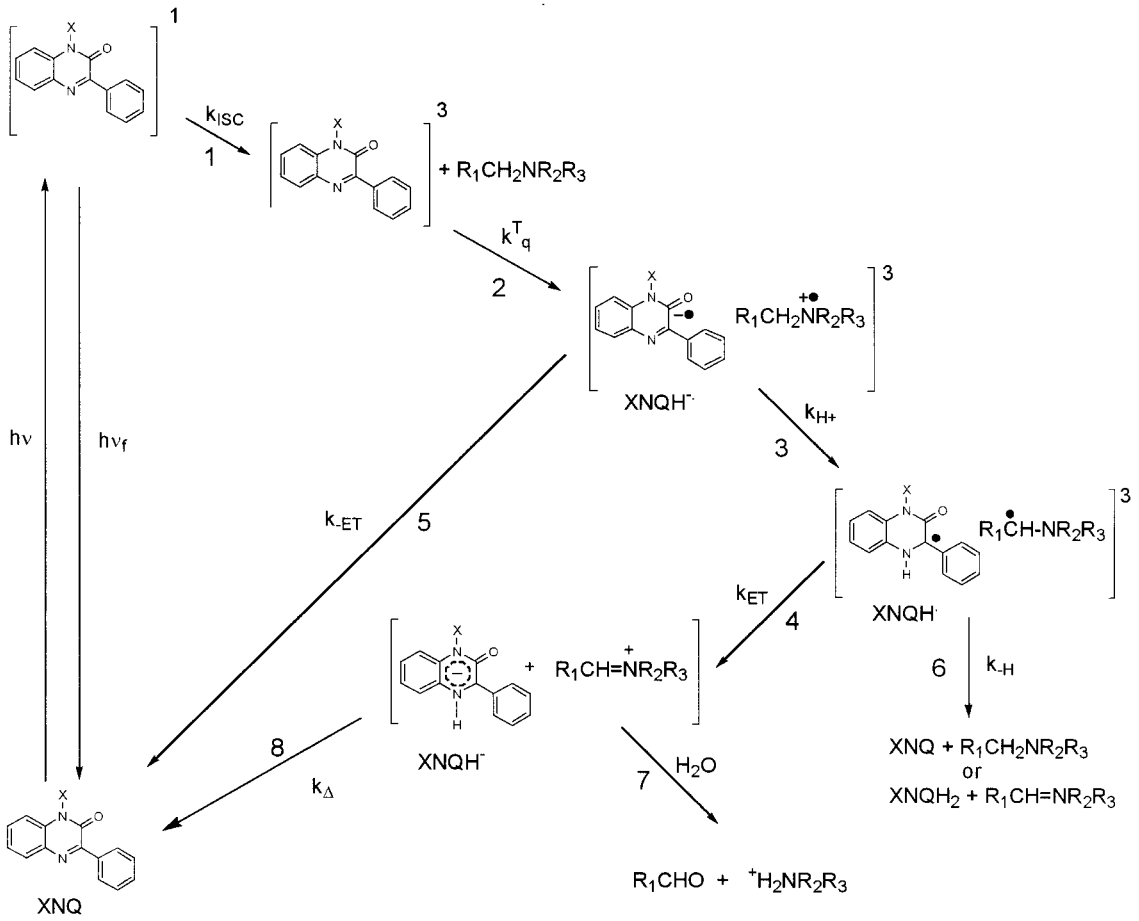
Scheme 1



Scheme 2



second electron transfer, resulting in a net hydride transfer within the quenching complex.[22] This process leads to reactive even-electron ion pairs that are, however, more stable kinetically than ion-radical pairs.[20] The reaction should then be reversible, and one or both of the reactants will be recyclable. However, examples are relatively rare, because the reversibility of the system depends largely on the thermodynamic stability of these intermediates or metastable products relative to other reaction pathways.[23]

In this study we report the unexpected photophysical and photochemical behavior of quinoxalin-2-one derivatives, the amine-induced enhancement of emission of 3-phenylquinoxalin-2-ones (HNQ), and the nearly quantitative reversible photoreduction of 1-methyl-3-phenylquinoxalin-2-one (MeNQ) and HNQ by amines. (The structures of these compounds are shown in Schemes 1 and 2). Although photoreductions of quinoxalin-2-ones by amines are well studied, this reversible photobleaching process has not been reported.

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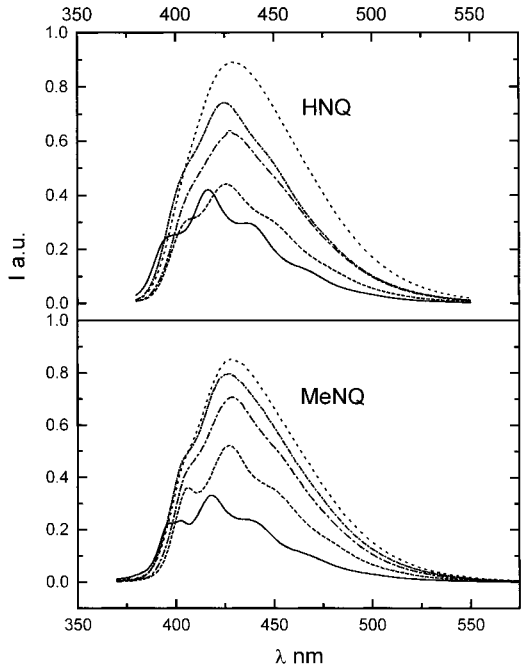

Figure 1. Emission spectra of absorbance-matched solutions of 3-phenylquinoxalin-2-one (HNQ) and 1-methyl-3-phenylquinoxalin-2-one (MeNQ) in *n*-hexane, benzene, acetonitrile, chloroform, and methanol, ordered from bottom to top.

Table 1. Fluorescence Quantum Yields and Stokes Shift for 3-Phenylquinoxalin-2-ones in Various Solvents at 20 °C

	HNQ		MeNQ	
solvent	Φ_f [a]	$\Delta\nu$ cm^{-1}	Φ_f [a]	$\Delta\nu$ cm^{-1}
n-hexane	0.010	3739	0.011	3086
benzene	0.011	4303	0.017	3857
chloroform	0.020	4248	0.029	4142
acetonitrile	0.017	4358	0.025	4187
methanol	0.025	4467	0.032	4267
DMF	0.016	4683	0.025	4082
ethanol			0.034	4097

[a] Against fluorescence of quinine sulfate.

Results and Discussion

Both 3-phenylquinoxalin-2-ones, HNQ and MeNQ, show absorption bands with maxima centered around 300 and 360 nm that can be attributed to nπ^* transitions of the rigid N=C−C=O chromophore of the heterocycle, which are insensitive to solvent polarity or amine concentration. However, emission spectra of both compounds are very sensitive to solvent. The emission is structured in nonpolar solvents, e.g., *n*-hexane, but in polar solvents, e.g., acetonitrile or methanol, the vibronic structure is missing (Figure 1). Concomitantly with this loss of spectral structure, the fluorescence quantum yield and Stokes shift increase with the increase of solvent polarity (Table 1). These increasing quantum yields and the red shifts are consistent with a polar excited state, probably originated by intramolecular charge transfer. Also for both quinoxalin-2-ones fluorescence quantum yield depends on the solvent acidity as show by the correlation ($r > 0.85$) with Swain's "Acity" parameter.[24]

Effect of Amine Addition on Emission Spectra. Addition of amines to quinoxalin-2-one solutions produces two unexpected effects in the emission spectra depending on the 1,N substituent. The fluorescence emission of MeNQ is slightly quenched by amines following the usual Stern−Volmer kinetics. The lifetime is approximately 100 ps for the emission from MeNQ in N_2-purged acetonitrile from phase-shift experiments. The same lifetime, within experimental error, was observed in aerated solutions. Quenching of MeNQ emission by various amines was carried out in N_2–purged acetonitrile and gives deactivation constants, k_q, near the diffusion limit (Table 2) that correlate approximately with amine oxidation potentials, suggesting deactivation of excited MeNQ by electron transfer.

Fluorescence quenching of HNQ with DABCO and aniline follows normal Stern−Volmer kinetics. Slopes of Stern−Volmer plots for these amines were 9.24 ± 0.48 and 2.78 ± 0.07 M^{-1}, respectively. Lifetimes for HNQ were ca. 90 ps in aerated or N_2-purged solutions.

There was an emission enhancement with a bathochromic shift of the whole emission band when triethylamine, TEA, or other aliphatic amines were used as quenchers in various solvents. In some of the solvents, a clear isoemissive point appears with increasing amine concentration, suggesting an equilibrium between two emitting species, namely, HNQ* and a complex [HNQ−amine]*. At high amine concentrations the emission intensity decreases, possibly as a result of quenching of the remaining free excited HNQ* and/or the excited complex, reflecting competition between complexation and quenching.

Remarkably, the absorption spectra did not change when the amine concentration was increased, precluding a ground-state charge-transfer interaction between HNQ and the amine. Nevertheless a shoulder appeared in the excitation spectra that grew with amine concentration, indicating the excitation of at least two molecular species. In Figure 2 are shown the absorption and excitation spectra of HNQ in the presence of DEA showing the apparition of new bands and hypsochromic shift in the excitation spectra. At high amine concentrations a slight hypsochromic shift in the absorption band at 300 nm is observed.

However, with HNQ/TEA in CD_3CN, the ^{1}H NMR N-H signal of HNQ at 10.8 ppm first broadens and then disappears on increasing the molar ratio of TEA/HNQ from 0.1 to 0.6, reflecting proton exchange between HNQ and TEA, which is strong evidence that HNQ and TEA associate via hydrogen bonding. Other indirect evidence for hydrogen bonding is the lack of an auxochromic effect with MeNQ. However, partial or total intramolecular proton transfer from ground-state 3-phenylquinoxalin-2-one to the amine is possible.

An alternative explanation of emission enhancement could be an equilibrium between HNQ and its enolic form, but it was excluded because absorption spectra did not change with solvent polarity. In addition, association in the excited state is ruled out by the short lifetime of the species involved.

The auxochromic effect due to addition of amines to HNQ can be explained by considering the processes in Scheme 1, where ground-state equilibrium is established between free species and an HNQ−amine complex. As noted this complex could involve hydrogen-bonding interactions between the amine lone pair and the N-H of 3-phenylquinoxalin-2-one.

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Table 2. Fluorescence Quenching Constants (k^S_q) for MeNQ by Amines and Apparent Complexation Constants (K) for HNQ by Amines in Different Solvents

k^S_q[a] at 20 °C [E_{ox}[b] (V)]

amine					
DABCO	TEA	aniline	DEA (Et_2NH)	t-$BuNH_2$	i-$PrNH_2$
5.6×10^{10} [0.292]	2.3×10^{10} [0.450]	3.7×10^{10} [0.475]	0.94×10^{10} [0.702]	*c* [1.300]	*c* [1.250]

K[d] at 20 °C (M^{-1})

	solvent					
amine	$CHCl_3$	CH_2Cl_2	C_6H_6	CH_3OH	CH_3CN	DMF
TEA	3.92 ± 0.3	5.72 ± 0.5	7.3 ± 0.2	59.1 ± 0.2	71.4 ± 0.6	119 ± 1.7
DEA	7.57 ± 0.2			136.7 ± 1.3	14.9 ± 0.7	
n-$BuNH_2$				110.2 ± 2.3	6.6 ± 0.7	

[a] Bimolecular quenching constant estimated from Stern−Volmer constants and fluorescence lifetimes. [b] Reference 27. [c] Fluorescence quenching was not observed for *tert*-butylamine and isopropylamine. [d] K obtained from plots [$I°/(I - I°)$] vs 1/[amine], correlation coefficients > 0.98.

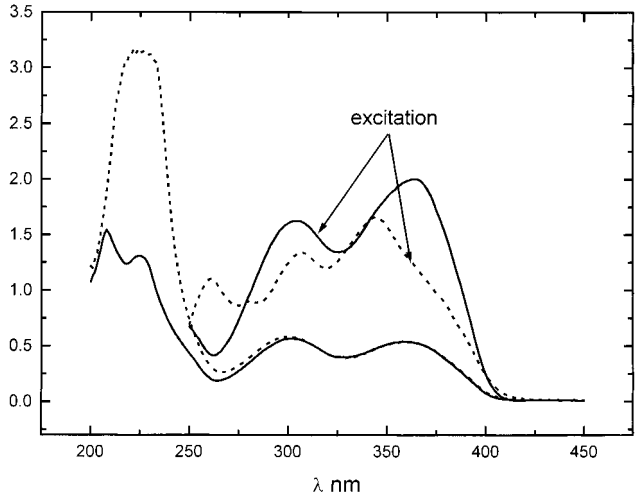

Figure 2. Absorption and excitation spectra of HNQ in acetonitrile in absence of DEA (continuous line) and with 32 mM DEA (broken line).

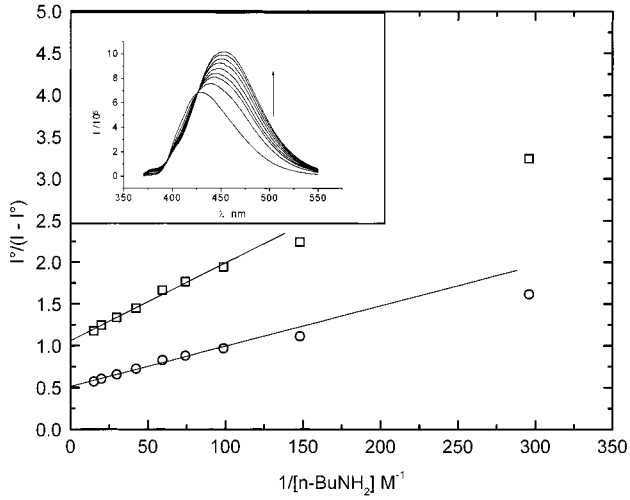

Figure 3. Fluorescence of HNQ at 450 and 475 nm in methanol titrated by *n*-butylamine. The data presentation corresponds to method 3 described by Valeur et al.[24]

Changes in fluorescence of HNQ with amine addition resemble those in various ion-responsive fluorescent compounds, where alkaline cation binding to the azacrown ether moiety of the fluorophore, L, induces hypsochromic and hyperchromic effects on the fluorescence emission.[25,26] These effects are related to complexation of a metallic cation M by the fluorophore L in the equilibrium M + L = ML, where there is emission from both excited species L* and ML*.

Fluorometric titrations of 3-phenylquinoxalin-2-one, in aerated or N_2-purged solutions, with addition of known quantities of amine, gave a monotonic enhancement of emission and often a bathochromic shift (Figure 3, insert).

The stability constant K for the complex HNQ−amine was calculated by plotting $I°_F/(I_F - I°_F)$ against 1/[amine],[25] where $I°_F$ and I_F are fluorescence intensities at a given wavelength in the absence and presence of amine. A typical plot of HNQ fluorescence with titration by *n*-butylamine in methanol is shown in Figure 3. The ratio intercept/slope of this plot gives apparent complexation constants of 114 and 108 M^{-1} for 450 and 475 nm, respectively, with correlation coefficients > 0.995. The insert show how the emission spectra is modified by an increase of amine concentration from 0 up to 67 mM, showing an isoemissive point.

The apparent stability constants K for the HNQ/TEA system in various solvents are in Table 2. The values show an approximate dependence on the ability of the solvent to stabilize hydrogen bonds. The dependence is complicated by the competition between complexation and quenching. On the other hand the low fluorescence quantum yields and short fluorescence lifetimes of both quinoxalin-2-ones and the Stern−Volmer constant for the fluorescence quenching of MeNQ indicate that any excited-state reaction of these compounds occurs mainly, if not exclusively, from the first triplet state of the quinoxalin-2-ones.

Photochemistry. Both 3-phenylquinoxalin-2-ones are photostable to irradiation at 366 nm and are not degraded in aerated solutions after 48 h of photolysis. In degassed or N_2-purged solutions photoconsumption was only 3% after 24 h of photolysis. However, with excess TEA (10:1−500:1 molar ratios), long-term photolysis of degassed solutions gives the respective dihydro-3-phenylquinoxalin-2-ones. These products were identified by their EI mass spectra[17] or by comparison with the mass spectra of authentic samples obtained by GC−MS.

Nevertheless, in the presence of TEA there is a fast photobleaching of the absorption bands of quinoxalin-2-

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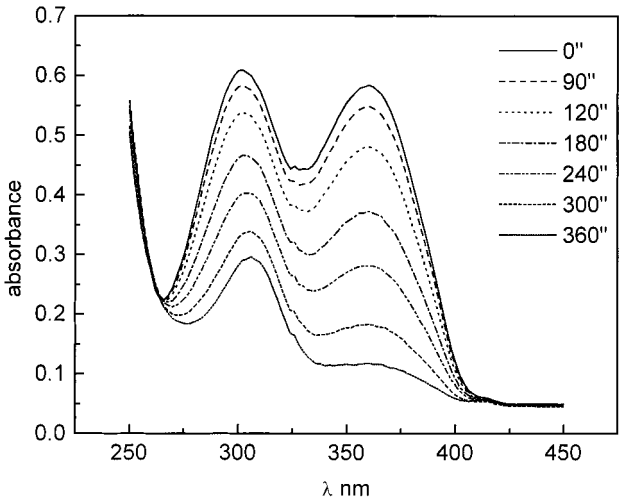

Figure 4. Absorption spectra during anaerobic bleaching at 366 nm of HNQ/TEA system; [HNQ] = 5.5×10^{-5} M, [TEA] = 1.46 mM.

ones after brief photolysis (Figure 4). Concurrently with the bleaching, the distinctive blue fluorescence of quinoxalin-2-ones disappears. The main photoproduct appears only at long photolysis times (>5 h), greater than that required for total bleaching of absorption at 360 nm. All attempts to detect dihydro products during photobleaching were unsuccessful.

The bleaching rate depends, among other factors, on the molar ratio TEA/quinoxalin-2-one. When this ratio is lower than or close to unity, there is a short induction time and the extent of bleaching is proportional to amine concentration, in an approximately stoichiometric relationship to quinoxalin-2-one consumption. When this ratio is higher than 10:1, there is no induction period and bleaching proceeds completely with a final spectrum similar to that of the corresponding dihydro-quinoxalin-2-one, indicating loss of conjugation of the N=C−C=O chromophore. From bleaching data for MeNQ the estimated extinction coefficients for $MeNQH^-$ were 4010 ± 80 and 635 ± 18 M^{-1} cm^{-1} at 300 and 360 nm, respectively; no other absorption appear at longer wavelength.

Samples irradiated to total bleaching revert slowly and almost quantitatively to the starting quinoxalin-2-ones within 12−72 h in the dark, depending on initial concentrations.

For the quinoxalin-2-one/TEA systems in acetonitrile, benzene, or methanol, recovery of quinoxalin-2-one is >98% (GC or UV spectrophotometry). These results suggest that steady-state irradiation of quinoxalin-2-one in the presence of TEA generates a metastable intermediate that accumulates and then reacts thermally to form the stable dihydro-quinoxalin-2-one under continuous irradiation conditions but reverts to the parent quinoxalin-2-one in the dark. Experiments to obtain information on the nature of the metastable intermediates were carried out with amines and electron donors of different oxidation potentials and some containing hydrogen, which could be donated.

Photobleaching, followed by almost quantitative dark recovery, is observed for quinoxalin-2-ones HNQ and MeNQ in the presence of diethylamine, 2-propylamine, and 1-butylamine, in different solvents. Photolysis of MeNQ in the presence of excess piperylene gives partial bleaching without dark recovery. In these conditions a photoproduct, mass 304, was detected by GC−MS, suggesting formation of a MeNQ−piperylene adduct, probably through [2 + 2] cycloaddition, as reported for reactions of quinoxalin-2-ones with alkenes.[13]

With *tert*-butylamine or diazabicyclo[2.2.2]octane (DABCO) as reductant there is no bleaching, while with aniline there is only partial bleaching but no dark recovery. With *tert*-butylamine the lack of bleaching is explained by its high oxidation potential (1.281 V vs ferrocene/ferrocenium in acetonitrile),[27] which inhibits electron transfer to the excited quinoxalin-2-one as seen on quenching of MeNQ fluorescence. However, the low oxidation potential of DABCO does not explain the lack of bleaching; DABCO is a good quencher of MeNQ or HNQ fluorescense, but its radical cation is a poor hydrogen donor. Therefore, it appears that quenching of the excited state of quinoxalin-2-one by DABCO generates a caged singlet ion-radical pair (eq 1), that reverts to the quinoxalin-2-one ground state by a rapid back electron transfer (eq 2), inhibiting further reactions of the ion-radical pair:

$$XNQ^* + DABCO \rightarrow [XNQ^{-\bullet}, DABCO^{+\bullet}] \quad (1)$$

$$[XNQ^{-\bullet}, DABCO^{+\bullet}] \rightarrow XNQ + DABCO \quad (2)$$

$$X = H \text{ or } Me$$

Aniline, with an oxidation potential 0.227 V lower than that of DEA,[27] should be a good reductant for quinoxalin-2-ones, but aniline has no α-hydrogen. Irradiation of both quinoxalin-2-ones in the presence of aniline shows partial photobleaching together with changes in the absorption spectra but no reversal in the dark. The permanent changes in the UV−vis spectrum suggest generation of stable photoproducts, probably via an addition reaction (eqs 3 and 4). We did not attempt to identify them.

$$XNQ^* + PhNH_2 \rightarrow [XNQ^{-\bullet}, PhNH_2{}^{+\bullet}] \quad (3)$$

$$[XNQ^{-\bullet}, PhNH_2{}^{+\bullet}] \rightarrow \text{Products} \quad (4)$$

If metastable photobleaching products are formed by single-electron transfer, followed by proton transfer, with formation of a radical pair (reactions 5 and 6), a long-lived radical pair (12−72 h) will be generated ,and this should be detectable by ESR. Also if long-lived metastable photoproducts were radical pairs (eq 6), some should diffuse from the solvent cage. Then radical traps added to previously bleached solutions would capture free radicals and terminate reaction, inhibiting dark recovery.

$$XNQ^3 + R1R2{-}N{-}CH_2CH_3 \rightarrow [XNQ^{-\bullet}, R1R2{-}N{-}CH_2CH_3{}^{+\bullet}]^3 \quad k^T_q \quad (5)$$

$$[XNQ^{-\bullet}, R1R2{-}N{-}CH_2CH_3{}^{+\bullet}]^3 \rightarrow [XNQH^{\bullet}, R1R2{-}N{-}CHCH_3{}^{\bullet}]^3 \quad k_{H+} \quad (6)$$

Reactions 7 and 8 showing disproportionation of radical pairs and deactivation of ion-radical pair by electron

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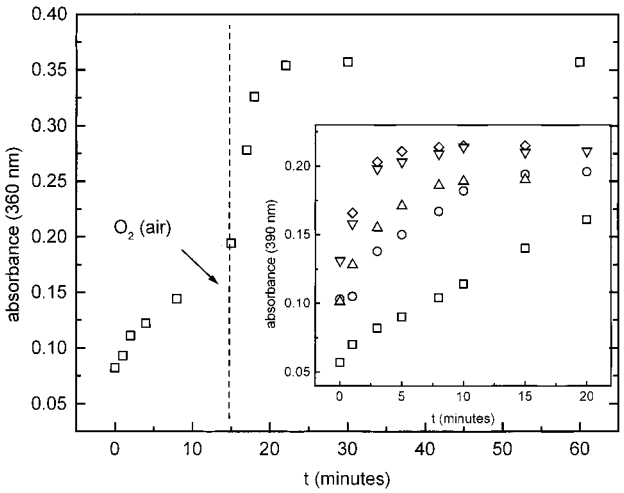

Figure 5. Anaerobic recovery of absorbance at 360 nm of MeNQ/TEA system. At 15 min air was admitted and the rate increased. Insert shows recovery curves at 390 nm with the specified concentrations of POBN: (□) 0; (○) 2.1×10^{-4}; (△) 8.5×10^{-4}; (▽) 1.3×10^{-3}; and (◊) 2.1×10^{-3} M.

retrotransfer must be also considered.

$$[XNQH^{\bullet}, R1R2{-}N{-}CHCH_3^{\bullet}]^3 \rightarrow XNQ + R1R2{-}N{-}CH_2CH_3 \quad k_{-H} \quad (7)$$

$$[XNQ^{-\bullet}, R1R2{-}N{-}CH_2CH_3^{+\bullet}]^3 \rightarrow XNQ + R1R2{-}N{-}CH_2CH_3 \quad k_{-ET} \quad (8)$$

Attempts to detect radical pairs by ESR during irradiation were unsuccessful. Also, photolysis of the deaerated MeNQ/TEA system in the presence of spin traps, e.g., TEMPO or α-(4-pyridyl-1-oxide)-*N*-*tert*-butylnitrone (POBN), showed neither bleaching nor disappearance of the quinoxalin-2-one fluorescence.

When radical scavengers such as TEMPO or POBN were added to previously bleached MeNQ/TEA (with disappearance of the blue emission), the recovery reaction was accelerated without consumption of the quinoxalin-2-one. The insert of Figure 5 shows the recovery curves with the MeNQ/TEA system at 390 nm with variable [POBN]. Addition of air oxygen to partially recovered bleached solutions also accelerates recovery of the original quinoxalin-2-one (Figure 5).

These results are evidence for rejecting the radical-pair nature of the metastable photoproduct, suggesting that the process is not simply SET followed by a proton transfer and is probably followed by a second electron transfer. Dye photoreductions by amines typically proceed by electron transfer, followed by proton transfer from the α-carbon, generating a radical pair, and in some selected systems a second electron transfer leads to ion pairs.[19−23,28,29]

The $TEA^{+\bullet}$ radical cation is a strong acid and deprotonation to $CH_3C{\cdot}H{-}NEt_2$ forms a stronger reducing agent than TEA,[29,30] with transfer of a second electron to $XNQH^{\bullet}$. The sequence of reactions generating metastable products can be represented by eqs 5−9:

$$[XNQH^{\bullet}, R1R2{-}N{-}C{\cdot}HCH_3^{\bullet}]^3 \rightarrow [XNQH^{-}, R1R2{-}N^{+}{=}CH{-}CH_3] \quad k_{ET} \quad (9)$$

The coupling of the processes of eqs 5, 6, and 9 allows a direct two-electron redox reaction to occur to an extent corresponding to net hydride ion transfer.

A similar mechanism with formal hydride transfer in coupled steps of an electron−proton−electron transfer has been reported for some particular chromophore/amine pairs by Whitten et al.[20−22,28,29]

^{1}H NMR Spectroscopy. The persistent primary metastable photoproduct was characterized by ^{1}H NMR spectroscopy. Direct photobleaching in NMR tubes of N_2-purged solutions of XNQ in the presence of excess TEA in CD_3CN provides strong evidence for the sequence of reactions involving formation of the semireduced hydroquinoxalin-2-one $XNQH^-$. Several ^{1}H NMR spectra were obtained during photobleaching of solutions of MeNQ/TEA (1:3 molar ratio, in CD_3CN). With 15 min of irradiation, the ^{1}H NMR spectrum shows new signals of $MeNQH^-$ and diethylamine, DEA. Additionally two signals at 2.0 ppm (doublet, 3 H) and 9.50 ppm (quartet, 1 H) can be assigned to acetaldehyde, probably formed by hydrolysis of an iminium ion by adventitious water (eq 10). Acetaldehyde has been observed as a photoproduct in similar systems.[19,31]

$$Et_2N^{+}{=}CH{-}CH_3 + H_2O \rightarrow Et_2NH_2^{+} + CH_3CHO \quad (10)$$

Bleaching is nearly complete after 20 min of photolysis, and the ^{1}H NMR spectrum of MeNQ/TEA clearly shows signals at 7.95 (broad, 1 H) assigned to N-H, position 4; 7.62 (doublet, 2 H); 7.15 (multiplet, 3 H); 6.95 (doublet, 1 H); 6.83 (triplet, 1 H); 6.65 (multiplet, 2 H), and 3.10 (singlet, 3 H) corresponding to the *N*-methyl of $MeNQH^-$. Two signals at 2.50 (quartet, 4 H) and 0.95 (triplet, 6 H) were assigned to hydrogen of DEA and were identified by adding DEA to bleached solutions.

However, consumption of quinoxalin-2-one is not stoichiometric with DEA production, suggesting that an iminium cation or its radical precursor have other secondary reaction paths to stable products that are not identified by ^{1}H NMR spectroscopy.

Figure 6 shows the NMR spectra obtained in CD_3CN during photobleaching of MeNQ/TEA. The upper spectrum corresponds to that of the aromatic rings of MeNQ before photolysis. The middle spectrum shows the decrease of the above signals and appearance of new signals. The final spectrum shows the signals after complete bleaching of the absorption at 360 nm, which were assigned earlier. The NMR spectrum of material stored overnight in the dark shows the recovery of signals of MeNQ (not shown in Figure 6).

The ^{1}H NMR spectrum of photolyzed HNQ/TEA is as above. Figure 7 shows the spectra, and from top down the first shows the aromatic region of HNQ with TEA at 0 time of photolysis, the second shows the spectrum at 15 min of irradiation when it was stopped, and the third shows recovery of signals corresponding to HNQ, after overnight dark storage. The last spectrum shows the

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(30) Nicholas, A. M. de Pe; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165−2179.
(31) Ci, X.; Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 3893−3904 and references therein.

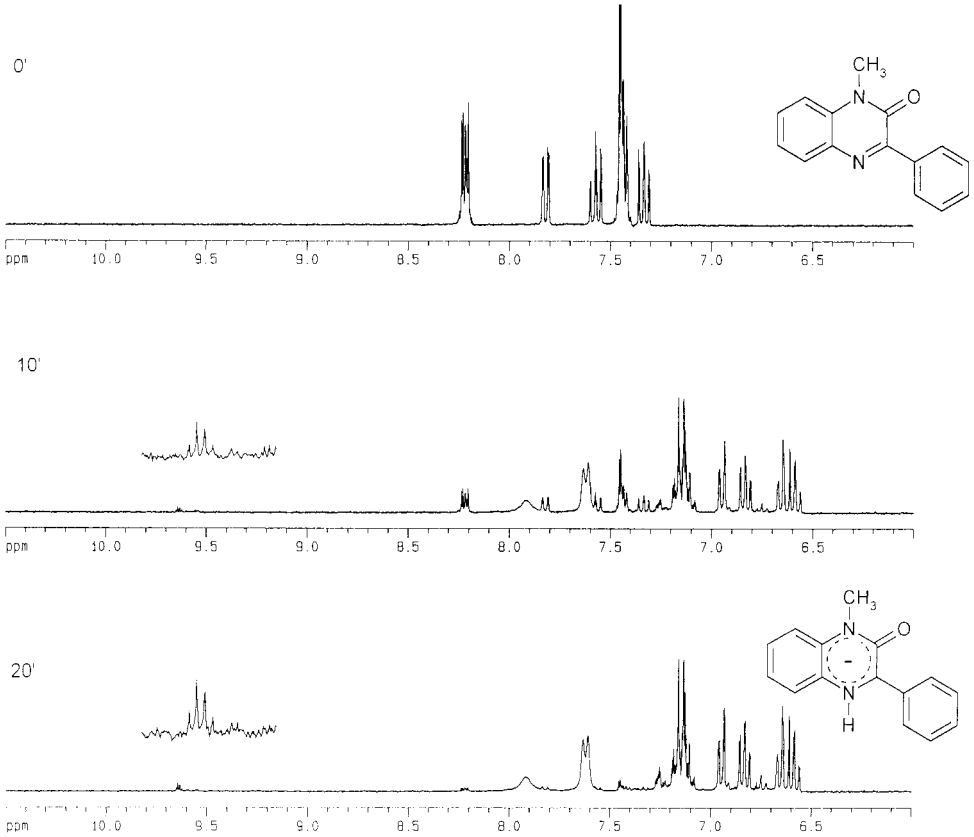

Figure 6. ^{1}H NMR spectra of MeNQ/TEA system in deoxygenated CD_3CN; see text. The middle and lower spectra show a zoom of the quartet at 9.62 ppm assigned to acetaldehyde.

difference between the spectrum after 15 min of bleaching and that of the initial HNQ/TEA. These signals were assigned to metastable $HNQH^-$.

Both metastable photoproducts of quinoxalin-2-ones show an upfield shift of the aromatic protons, and also $MeNQH^-$ shows the upfield shift of the *N*-methyl hydrogens. These effects can be rationalized by considering the increase of charge in the $XNQH^-$ anion and its stabilization by resonance. Although from the ^{1}H NMR spectra we cannot rule out formation of an adduct of $XNQH^-$ and iminium or ammonium ions, the COSY spectrum of previously photobleached MeNQ/TEA shows no correlation between signals assigned to $MeNQH^-$ and TEA or DEA, making adduct formation unlikely. The thermal instability of the metastable photoproducts and its possible reaction with oxygen precludes their isolation and purification.

Photobleaching Quantum Yield. In the previous paragraph we stated that the short fluorescence lifetime of 3-phenylquinoxali-2ones and the low values of $k^S_q\tau^S_0$ for quenching of MeNQ by amines preclude photoreaction from the excited singlet state, and any photoproduct should be formed from the first triplet state of the quinoxalin-2-ones.

Considering processes that generate triplet state XNQ, the quantum yield is given by $\Phi^T = k_{ISC}/(\Sigma k_d^S + k_q^S[Q])$, where k_{ISC} is the intersystem crossing constant, Σk_d^S represents all first-order decay paths of the singlet state, and $k_q^S[Q]$ is the second-order quenching of singlet XNQ by amines.

The metastable product formation quantum yield, Φ_{XNQH^-} (eq 12) is obtained from eqs 5−9, and Φ^T and eq 11 account for the triplet state deactivation. The recipro-

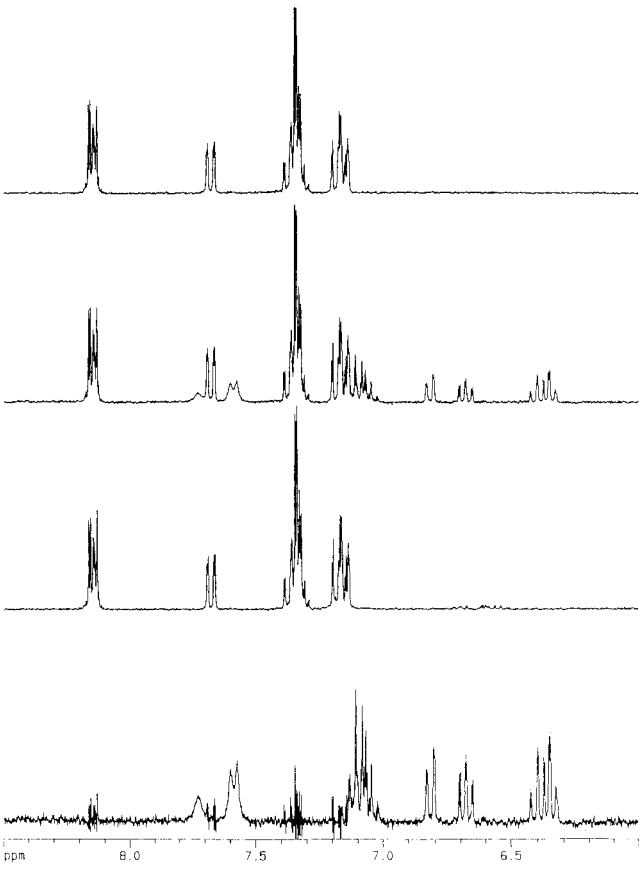

Figure 7. ^{1}H NMR spectra of HNQ/TEA system in deoxygenated CD_3CN; see text.

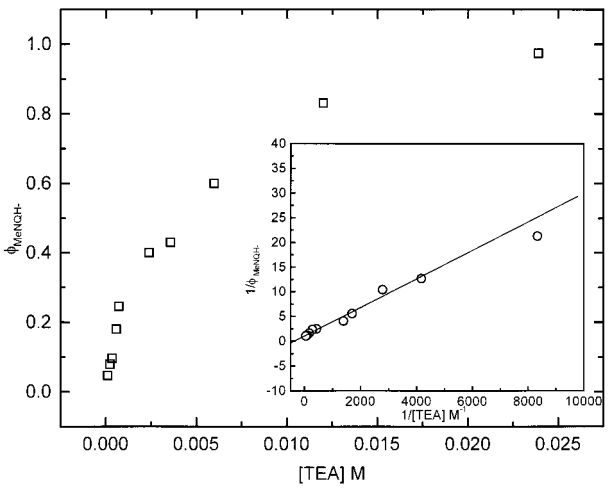

Figure 8. Quantum yield of $MeNQH^-$ (Φ_{MeNQH^-}) as a function of [TEA] with deoxygenated samples irradiated at 366 nm at 5.5×10^{-5} M MeNQ. Insert shows the double reciprocal plot.

cal of eq 12 gives eq 13, which predicts a linear relationship between $1/\Phi_{XNQH^-}$ and 1/[amine], with an intercept/slope of $k^T_q\tau^T_0$.

$$XNQ^3 \rightarrow XNQ \quad k^T_d \tag{11}$$

$$\Phi_{XNQH^-} = \frac{\Phi^T k_{ET} k_{H^+} k^T_q [\text{amine}]}{(k_{-H} + k_{ET})(k_{-ET} + k_{H^+})(k^T_d + k^T_q[\text{amine}])} \tag{12}$$

The quantum yield of the photoreduction of MeNQ by TEA in purged acetonitrile, as predicted by eq 12, shows a high dependence upon the concentration of amine with a monotonic increase to a limit approaching 1.0 (Figure 8). For HNQ with [TEA] = 0.03 M, $\Phi_{HNQH^-} = 0.97$, suggesting a limiting value of 1.0 for photoreduction of HNQ.

These limits values for Φ_{XNQH^-} indicate that the triplet quantum yield should be near unity and that processes 7 and 8 that deactivate the radical and the ion-radical pairs by atom and electron transfer respectively, are relatively inefficient.

$$\frac{1}{\Phi_{XNQH^-}} = \frac{(k_{-H} + k_{ET})(k_{-ET} + k_{H^+})}{\Phi^T k_{ET} k_{H^+}} \left[1 + \frac{1}{k^T_q \tau^T_0} \times \frac{1}{[\text{amine}]}\right] \tag{13}$$

The double reciprocal plot in the insert of Figure 8 gives an intercept/slope $k^T_q\tau^T_0$ of 370 M^{-1}, which is 150-fold larger than that obtained for singlet state quenching in acetonitrile. Assuming diffusion-controlled triplet state quenching ($k^T_q = 5 \times 10^9$ $M^{-1}s^{-1}$) a short lifetime of about 75 ns can be estimated for triplet state MeNQ. Taking the limit $\Phi^T = 1.0$, the fluorescence quantum yield, Φ_f, and the lifetime of the singlet state we estimate $k_{ISC} = 10^{10}$ s^{-1}, which agrees with the growth of triplet absorption time of 40 ps for quinoxaline ($k_{ISC} = 2.5 \times 10^{10}$ s^{-1})[32] and with the estimated k_{ISC} of 10^{11} s^{-1} for chloranil.[33]

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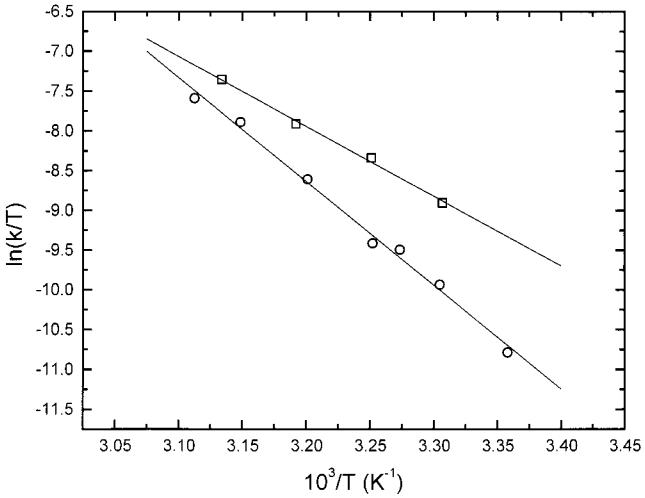

Figure 9. Plots of ln(k/T) vs $1/T$ for the dark recovery reaction of MeNQ/TEA system in acetonitrile (□) and benzene (○) (correlation coefficient > 0.997).

Dark Recovery Reaction. Experiments were carried out to obtain the reaction order for the dark recovery reaction of semireduced quinoxalin-2-ones, $XNQH^-$ and TEA. Deaerated solutions with molar ratios of TEA/XNQ from 10 to 500 and constant [TEA] or [XNQ], were photolyzed to obtain the reaction orders, following procedures described in the Experimental Section.

We obtained first-order kinetics for the disappearance of $HNQH^-$ and $MeNQH^-$ in acetonitrile, methanol, chloroform, and benzene, from initial rates, at different initial concentrations of $XNQH^-$ and found that the mechanism of the dark reaction did not change with the solvent. Experiments at variable [TEA] showed no dependence of the recovery rate on amine concentration. These studies were carried out with both quinoxalin-2-ones and in various solvents. The solutions were irradiated until the blue fluorescence disappeared, and then recovery of absorption at 360 nm was monitored spectroscopically. The absorbance depletion at 360 nm is proportional to the concentration of the metastable photoproduct; no other photoproducts are observed. The consumption rate of $XNQH^-$ can be measured by monitoring the increasing absorbance of bleached solutions.

A first-order dark recovery reaction could be rationalized by assuming a strong contact ion pair of $XNQH^-$ and the iminium ion[20] generated in reaction 9 or with the ammonium ion formed by reaction 10. Although formation of an adduct that can return to the parent compounds would also fit first-order kinetics, we have no evidence of its formation and it is not seen in the NMR spectra.

Kinetic parameters for the dark reaction were calculated from rate constants at various temperatures for the MeNQ/TEA system in acetonitrile and benzene. Activation free energies for the dark disappearance of $MeNQH^-$ were 17.4 ± 0.8 and 25.9 ± 0.9 kcal/mol in acetonitrile and benzene, respectively; plots of ln(k/T) v/s $1/T$ are shown in Figure 9. The difference of 8.5 kcal/mol in activation free energies is explained by stabilization of a charged activated complex by the more polar solvent.

The thermal oxidation reaction of dihydroanthraquinone and a stabilized iminium salt, leading to the anthraquinone,[20] behaves similarly to the dark recovery reaction of $XNQH^-$. This first-order reaction of dihy-

droanthraquinone and iminium ion, occurring via a sequence of electron and hydrogen atom transfer, has an activation free energy of 25.9 kcal/mol.[20] This value is in agreement with the activation free energy obtained for the MeNQ/TEA system and supports a sequence of electron and hydrogen atom transfer for the thermal recovery of $XNQH^-$ to the parent quinoxalin-2-ones.

Conclusion

The preceding results support the mechanism shown in Scheme 2. Photoexcitation of XNQ leads to its first singlet state, which is converted into the triplet via an efficient intersystem crossing, step 1, with $k_{ISC} = 10^{10}$ s^{-1} for MeNQ. The triplet state is quenched by amine via electron transfer, step 2, giving the triplet radical-ion pair. The ion-radical pair can then decay to the starting compounds, step 5, but back electron transfer seems to be inefficient, probably as a result of a spin forbidden transition. A rapid proton transfer, step 3, to yield $XNQH^•$ and the *N*-methylene radical pair follows formation of the ion-radical pair in step 2. The radical pair can give by a second electron transfer, step 4, the ion pair in a more efficient reaction than step 6 involving homolytic bond cleavage to transfer a hydrogen atom. Reactions 4 and 6 require intersystem crossing from the presumed triplet radical pair that precedes them. The quantum yield of $XNQH^-$, $\Phi_{XNQH^-} = 1.0$, shows that the proton-transfer step is faster than competitive disproportionation of a radical pair in step 6. Also step 6 fits formation of dihydro-quinoxalin-2-ones, $XNQH_2$. The ion pair formed in step 4 can diffuse out of the solvent cage, and in the presence of water, the iminium ion will be hydrolyzed to $H_2N^+R_2R_3$ and R_1CHO in step 7, as supported by detection of DEA and acetaldehyde in the photolysis of MeNQ/TEA and HNQ/TEA.

The reverse dark reaction could follow a stepwise pathway, step 8 of Scheme 2. An electron transfer from $XNQH^-$ to the iminium ion could be induced thermally to regenerate the singlet radical pair, followed by back hydrogen atom transfer, leading to the starting quinoxalin-2-ones. The activation free energies of 17.4 and 25.9 kcal/mol in acetonitrile and benzene seem reasonable for the proposed sequence of electron and atom transfers for this thermal back reaction.[20]

The high yield of dihydro products $XNQH_2$ on continuous irradiation reported by Nishio[17] can be explained by considering the high stationary concentration of $XNQH^-$ that can react thermally to give $XNQH_2$ or from disproportionation of the radical pair in equilibrium with the ion pair.

Experimental Section

Acetonitrile, hexane, chloroform, ethanol, methanol, dichloromethane, and *N*,*N*′-dimethylformamide were Merck HPLC grade. Benzene-d_6, acetonitrile-d_3 99%, and chloroform-d_1 99.5% were Merck spectroscopic grade. These solvents were used as received.

Triethylamine, diethylamine, isopropylamine, *n*-butylamine, tertbutylamine, and aniline (Fluka) were stored over potassium hydroxide pellets and vacuum distilled trap-to-trap, sealed into glass tubes at 10^{-4} mmHg, and stored at −18 °C. Before each experiment a new tube was opened to ensure freshness of the amine. DABCO from Aldrich was used as received. DABCO solutions were prepared immediately before use.

Radiant Flux Determination. A solution of Aberchrome 540, ca. 1.0 mM in toluene, was used to estimate the radiant flux from the Hg lamp at 366 nm. Absorbance at 494 nm was measured every 30 s of irradiation, and the photon flux was calculated from the slope of the plot A_{494} vs time, with $\epsilon_{494} = 8200$ M^{-1} cm^{-1} and $\phi = 0.20$.[34,35]

Quantum Yield. The quinoxalin-2-one photobleaching quantum yield was estimated by using the time-integrated absorbed light at 366 nm and the absorbance at 360 nm, with $\Phi_{XNQH^-} = [(\Delta A_{360}/\epsilon_{360})/(I^\circ \times S)](v/1000)$, where ΔA_{360} is the absorbance difference at 360 nm, ϵ_{360} is the molar extinction coefficient of quinoxalin-2-one at 360 nm, I° is the photon flux in Einstein s^{-1}, S is the time-integrated absorbed light, and v is the volume of irradiated solution.

General Procedure for Photobleaching Studies. Solutions (3 mL) of quinoxalin-2-one with absorbances between 0.20 and 1.40 at 360 nm were purged with N_2 for 20 min in a 10 mm fluorescence quartz cell sealed with a septum. Immediately after purging an aliquot of pure or diluted amine was added through the septum. The solutions were photolyzed with a Black Ray UV lamp with a 366 nm filter, and the absorbance was measured every 30 s at 360 nm on ATI Unicam UV2 or UV4 spectrophotometers with Vision 2.11 software. In experiments at high amine concentrations, neutral filters were used to reduce the photon flux from the lamp to keep total bleaching times within 5−10 min. For each experiment, the radiant flux was determined as described previously.

Dark Recovery. This determination was carried out with solutions prepared as described for bleaching. A thermostated cell holder was used to control temperature before and after bleaching. In these experiments the lamp was at a very short distance in order to obtain photobleaching times less than 60 s, and the temperature was varied between 20 and 50 °C. Bleaching was stopped when the blue fluorescence of the quinoxalin-2-one disappeared to the eye. In all experiments the final absorbance at 360 nm (A_{360}) was about 0.020 at the end of bleaching. Absorbance at 360 nm was measured at time intervals of 60 s up to 5 min and then each 5 min for 1 h. To minimize further photobleaching by the spectrophotometer beam, a black shutter interrupted the beam between measurements.

Metastable Product Detection. Experiments were performed in a Bruker Avance DRX-300 (300 MHz) spectrometer. Reactions were carried out by direct photobleaching of N_2-purged solutions containing a weighed amount of the respective quinoxalin-2-one and excess TEA in CD_3CN. Solutions were prepared directly in a NMR tube and sealed with a septum. During photobleaching some ^1H NMR spectra were taken in order to test for the maximum concentration of the metastable species. COSY spectra were taken when the lifetime of the metaestable photoproduct was long enough. It was not possible to obtain a ^{13}C NMR spectrum of the irradiated samples of XNQ/TEA because of the low concentration of $XNQH^-$ generated and the necessary number of scans.

Fluorescence Quenching and Enhancement of Emission. Measurements were made in a Spex Fluorolog Tau 2 system with DM 3000 software, all at 20 °C, by using the corrected fluorescence method. Quenching experiments were performed at absorbance 0.2 at 360 nm, in aerated or N_2-purged solutions. The entire spectra were scanned to test for possible bathochromic shifts. Enhancement of emission was also measured by using the corrected fluorescence method in N_2-purged solutions. A 10 mm square quartz cell sealed with a septum was used in both experiments, and pure or diluted amine was added through the septum. The absorbance of the solutions was checked between scans to show that quinoxalin-2-one was not consumed.

Fluorescence Yields. Yields were determined from the

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(35) *The Use of Aberchrome 540 in Chemical Actinometry*; Aberchromic Ltd., School of Chemistry and Applied Chemistry, University of Wales, College of Cardiff, PO Box 912, Cardiff CF1 3TP, U.K.

wavenumber integrated corrected fluorescence spectra of quinoxalin-2-ones, by using quinine sulfate as actinometer.

The 1,4-quinoxalin-2-ones were prepared from the required *o*-phenyldiamine and methyl benzoylformate in THF/pyridine (10:1). The mixture was heated at 110 °C for 0.5−1 h, and the reaction mixture was then concentrated. The solid residue was collected by filtration, washed with ethyl ether, and finally recrystallized from acetonitrile. Products were characterized by NMR and melting point.[13]

The 3-phenyl-3,4-dihydro-quinoxalin-2-ones were prepared by hydrogenation of the respective quinoxalin-2-ones in $CHCl_3$ with 10% Pd/carbon, in a Parr apparatus at 20 psi of H_2 and 25 °C. The CH_3Cl solution was filtered and concentrated, and the solid residue was recrystallized from methanol. Dihydro-products were characterized by NMR and melting point.[17]

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