

A Sterically Controlled Recyclable System: Reversible Photoredox Reactions between Anthraquinone and Hindered Tertiary Amines

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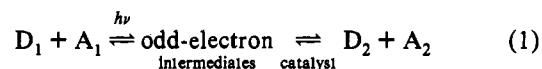
Abstract: Photochemical reactions of 9,10-anthraquinone (AQ) with sterically hindered tertiary amines have been studied. The reactivity and products are strongly dependent on the structure of the tertiary amine. Irradiation of AQ in the presence of the sterically hindered amine 1,2,2,6,6-pentamethyl-4-piperidinol (**3**) (or 1,2,2,6,6-pentamethylpiperidine (**5**)) in degassed dry benzene leads chiefly to the formation of 9-hydroxy-9-[*N*-(2,2,6,6-tetramethyl-4-piperidinol)-methyl]anthrone (**8**), which is found to be metastable at room temperature under vacuum. The reaction may be thermally reversed to regenerate the starting materials. The photolysis products and thermal reversion are solvent dependent. While in dry benzene adduct **8** is the major product, in dry acetonitrile the ionic redox products AQH⁻ and iminium cation are detected and no thermal reversal occurs. The results are explained in terms of equilibrium between a product ion pair (AQH⁻, iminium⁺) and a metastable adduct **8**. In the presence of water, the reaction leads to the formation of a stable product, 9-hydroxy-9-(hydroxymethyl)anthrone (**6**). Different reactivity is observed upon irradiation of AQ in the presence of the sterically less hindered tertiary amine *trans*-tropine (**1**).

Introduction

Photoinduced single-electron transfer (SET) provides a versatile means of generating energy-storing and reactive ion-radical intermediates; a chief impediment to their utilization is the rapid decay of these intermediates, especially when generated as contact or solvent-separated radical ion pairs, by rapid return-electron-transfer processes.¹⁻⁷ SET quenching of excited states can lead to permanent photoproducts with reasonable efficiency where steps subsequent to the quenching such as proton transfer⁸⁻¹⁰ or bond cleavage¹¹ can occur in competition with return electron transfer. These steps are often exothermic and can result in conversion of the ion-radicals into stable products. However, for some donor-acceptor combinations a sequence of SET quenching followed by proton transfer and a second electron transfer leads to an even-electron ion pair which can store considerable energy or have high potential reactivity yet possess reasonable kinetic stability compared to ion-radical pairs.¹² In these cases the reactions should be reversible and one or both of the product reagents produced should be recyclable. However examples of this type of reaction leading to energy storing and recyclable products via net two-electron redox are relatively rare, since the reversibility of the particular system depends largely on the thermal stability of these "intermediates" or metastable products to other decomposition pathways.¹³ In principle, the energy-rich products could be accumulated and used selectively

if the secondary reactions can be controlled or eliminated by the design of reagent structure.

Since the photoinduced net two-electron-transfer reaction is a redox reaction, a recyclable photoinduced electron-transfer reaction will involve two interconvertible redox pairs, as shown in eq 1. As a reasonable candidate for a recyclable donor, we

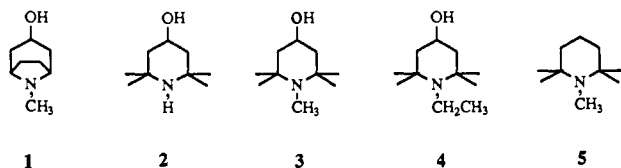


have previously examined the photoredox behavior of a number of tertiary amines. Photooxidation of these tertiary amines by excited electron acceptors leads to a variety of products;¹³⁻²³ iminium ions are precursors in several cases to the final isolable products.¹⁷⁻²³ Although some are relatively stable and have been synthesized independently,²⁴ iminium ions from these two-electron photoredox reactions are generally not isolated, due to their reactivity toward nucleophiles present under the experimental conditions. A further complication in the tertiary amine-iminium ion interconversion is the subsequent deprotonation of several iminium ions to afford enamines, which being good nucleophiles show a high tendency to self-condense with residual iminium ions to result in irreversible loss of the donor molecule.

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One possibility for avoiding paths involving iminium ion-enamine condensations and other decomposition routes could involve the use of amine donors which can undergo two-electron redox to iminium ions but are unable to react further to the enamine. By utilizing this strategy, a recyclable system has been designed. Herein, we report a simple process, involving photo-induced electron transfer, followed by proton transfer and a second electron transfer, which is at least partially reversible. The two redox pairs used in our study are *N*-alkylamines (1, 3, 4, and 5)/iminium ions and 9,10-anthraquinone (AQ)/9,10-anthrahydroquinone (AQH₂).



Previous investigations have established that irradiation of quinones (Q) in the presence of potential reductants such as amines or alcohols leads to the formation of the corresponding dihydroquinones (QH₂).^{15,25,26} It has also been shown that dihydroquinones can be converted to quinones under relatively mild oxidation conditions.²⁷ For example, AQH₂ is very easily oxidized by oxygen at room temperature to AQ.¹⁵ In the present study we find that the iminium ions produced by oxidation of amines 3 and 5 are still quite reactive; however, we find that they are sufficiently selective in their reactivity, due at least in part to steric shielding, to form metastable adducts with reduced quinone which can be stored or recycled on a very slow time scale.

Results and Discussion

The study in the present paper involves AQ as the excited-state substrate. Since AQ has a very high intersystem crossing efficiency ($\Phi_{isc} > 0.9$)²⁸ from excited singlet to triplet state, only triplet-state reactions are considered. Amines 1, 2, and 5 are commercially available, while amines 3 and 4 are obtained by treatment of 2 with methyl iodide and ethyl iodide, respectively. In the latter case, base catalysis was used to force the alkylation to completion. In typical experiments, solutions of *N*-alkylamine and AQ in a chosen solvent (benzene or acetonitrile, wet or dry) are degassed by freeze-pump-thaw cycles, sealed under high vacuum in the reaction vessel, and irradiated with a light source fitted with an appropriate filter system (irradiation wavelength > 310 nm, where only AQ absorbs). The course of the reaction is followed by either UV-vis or NMR spectra.

The photoreduction of AQ by alcohols (for example ethanol and isopropanol) and amines normally produces AQH₂, which can be readily detected by its characteristic UV absorption spectrum (380 nm).¹⁵ In the former case, the reduction is attributed to a hydrogen atom abstraction mechanism, while, in the second case, a mechanism of electron transfer followed by proton transfer is usually accepted (even though hydrogen abstraction will give the same results). In the present study, the photoreduction of AQ by amine is anticipated to occur via the electron-transfer mechanism, since the one-electron reductions of the AQ excited triplet²⁹ by amines 1–5 are all exothermic by more than 0.6 eV (Table I). All of these amines quench the fluorescence of 9,10-dicyanoanthracene (DCA has a similar reduction potential and excited-state energy³⁰) with a diffusion-controlled rate. The electron-transfer mechanism is further supported by the lack of reaction between AQ and 2. Since the

Table I. Free Energy for Electron-Transfer Reactions

amine	1	2	3	4
E_p (V) ^a	0.933	1.220	0.983	1.095
ΔG_{et}^* (eV) ^b	-0.887	-0.600	-0.837	-0.725
ΔG_{et} (eV) ^c	1.813	2.100	1.863	1.975

^a The oxidation of amines 1–4 is irreversible. Peak potentials are reported vs SCE. ^b Excited-state electron-transfer free energy with $E_{AQ^*/AQ} = 1.82$ eV (AQ triplet-excited-state energy is 2.7 eV). ^c Ground-state electron-transfer free energy with $E_{AQ/AQ} = -0.88$ eV vs SCE.

Table II. Quantum Yields of AQ Photoreduction^a

[AQ] (M)	[3] (M)	Φ
1×10^{-4}	0.01	0.37 ± 0.03
1×10^{-4}	0.10	0.46 ± 0.02
1×10^{-4}	1.00	0.25 ± 0.02

^a Data are average of four replicate experiments in each case. Solvent: acetonitrile with 0.1% water.

amines (1–4) contain a secondary alcohol group which is known to reduce AQ photochemically by a hydrogen abstraction mechanism,^{31,32} the lack of permanent AQ reduction in the presence of 2 is a clear indication of the electron-transfer-quenching mechanism which effectively precludes the hydrogen abstraction pathway in this case.

(1) Orbital Overlap and Kinetic Acidity of *N*- α -Protons. Since amine 2 does not have an α -proton, it is not surprising that there is no net chemical reaction when AQ and 2 are irradiated. After electron-transfer quenching, return electron transfer is the most likely pathway. However, the unreactivity of amine 4 toward the photoreduction of AQ was unexpected, initially, because photoreduction of AQ by its analog triethylamine proceeds quite smoothly.¹⁵ Furthermore, for amines 3 and 5, the reduction occurs with relatively high efficiency under the same experimental conditions. The quantum yields of AQ photoreduction by 3 are listed in Table II. Since amines 3 and 4 are quite similar in terms of structure and energy (Table I), the unreactivity of amine 4 is probably due not to a lack of AQ excited-state quenching but rather to the impedance of the subsequent steps. The quenching of the AQ excited state by 3 or 4 will generate the AQ anion radical and amine cation radical pair. At this stage, the subsequent proton-transfer step must compete with the return-electron-transfer process. The rate of proton transfer is, however, dependent on the kinetic acidity of the α -protons.^{8–10,33} Molecular modeling calculations suggest that the α -proton of the cation radical from 4 should be less acidic kinetically than that of 3. In the most stable predicted conformation, strong overlap should occur between the nitrogen lone-pair nonbonding orbital and the α -C–H bond orbital for 3. However, in the case of 4, the nitrogen lone-pair orbital is constrained to overlap only with the C–CH₃ bond. As a consequence, the α -proton of the cation radical of 3 is a stronger acid kinetically and the proton-transfer process can effectively compete with the return electron transfer. In contrast, return electron transfer is predominant when amine 4 is used.

(2) Photoreduction of AQ by 3 in Wet Solvent and the Subsequent Dark Reaction. Previously, we reported that the photolysis of 9,10-anthraquinone with 3 in the presence of water leads to the clean formation of 6 and the secondary amine 2 (eq 2).²³ These investigations indicated that 6 and 2 are derived from a secondary dark reaction. It was proposed that the reactive intermediates are iminium ions, which are trapped by water and hydrolyzed to secondary amine 2 and formaldehyde (detected by

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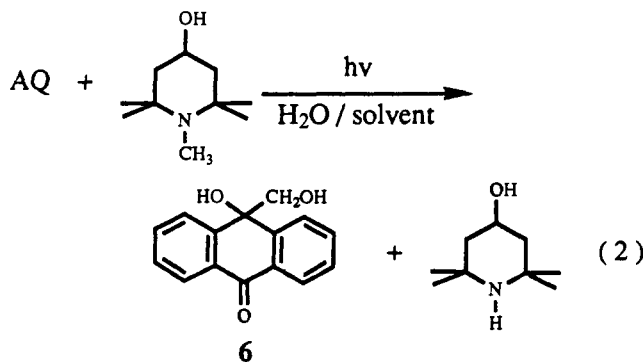
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$^1\text{H-NMR}$ ³⁴; the formaldehyde further reacts with 9,10-anthrahydroquinone anion via a dark reaction to afford **6** as the final product. Although AQH_2 was not obtained as a final product as observed in the other cases,¹⁵ its presence as a reaction intermediate was clearly indicated by the observation of its characteristic blue fluorescence during the photolysis and the UV absorption at 380 nm (Figure 1). The absorption of AQH_2 decays concomitant with the formation of **6**. The reaction proceeds smoothly in acetonitrile and several other solvents (benzene, dichloromethane, and acetone). Similar reaction has been observed with amine **5**. The structure of **6** suggests that it can be derived from an aldol condensation between formaldehyde and AQH_2 anion. Accordingly, we found that synthetically prepared AQH_2 reacts with formaldehyde, in the presence of base (either amine **2** or **3** or NaOH), to form adduct **6** as the only isolable product. However, in the absence of base there is no detectable reaction between AQH_2 and formaldehyde, and thus the reaction observed under the photochemical conditions (excess **3** or **5**) is base catalyzed. The thermal reaction can be monitored conveniently by generating AQH_2 photochemically (assuming that iminium ion hydrolysis is rapid), and it is found to follow second-order kinetics (Figure 2) with a fairly low activation energy ($E_a = 15.3$ kcal/mol). The overall reaction according to eq 2 thus consists of a photochemical stage, involving electron transfer, proton transfer, and second electron transfer, resulting in formation of AQH_2 and iminium ion, and a dark process in which adduct **6** is generated via a base-catalyzed aldol condensation. Interestingly, we find that AQH^- does not condense with acetone and benzaldehyde, and neither of them inhibit the formation of **6** in the above described overall photochemical reaction. To our knowledge, this is the first evidence that AQH^- reacts with a carbonyl group to form an anthrone-type adduct.

(3) **Steric Effect.** The photoreaction of AQ with the sterically less hindered amine **1** in both wet and dry solutions yields an anthrone-type product which is different from **6**. Although the product is both thermally and air stable, it decomposes to anthraquinone and other unidentified products on silica gel. Attempts to isolate this product from the reaction mixture were unsuccessful. The structure of the adduct is tentatively assigned as **7** (Scheme I) on the basis of the new $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ signals from it in the reaction mixture. Amines **1** and **3** are very similar in terms of their structure and reaction center. However, the finding of quite different products from these two amines clearly indicates the importance of the steric effect. Steric hindrance in the tetramethyl-substituted iminium ions (derived from **3** or **5**) evidently restricts their reactions with the bulky nucleophile, the 9,10-anthrahydroquinone anion. However small nucleophiles, such as water, can attack the hindered iminium ion and gave stable products. In the case of amine **1**, the iminium ion intermediate should not be as sterically hindered. It can react with nucleophiles both large and small. While the radical coupling mechanism cannot be ruled out for the formation of **7**

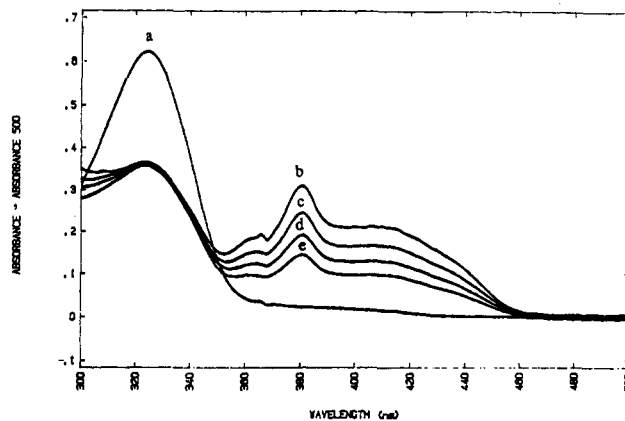


Figure 1. (a) AQ (1.253×10^{-4} M) and **3** (9.972×10^{-3} M) in acetonitrile (containing 0.1% water). (b) 5-min irradiation. (c) 2 min after irradiation. (d) 5 min after irradiation. (e) 10 min after irradiation.

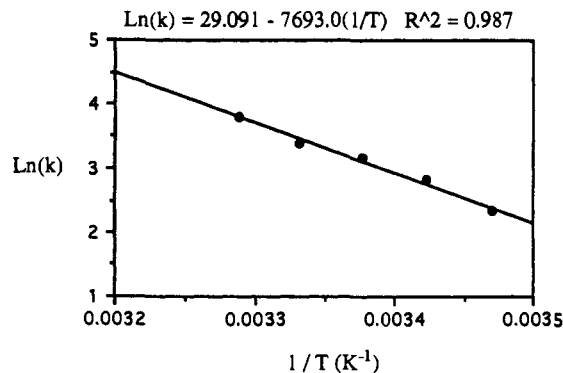
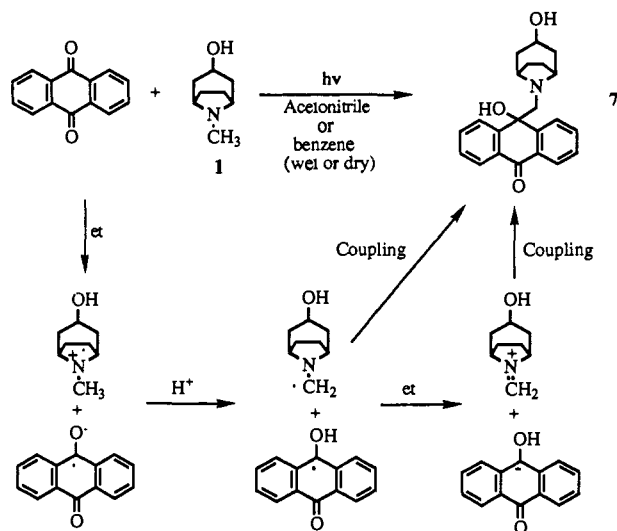


Figure 2. Kinetics of dark reaction.

Scheme I. Photoreaction of AQ with the Sterically Less Hindered Amine **1**



(Scheme I),¹³ it could, however, be prohibited in the case of amines **3** and **5** due to the unfavorable steric interaction within the radical pair.

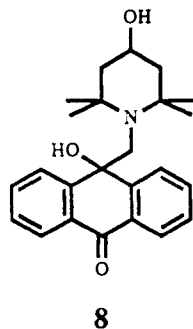
(4) **Photoreaction of AQ with **3** in Dry Solvent.** As discussed above, the photoreaction of AQ and amines **3** and **5** should lead to the formation of AQH^- and the iminium ions as the primary products. In the presence of water, the resulting iminium ion from **3** is evidently hydrolyzed to secondary amine **2** and formaldehyde, which reacts with AQH^- thermally to afford **6** as the stable and isolable product. However, when AQ and amine **3** or **5** are photolyzed in rigorously dry degassed benzene solution, quite different overall reactivity is observed. While similar overall reactivity is observed for both **3** and **5**, we will discuss in detail

(34) A sharp singlet at δ 9.6 ppm in acetonitrile- d_3 , which disappeared after the dark reaction.

only the reactivity of **3**, which has been followed most closely. Other than **2** and **6** (a trace of water, which was consumed completely after the irradiation, is evidently responsible for the formation of these products), metastable photoproducts are observed which are found to be thermally unstable and sensitive to air. In contrast to the observation for "wet" solution, the UV absorption spectrum of the irradiated sample (AQ, 1×10^{-3} M; **3**, 1×10^{-2} M; with 50% conversion) shows only a very weak AQH₂ (or AQH⁻) absorption at 380 nm. However, about 40% recovery of AQ ($\lambda_{\text{max}} = 326$ nm) was detected upon 2 h of heating of the degassed product solution at 95 °C. No recovery, however, is observed when 0.1% water is present in the reaction solution.

The thermal reversal of the photoreaction can also be followed by ¹H-NMR spectra of both AQ and amine **3**. In a typical experiment, 20-min irradiation of AQ (1.7×10^{-2} M) and **3** (2.8×10^{-2} M) solution (in freeze-pump-thaw degassed dry benzene-*d*₆, internal standard, benzene) leads to 85% conversion of AQ and 61% conversion of **3** and gives very clean formation of the metastable photoproduct which is easily detected due to its characteristic proton signals (the NMR data for this intermediate are reported in the Experimental Section). This photoproduct is stable at room temperature; however, when the sample was opened to the air, it disappeared with the coincident recovery of AQ. If the irradiated sample is heated in a water bath (95 °C), the recovery of both AQ (up to 55.7%) and **3** (up to 28.9%) is observed by NMR concurrent with the decrease of the photoproduct signals on the same time scale. Further irradiation of the above sample yields the same metastable product, which again can be thermally reverted to the starting materials. Experimental studies showed that **6** is thermally stable at this temperature. There is no decomposition detected when **6** is heated at 100 °C for 14 h in degassed solutions. Therefore, the AQ recovery must come from the metastable photoproduct.

Since we are unable to detect any radical signal in an ESR experiment, it appears unlikely that the metastable compound is a radical species. The ¹H-NMR signals in the aromatic region (four peaks with two doublet and two triplet) suggest an anthrone-type structure. The multiplet at δ 3.40 ppm (methine proton α to hydroxy group) and two sharp singlets at δ 0.60 and 0.28 ppm (four α -methyl substituents) indicate the presence of the piperidinol ring structure. The sharp singlet signal at δ 2.72 ppm from the *N*-methylene group is the key for the assignment of the structure for the metastable intermediate. The chemical shifts of these signals are consistent with the structure of coupling product **8**. However, the NMR spectrum does not immediately



rule out the possibility of an AQH⁻/iminium ion pair, since the face-to-face arrangement of a contact ion pair could put the iminium ion very close to the anthrahydroquinone anion. An upfield shift of the iminium ion proton signals would be expected due to the ring-current effect. Since AQH₂ can be oxidized quantitatively by oxygen to AQ,¹⁵ the sensitivity of the metastable product toward air is also consistent with the ion pair structure. However, the lack of a strong UV absorption of AQH₂ (see below) from the reaction mixture suggests that an iminium ion/AQH⁻ ion pair is not a major component of the product and supports the assignment of structure **8** for the predominant species in the

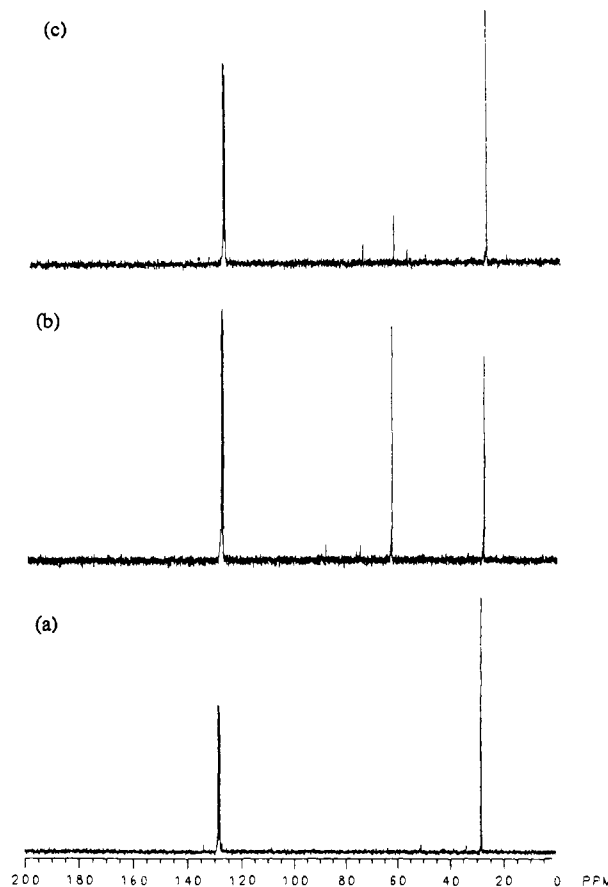


Figure 3. ¹³C-NMR of AQ and **3a** in dry C₆D₆ (The signal from benzene, δ 128.0 ppm, is the "constant" internal standard for each spectrum): (a) before irradiation, *N*-methyl from **3a** (δ 28.1 ppm); (b) 20-min irradiation, bleaching of **3a** and formation of **8a** (δ 62.6 ppm) and **6a** (δ 74.6 ppm); (c) 180-min thermolysis at 88 °C after irradiation, bleaching of **8a** and recovery of **3a**.

metastable product mixture. Because the metastable compound(s) are thermally unstable and sensitive to air, their isolation and purification has not been possible. However, we have obtained additional evidence supporting the role of **8** and iminium ion/AQH⁻ in equilibrium as follows.

(5) Metastable Photoproducts and Thermal Reaction. To determine more precisely the structure of the metastable products and the mechanism of the thermal "retroreaction", the methyl-C-13 labeled compound **3a** was synthesized. Through ¹³C-NMR it is possible to follow quite closely both the photochemical reaction and the thermal return to starting materials. In a decoupled experiment, compound **3a** shows a very sharp peak at δ 28.1 ppm in benzene-*d*₆. In the nondecoupled experiment, the signal splits into a quartet, a clear indication of a methyl group. When a mixture of AQ (1.202×10^{-2} M) and **3a** (2.032×10^{-2} M) in dry benzene-*d*₆ is irradiated in degassed solution, the signal at δ 28.1 ppm bleaches while a new signal at δ 62.6 ppm shows up, along with the appearance of a small peak at δ 74.6 ppm (Figure 3). The signal at δ 74.6 ppm is assigned to compound **6a** (consistent with the signal from the methylene carbon in **6**), which grows only during the initial period of irradiation. This observation is attributed to the presence of a trace of water which was completely consumed during the initial period of photolysis, as further supported by ¹H-NMR observation (the broad singlet at 0.6 ppm for water disappeared after 5 min of irradiation). After 20-min irradiation, 54% conversion of amine **3a** (followed by ¹³C-NMR) (Figure 3) and 80% conversion of AQ (followed by ¹H-NMR) to photoproduct were observed. The signal at δ 62.6 ppm bleaches upon thermolysis at 88 °C with the concurrent recovery of starting amine **3a** (δ 28.1 ppm) (Figure 3). At the same time, the percentage recovery of AQ can be calculated from ¹H-NMR

Table III. Thermal Reversion of **8a** to AQ and **3a** at 88 °C

	0 min	30 min	90 min	180 min
% recovery ^a of 3a ^b	0.0	13.3	34.5	50.0
% recovery ^a of AQ ^c	0.0	18.2	31.7	46.2
relative ratio ^b [8a]/[8a] ₀	1.0	0.66	0.41	0.26

^a Calculated based on consumed starting materials. ^b Calculated from ¹³C-NMR (in dry C₆D₆). ^c Calculated from ¹H-NMR (in dry C₆D₆).

spectra. The results are listed in Table III. The disappearance of the metastable photoproduct follows first-order kinetics, and the rate constant at 88 °C is estimated to be $1.2 \times 10^{-4} \text{ s}^{-1}$. The recovery ratio of AQ to **3a** is approximately 1:1. From the chemical shift of this new signal (δ 62.6 ppm, split into a triplet if uncoupled, quite similar to the ¹³C-NMR value for the analogous carbon in **7**, δ 63.8 ppm), the metastable photoproduct is assigned as adduct **8a**, which is also consistent with its ¹H-NMR spectrum. However, the persistence of a yellow color in the irradiated reaction mixture suggests the presence of at least a small amount of 9,10-anthrahydroquinone (or AQH⁻) and the iminium ion from **3a**, which should be in equilibrium with **8a** (the characteristic blue fluorescence of AQH₂ is also readily observable). The failure to detect the iminium ion by ¹³C-NMR is probably due to its low steady-state concentration. For dry benzene, the ¹³C-NMR signal integration from the starting **3a** remains close to the total ¹³C signal integration attributed to the labeled carbon from residual **3a**, **6a**, and **8a**. Additional evidence also suggests the existence of an equilibrium between **8a** and the ion pair AQH⁻/iminium ion. When an irradiated solution is exposed to air, the yellow color of the reaction solution bleaches out rapidly and completely. Although the intensity of the signal from **8a** at δ 62.6 ppm decreases, the decrease in its intensity is much slower and it can still be clearly detected by ¹³C-NMR up to 1 h after opening the sample. Moreover, if the opened sample is left unshaken under air, the yellow color reappears but bleaches out immediately upon shaking. The oxidation products observed upon exposing the photoproduct solution to air were identified by ¹³C-NMR and ¹H-NMR as AQ, amine **2**, and formaldehyde derivatives. From these observations it seems reasonable to infer that compound **8a** is stable to air; in degassed solution an equilibration between **8a** and the ion pair is established; and upon exposure to air, the anthrahydroquinone anion is oxidized by oxygen to AQ, which shifts the equilibrium to the ion pair (thus the reappearance of the yellow color). The iminium ion is decomposed either by reacting with water (from the air) or hydroperoxide (formed through oxidation of AQH₂).

If the above explanation is correct, we should anticipate a possible solvent effect. Since a polar solvent can stabilize the ion pair, the equilibrium should shift to the ion pair side when a polar solvent, such as acetonitrile, is used. Under such conditions, we should be able to detect the iminium ion by ¹³C-NMR. This apparently is the case. When AQ and **3a** are irradiated in a mixed solvent (benzene-*d*₆/acetonitrile-*d*₃ = 1:5), a small signal at δ 154.6 ppm was clearly detected, which has been determined to be a methylene group on the basis of a nondecoupled experiment. The chemical shift of this signal is consistent with that of the iminium ion methylene carbon.³⁵ Although the iminium ion has been detected in the polar solvent, it was found to be very reactive. The signal at δ 154.6 ppm disappeared completely in a few hours at room temperature. At higher temperature, 90 °C, it bleached out within 1 h. However, **3a** was not regenerated under these conditions. Some unidentified secondary products were formed. The results were further supported by a UV-vis experiment. In dry benzene, the bleaching of AQ with **3** in dilute solution leads

(35) See: Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; John Wiley & Sons, Inc.: New York, 1972; 473 (and also entry 35 for a closely related compound).

(36) Both reactions 4 and 5 require intersystem crossing from the (presumed) triplet radical pair which precedes them; it is assumed that proton transfer (step 3) is probably faster than intersystem crossing, but we have no direct evidence concerning the rate of intersystem crossing, since transient spectroscopy provides little in the way of defining the different intermediates.

to **8** as major product with very little absorption in the visible region corresponding to AQH⁻. However, when the solvent polarity is increased (mixture of benzene and acetonitrile), more reduced anthraquinone is detected by UV absorption spectra (380 nm). When the reaction is carried out in dry acetonitrile, AQH₂ accumulates and is found to be stable even at high temperature (90 °C). Thus in dry polar solvent neither of the dark reactions (formation of **6**, which requires the presence of water, or the regeneration of starting materials) occurs.

(6) Mechanism of the Reversible Reaction. The results from our study support the mechanism shown in Scheme II. Photoexcitation of AQ leads to its singlet excited state, which is converted to the triplet via an efficient intersystem crossing (step 1). The triplet state is quenched by amine **3** via an electron transfer (step 2), followed by a proton-transfer step (step 3), to yield the semiquinone radical and *N*-methylene radical pair. Although a hydrogen abstraction mechanism can also lead to the same intermediates, this pathway, however, is regarded as less likely as discussed above. At this stage, the radical pair can decay to starting material (step 4) or further react to yield adduct **8** either by direct radical coupling or through a two-step mechanism, that is a second electron transfer (step 5), followed by a zwitterion ion coupling (step 6).³⁶ We believe the reaction follows the stepwise pathway, because the photolysis of AQ and **3** in benzene under air leads only to the formation of AQH₂ (evidenced by the blue fluorescence), **2**, and formaldehyde derivatives; under these conditions compound **8** is not detected. If the reaction were to follow the radical-coupling pathway, we would expect that **8** could be detected due to its stability toward air (*vide supra*). The second electron transfer thus leads to the formation of the ion pair. In the presence of water, the iminium ion will be hydrolyzed to **2** and formaldehyde, which reacts with AQH⁻ to afford adduct **6** (step 7). In contrast, under dry and degassed conditions, the ion pair reacts to form **8** in an equilibrium process. We can estimate the equilibrium constant to be roughly 70 in benzene.³⁷ This suggests that adduct **8** is about 2–3 kcal/mol more stable than the iminium ion pair in this solvent.

The reverse reaction could follow the pathways outlined in Scheme II. Heterolytic C–C bond cleavage of **8** (step 6) followed by electron transfer from AQH⁻ to the iminium ion (step 5) could be induced thermally to generate the radical pair. The free energy of this process is estimated to be around 26–27 kcal/mol,³⁸ which is in good agreement with the estimated free energy of activation of the thermal reaction (27.8 kcal/mol) in our kinetic analysis. Hydrogen atom transfer from the semiquinone radical to the amine radical within the pair (step 4) will lead to the regeneration of starting materials. Even though a homolytic C–C bond cleavage of **8** could also lead to the formation of the radical pair intermediate, the pathway of nitrogen lone pair electron assisted heterolytic C–C cleavage followed by thermally induced electron transfer appears more likely, since more energy should be required to break the C–C bond homolytically. We have also found that AQH₂ can be thermally oxidized to AQ by reaction with the excess stabilized iminium salt **9** (Figure 4).⁴¹ The bleaching of AQH₂ follows pseudo-first-order kinetics, and the free energy of activation is estimated to be 25.9 kcal/mol. This further supports the sequence of electron transfer, hydrogen atom transfer for the thermal reaction.

(37) Estimated by the absorption of AQH⁻ in the reaction mixture using the following equation:

$$K = \frac{[\text{adduct } \mathbf{8}]}{[\text{AQH}^-/\text{iminium ion}]}$$

(38) Estimated by the reduction potential of the iminium ion ($\sim -1.0 \text{ eV}$ vs SCE),³⁹ the oxidation potential of the hydroquinone anion⁴⁰ ($\sim 0.023 \text{ eV}$ vs SCE at pH 13.5), and the heat of reaction of the heterolytic C–C bond dissociation (2 to 3 kcal/mol).³⁷

(39) Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130–137.

(40) Steenken, S.; Neta, P. *J. Phys. Chem.* **1982**, *86*, 3661–3667.

(41) AQH₂ does not convert to AQ in the absence of **9**.

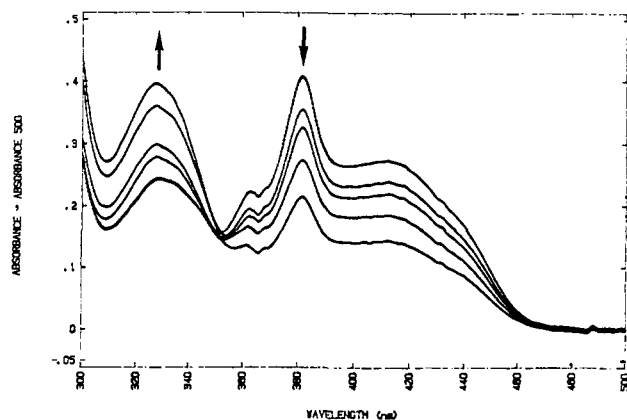
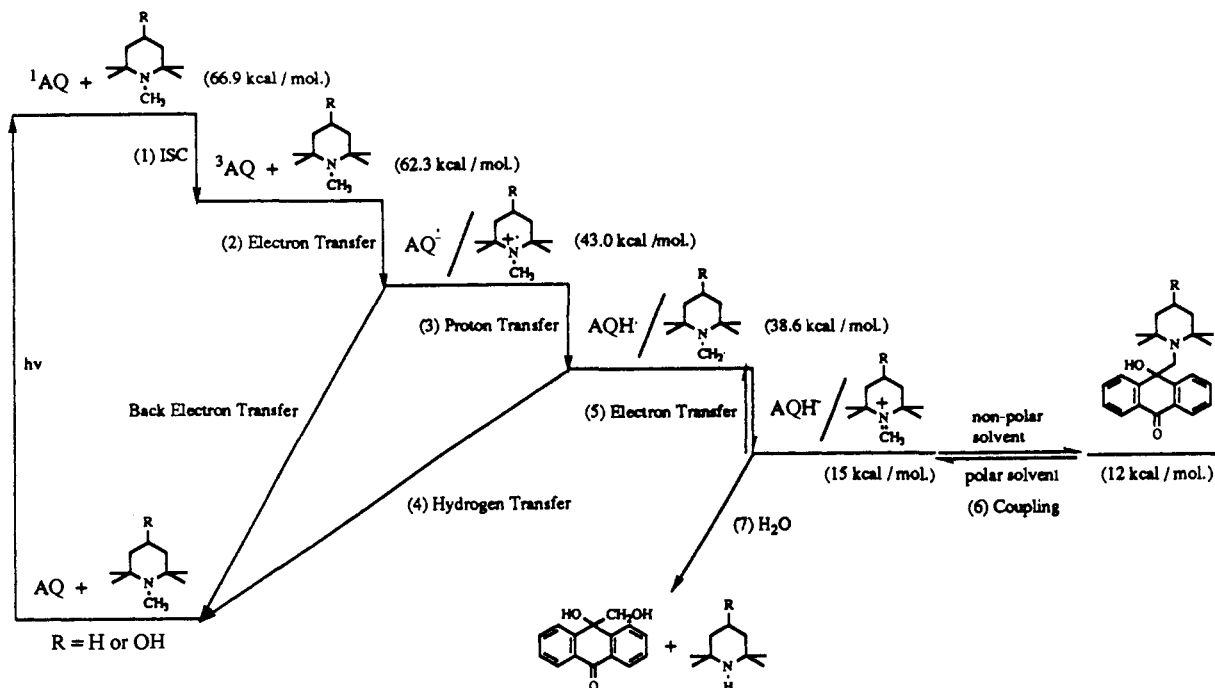
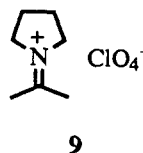
Scheme II. Energetics of the Intermediates and Mechanism of the Photoinduced Electron-Transfer Reaction: Reaction of AQ with Sterically Hindered Amines **3** and **5**

Figure 4. Thermal oxidation of AQH₂ ($\sim 10^{-4}$ M; generated from photoreduction of AQ by triethylamine) by iminium salt **9** ($\sim 10^{-2}$ M) in the presence of triethylamine ($\sim 10^{-2}$ M) under vacuum in benzene/acetonitrile (1:1).

**Summary**

In conclusion, this study shows that utilization of photoinduced net two-electron redox reactions in a simple organic system as a light harvesting and storage process might be a reasonable process given appropriate donor and acceptor structure. In the present case the results clearly demonstrated the importance of the steric substituent effect and the reaction conditions on the reactivity of the reactive intermediates. We have also been able to detect the iminium ion by ¹³C-NMR in dry acetonitrile from a photoinduced electron-transfer oxidation of a tertiary amine. In dry benzene, a metastable product **8** is formed, which at least can be partially reconverted to AQ and **3** under controllable conditions. By utilizing Benson's additivity rules, the enthalpy of the reaction to produce adduct **8** from AQ and amine **3** is estimated to be

around 12 kcal/mol (Scheme II). Accordingly, the relative energies of the reactive intermediates have been estimated from the thermochemical calculation and the redox potentials of the corresponding substances (Scheme II).⁴² Although the energy stored is relatively low, the finding of a long-lived but recyclable system in this study is promising. With a better understanding of the factors that affect the pathway of this reaction, we may be able to design a better and more efficient system.

Experimental Section

The deuterated NMR solvents, chloroform, benzene, acetonitrile, and acetone, were used as received (Cambridge Isotope Laboratories; MSD Isotopes). Dry benzene-*d*₆ was obtained by refluxing over sodium and distillation. Dry acetonitrile-*d*₃ was obtained by distillation over lithium aluminum deuterate. Spectroscopic grade benzene and HPLC grade acetonitrile were dried by refluxing with lithium aluminum hydride. The solvents were freshly distilled prior to use.

Iodomethane (Aldrich, 99%), iodomethane-¹³C (Aldrich, 99 atom% ¹³C), iodoethane (Aldrich, 99%), 2,2,6,6-tetramethyl-4-piperidinol (**2**) (Aldrich, 98%), *trans*-tropine (**1**) (Riedel-de Haen, 98%), and 1,2,2,6,6-pentamethylpiperidine **5** (Aldrich, 97%) were used as received. 9,10-Anthraquinone (Aldrich, 97%) was recrystallized from chloroform.

Preparation of 1,2,2,6,6-Pentamethyl-4-piperidinol (3). Iodomethane (4.0 mL, 9.12 g, 6.43×10^{-2} mol) was added to a solution of 2,2,6,6-tetramethyl-4-piperidinol (**2**) (2.00 g, 1.27×10^{-2} mol) in 5.0 mL of methanol. A white precipitate formed after stirring the solution overnight at room temperature. Ether (20 mL) was added to the reaction mixture to induce more precipitation. The white solid was collected by filtration and was dissolved in 150 mL of 1.4 M NaOH and extracted with dichloromethane (5 × 50 mL). The organic phases were washed once with brine, dried over anhydrous MgSO₄, and filtered, and the solvent

(42) The free energy of reaction from AQ and **3** to **8** is estimated by Benson's additivity rules to be 12 kcal/mol; the AQ singlet excited state energy is 66.9 kcal/mol; the AQ triplet excited state energy is 62.3 kcal/mol; the energy of the AQ anion radical and amine **3** cation radical pair is estimated to be 43.0 kcal/mol by their redox potentials (Table I); and the relative energy of the AQH⁻ and iminium ion pair is estimated to be 15.0 kcal/mol. The energy of the semiquinone radical and amine-methylene radical pair is estimated to be 38.6 kcal/mol by using their estimated redox potentials.³⁸ The free energy of reaction from the AQ anion radical and **3** cation radical pair to the above radical pair equals -4.4 kcal/mol, which is in very good agreement with the calculated free energy of the deprotonation reaction of the trimethylamine cation radical (-5.5 kcal/mol).⁴³

(43) Armstrong, D. A.; Rauk, A.; Yu, D. *J. Am. Chem. Soc.* **1993**, *115*, 666-673.

was evaporated under reduced pressure, affording **3** as colorless needle crystals (1.7711 g, 81.5%). The compound was recrystallized from hexane to yield 1.5358 g of colorless crystals of **3** (70.7%): $^1\text{H-NMR}$ (C_6D_6) δ 3.61 (m, 1H), 2.05 (s, 3H), 1.59 (dd, 2H), 1.29 (d, 2H), 1.01 (s, 3H), 0.79 (s, 3H); $^{13}\text{C-NMR}$ (C_6D_6) δ 63.4, 55.0, 50.5, 33.5, 28.1, 20.6 ppm; mp 74–75 °C (lit.⁴⁴ 73–74 °C).

Preparation of 1-(^{13}C),2,2,6,6-Pentamethyl-4-piperidinol (3a). Iodomethane- ^{13}C (5.0 g, 3.50×10^{-2} mol) was added to a solution of 2,2,6,6-tetramethyl-4-piperidinol (**2**) (0.81 g, 5.15×10^{-3} mol) in 3.0 mL of methanol. The solution was stirred at room temperature for 3 days. A white precipitate formed. The reaction mixture was dissolved in 100 mL of 0.12 M KOH and extracted with dichloromethane (6 \times 50 mL). The organic layers were separated, washed once with brine (100 mL), dried over anhydrous MgSO_4 , and filtered. The solvent was removed under reduced pressure, affording a white solid (0.74 g), which was recrystallized from pentane. **3a** was obtained as colorless crystals (0.66 g, 74.4%): mp 79–80 °C; $^{13}\text{C-NMR}$ (CDCl_3) δ 28.0 ppm.

Preparation of 1-Ethyl-2,2,6,6-tetramethyl-4-piperidinol (4). Iodomethane (2 mL, 3.9 g, 2.50×10^{-2} mol) and 0.2 g of Na_2CO_3 were added to a solution of 2,2,6,6-tetramethyl-4-piperidinol (**2**) (0.52 g, 3.31×10^{-3} mol) in 2.0 mL of methanol. The reaction mixture was stirred and refluxed for 2 days. The solvent was evaporated. The solid residue collected was dissolved in 20 mL of 0.20 M Na_2CO_3 and extracted with dichloromethane (5 \times 20 mL). The organic layers were separated, washed once with brine (100 mL), and dried over anhydrous MgSO_4 . The solution was filtered and evaporated under reduced pressure. The white solid obtained was recrystallized from hot hexane to afford **4** as colorless crystals (0.40 g, 64.8%): $^1\text{H-NMR}$ (CDCl_3) δ 3.93 (m, 1H), 2.49 (q, 2H), 1.80 (dd, 2H), 1.31 (t, 2H), 1.14 (s, 3H), 1.02 (s, 3H), 0.99 (t, 3H); mp 92–94 °C (lit.^{45,46} 76.5–78.5 and 82–85 °C).

Preparation of 9-Hydroxy-9-(hydroxymethyl)anthrone (6). (a) Thermal reaction: A mixture of AQ (0.50 g, 2.404×10^{-3} mol), $\text{Na}_2\text{S}_2\text{O}_4$ (Aldrich, 85%; 0.50 g, 2.441×10^{-3} mol), and NaOH (0.45 g, 1.125×10^{-2} mol) in water (50 mL) was stirred and bubble-degassed with Argon for 15 min. The solution was heated at 60 °C under argon for 45 min and then cooled to room temperature. A deep-red solution was obtained. Formaldehyde (2 mL, 37 wt% in water) was added, and the solution was stirred at 60 °C under argon for 30 min. The resulting deep-red mixture was neutralized with concentrated HCl. The red color disappeared and a yellow precipitate was formed. The reaction mixture was worked up and chromatographed on silica gel with dichloromethane and ether as eluent, affording AQ (0.16 g, 31.8%) and **6** (0.41 g, 67.9%): $^1\text{H-NMR}$ (CDCl_3) δ 8.26 (d, 2H), 7.93 (d, 2H), 7.69 (t, 2H), 7.53 (t, 2H), 3.62 (d, 2H), 3.07 (s, 1H), 1.87 (t, 1H). Upon addition of D_2O , the signals at δ 3.07 and 1.87 ppm (hydroxy protons) disappeared and the signal at δ 3.62 ppm became a broad singlet. $^{13}\text{C-NMR}$ (CD_3CN) δ 184.6, 147.1, 134.0, 132.5, 128.7, 127.1, 126.9, 74.7, 73.8; UV (CH_3CN) λ_{max} = 274 nm (15 400); mp 165–170 °C dec. Elemental analysis: C, 74.51%; H, 5.03%. Calculated: C, 74.99%; H, 5.03%.

(b) Photochemical reaction: AQ (0.3144 g, 1.512×10^{-3} mol) and amine **3** (0.2580 g, 1.491×10^{-3} mol) were dissolved in 250 mL of dichloromethane. The solution was stirred and degassed with argon and irradiated with a 250-W tungsten lamp through a Corning 0–52 glass filter at room temperature for 3.5 h. The solvent was evaporated, and the yellow residue was chromatographed as described above, yielding AQ (0.2232 g, 71%), **6** (0.0859 g, 23.7%), **2** (0.0926 g, 39.1%), and **3** (0.1262 g, 48.9%).

General Procedure for Photolysis and Product Analysis. The solutions were irradiated with either a 200-W mercury lamp or a 250-W tungsten lamp with a Corning 0–52 cutoff filter or a monochromator (Bausch & Lomb) set at 313 nm to selectively excite only the 9,10-anthraquinone. The analysis of the photoproducts in most cases is complicated by the fact that some of the products formed are air sensitive. Therefore, all analytical experiments were carried out under degassed conditions. All the samples were degassed on a vacuum line through five to seven freeze–pump–thaw cycles in Kimax glass test tubes with or without an NMR tube as a side arm and sealed at $<5 \times 10^{-6}$ Torr. In the case of NMR studies, the sample was transferred into the side-arm NMR tube and sealed. The whole process was carried out in a dark room. The photolysis was performed either in the Kimax test tube or in the NMR tube. The progress of photoreactions was monitored by UV–vis (Hewlett Packard 8451 A diode array spectrophotometer) or NMR (300-MHz FT NMR; GE, Oxford Instrument) periodically. The photoproducts were identified by the analysis of their absorption spectra and their NMR spectra (proton and carbon-13). The stable products were analyzed after isolation and purification.

Photolysis of AQ in the Presence of *trans*-Tropine (1). A solution of AQ (0.0488 g, 2.346×10^{-4} mol) and *trans*-tropine (**1**) (0.0531 g, 3.760×10^{-4} mol) in acetonitrile (35 mL) was bubble-degassed with argon for 15 min. The solution was irradiated with a 250-W tungsten lamp through a Corning 0–52 glass filter at room temperature for 1 hour. The solvent was evaporated to afford a yellow, solid residue. $^1\text{H-NMR}$ indicated the formation of a new anthrone-type product. TLC (silica gel, ether) also indicated a new product with R_f = 0.72 (observed under UV light as well as in an iodine chamber). However, this product is not stable on a silica gel column, and attempts to isolate it through column chromatography failed. Only AQ and some decomposed products were obtained. The photoproduct is tentatively assigned as **7**. Its characteristic absorption signals in the reaction mixture are summarized as follows: $^1\text{H-NMR}$ (C_6D_6) δ 8.44 (d, 2H), 7.76 (d, 2H), 7.21 (t, 2H), 7.10 (t, 2H), 3.45 (br, 1H), 2.31 (br, 2H), 2.01 (s, 2H), 1.75 (d, 2H). Other signals overlap with signals from other reactants. $^{13}\text{C-NMR}$ (C_6D_6) δ 184.3, 147.9, 133.7, 132.1, 127.6, 126.5, 124.9, 73.2, 64.3, 63.8, 60.4, 40.4, 39.6.

Photolysis of AQ in the Presence of **3 or **5**.** A solution of AQ (0.0015 g, 7.212×10^{-6} mol) and **3** (0.0021 g, 7.749×10^{-6} M) in benzene- d_6 (freshly distilled from sodium, 0.6 mL) was vacuum-degassed via five freeze–pump–thaw cycles and sealed under high vacuum (5×10^{-6} Torr) in an NMR tube. The solution was irradiated with a 250-W tungsten lamp through a Corning 0–52 glass filter at room temperature for 20 min. Adduct **8** was formed. Since the product is unstable in air, its isolation from the reaction mixture was not attempted. The $^1\text{H-NMR}$ signals of adduct **8** from the reaction mixture are summarized as follows: $^1\text{H-NMR}$ (C_6D_6) δ 8.27 (d, 2H), 7.86 (d, 2H), 7.0–7.1 (m, 4H), 3.40 (m, 1H), 2.72 (s, 2H), 0.60 (s, 6H), 0.28 (s, 6H). Other signals overlap with signals from other reactants. When amine **5** is used, the product gives a similar $^1\text{H-NMR}$ spectrum: $^1\text{H-NMR}$ (C_6D_6) δ 8.28 (d, 2H), 7.90 (d, 2H), 7.0–7.1 (m, 4H), 2.79 (s, 2H), 0.61 (s, 6H), 0.31 (s, 6H). Upon heating the samples at 90 °C, the signals from the product bleached out with the concurrent recovery of AQ and **3** or **5**.

Kinetic Study of the Dark Reactions. The kinetics of the dark reaction between AQH₂ and formaldehyde was followed in a Kimax test tube. The reaction mixture of AQ (1.1526×10^{-4} M) and amine **3** (9.972×10^{-3} M) in acetonitrile (containing 0.1% water) was irradiated with a 250-W tungsten lamp through a Corning 0–52 glass filter at room temperature for 5 min. Then, the disappearance of AQH₂, generated from the above photolysis, at 15, 19, 23, 27, and 31 °C was monitored by UV–vis at 400 nm. The reaction was observed to follow second-order equal-concentration kinetics. On the basis of an Arrhenius plot, the activation energy is calculated to be 15 kcal/mol.

The kinetics of thermal reversion of adduct **8a** to AQ and amine **3a** was determined by following the reaction by $^{13}\text{C-NMR}$. The bleaching of peak intensity at δ 62.6 ppm for **8a** (with benzene as internal standard) upon thermolysis was analyzed (see Table III). The rate of disappearance of **8a** at 88 °C was calculated to be $1.2 \times 10^{-4} \text{ s}^{-1}$, and the free energy of activation was estimated by using the Eyring equation to be around 27.8 kcal/mol.

Quantum Yield of AQ Photoreduction. The quantum yields of AQ photoreduction were measured in acetonitrile (with 0.1% water) in the presence of **3**. The samples were irradiated with a 200-W mercury lamp through a monochromator (Bausch & Lomb) set at 313 nm. The progress of AQ reduction (bleaching of the absorption peak at 324 nm) was followed by UV–vis. The excitation light intensities were determined using potassium ferrioxalate actinometry.⁴⁷ The results are listed in Table II.

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