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Electron Transfer Induced Deazatization of Cyclic Azo Derivatives of Quadricyclane and Norbornadiene

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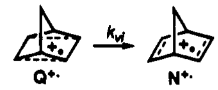
Abstract: The photosensitized oxidation of two cyclic azoalkane derivatives (**Azo-Q**, **Azo-N**) of quadricyclane (**Q**) and norbornadiene (**N**) has been investigated using steady-state and laser flash photolysis techniques as well as chemically induced dynamic nuclear polarization (CIDNP). Irradiation of acetonitrile solutions of 9,10-dicyanoanthracene (**DCA**), 2,6,9,10-tetracyanoanthracene (**TCA**), or chloranil (**Chl**) in the presence of **Azo-Q** results in rapid and efficient deazatization to afford **N**. Similar irradiation of **DCA**, **TCA**, and **Chl** in the presence of **Azo-N** yields **N** and **Q**. CIDNP experiments reveal that polarized **N** is formed as a cage product in the **Chl** sensitized photolysis of **Azo-Q** while polarized **N** and **Q** are *both* formed as cage products from **Azo-N**. The results are consistent with competitive fragmentation of **Azo-N**$^{•+}$ to **N**$^{•+}$ and **Q**$^{•+}$, and selective deazatization of **Azo-Q**$^{•+}$ to **N**$^{•+}$. Irradiation of 1-cyanonaphthalene in the presence of **Azo-Q** or **Azo-N** affords **Q** and/or **N** in chemical yields similar to those obtained from direct and naphthalene sensitized irradiations, indicative of singlet energy transfer quenching. Bimolecular rate constants for quenching by **Azo-N** and **Azo-Q** were determined by steady-state fluorescence methods for singlet sensitizers, or by laser flash photolysis (LFP) for ^{3}**Chl***.

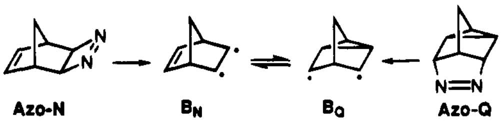
Introduction

The interconversion of quadricyclane (**Q**) and norbornadiene (**N**) has attracted considerable attention because of its potential for solar energy storage,[1] or as the basis for an optical memory system.[2] The exothermic conversion of **Q** to **N** may be facilitated by photosensitized one-electron oxidation (eq 1).[3–9] Chemically induced dynamic nuclear polarization (CIDNP) studies have established the existence of two distinct radical cations, **Q**$^{•+}$ and **N**$^{•+}$, and have provided indirect evidence for the valence isomerization of **Q**$^{•+}$ to **N**$^{•+}$.[10–13] *Ab initio* calculations also support two minima on the $C_7H_8^{•+}$ energy surface corresponding to **Q**$^{•+}$ and **N**$^{•+}$.[14] Recently, we reported the first direct detection of **Q**$^{•+}$ by time-resolved ESR, and estimated the rate constant for the valence isomerization to **N**$^{•+}$ ($k_{vi} \approx 10^6$ s^{-1}).[15,16]



(1)

Azoalkanes are convenient sources of radicals and biradicals.[18] We have previously employed cyclic azoalkanes *exo*-**Azo-N** and *endo*-**Azo-Q** as alternate precursors to the norbornadienyl and quadricyclanyl biradicals (**B**$_N$, **B**$_Q$) in attempts to elucidate the energy surfaces which interconnect **N** and **Q**[19] (eq 2).



(2)

One-electron oxidation of azoalkanes lowers the barrier to carbon–nitrogen bond fragmentation by several orders of magnitude, leading to rapid and efficient deazatization.[20–30] Thus, we have selected **Azo-N** and **Azo-Q** as alternate sources

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(16) A difference spectrum of two low-temperature spectra also was ascribed to **Q**$^{•+}$.[17] However, the resulting hyperfine pattern deviates noticeably from the (TR) ESR results,[15] the CIDNP pattern,[10,11] and the ab initio results.[14,17]

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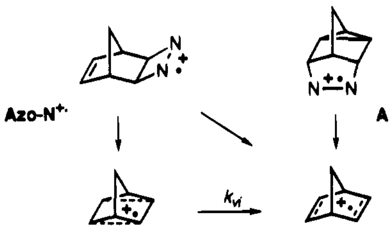
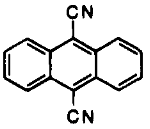
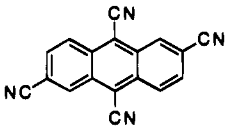
Scheme 1

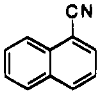


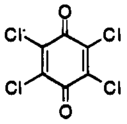
of the radical cations **N**$^{\bullet+}$ and **Q**$^{\bullet+}$ (Scheme 1); this reaction leads ultimately to formation of the neutral hydrocarbons **N** and **Q**.

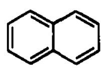
In this paper, we report results of the photosensitized decomposition of **Azo-N** and **Azo-Q** in acetonitrile. We have employed several singlet sensitizers, viz., 9,10-dicyanoanthracene (**DCA**), 2,6,9,10-tetracyanoanthracene (**TCA**), and 1-cyanonaphthalene (**CN**), and one triplet sensitizer, chloranil (**Chl**), which we expected to react by electron transfer, and one sensitizer, naphthalene (**Nap**), likely to react by energy transfer. The deazatization mechanism of the azoalkane radical cations was probed by CIDNP experiments. Bimolecular rate constants for quenching by **Azo-N** and **Azo-Q** were determined by steady-state fluorescence methods for singlet sensitizers, or by laser flash photolysis (LFP) for ^{3}**Chl***.


DCA


TCA

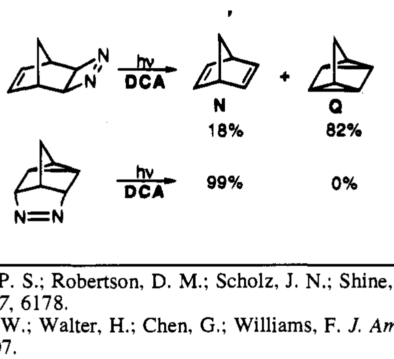

CN


Chl


Nap

Results

Product Studies. The photosensitized oxidation of the azoalkanes results in efficient deazatization affording **N** and **Q** as the major products with each of the sensitizers employed (Table 1). Steady-state photolysis (λ > 370 nm) of acetonitrile solutions of **DCA** or **TCA** in the presence of **Azo-Q** affords **N** in virtually quantitative yield at 2−50% conversion of **Azo-Q**; the valence isomer **Q** was not detected. Irradiation of **DCA** or **TCA** in the presence of **Azo-N** affords **N** (18%) and **Q** (82%) as the sole products (eq 3).



(3)

Table 1. Chemical Yields of Norbornadiene (N) and Quadricyclane (Q) from **Azo-Q** and **Azo-N** upon Direct Irradiation or Photosensitized Decomposition at 23 ± 2 °C^a

compound	conditions	% N	% Q	mechanism
 **Azo-Q**	**DCA**	99	0	ET to singlet state
	TCA	99	0	ET to singlet state
	Chl	24	0	ET to triplet state
	CN^b	59	41	singlet energy transfer
	Nap^b	62	38	singlet energy transfer
	direct^{b,c}	63	37	
	triplet^{c,d}	10	90	triplet energy transfer
 **Azo-N**	**DCA**	18	82	ET to singlet state
	TCA	19	81	ET to singlet state
	Chl	28	7	ET to triplet state
	CN^b	35	65	singlet energy transfer
	Nap^b	25	75	singlet energy transfer
	direct^{b,c}	29	71	
	triplet^{c,d}	10	90	triplet energy transfer

^{a} Determined by GC, relative to consumed starting azoalkane, after 5−20% conversion. Acetonitrile solution except where noted otherwise. Errors are ca. 10% of the stated values. ^{b} Percentages include only N and Q. At times small amounts (<10%) of norbornene, toluene, and cycloheptatriene were observed but not included in the percentages. ^{c} Pentane solution. Data from ref 19. ^{d} Benzophenone or acetophenone sensitization.

Photolysis (λ > 370 nm) of an acetonitrile solution of **DCA** and **Q** resulted in clean and quantitative production of **N**, which is photostable under these photolysis conditions.

Irradiation (300 nm excitation) of acetonitrile solutions of **CN** or **Nap** in the presence of **Azo-N** or **Azo-Q** again affords **N** and **Q**, however in yields markedly different from those obtained from **DCA** and **TCA** sensitization (eq 3). For example, **CN** sensitized photolysis of **Azo-Q** affords **N** and **Q** in 59% and 41% yield, respectively, quite similar to those obtained upon direct photolysis.[19]

The chloranil photosensitized reaction of the azoalkanes yields **N** and **Q** as the major C_7H_8 products, but they are formed in moderate overall yields (Table 1). For example, **Chl** sensitized irradiation of **Azo-Q** affords **N** in only 24% yield, whereas the corresponding reaction of **Azo-N** affords **N** and **Q** in 28% and 7% yield, respectively. Several products of higher molecular weight are formed from both azoalkanes; the GC mass balances are lower than for **DCA** and **TCA** sensitization. One additional product ($\sim$3−10% yield) has a mass spectrum consistent with an adduct between the C_7 hydrocarbon and **Chl** ($M^+ = 338$; $C_7H_8 + C_6Cl_4O_2$); such adducts have precedent.[31,32] Three other products have parent ions consistent with addition of H and Cl to the C_7−**Chl** adducts ($M^+ = 374$; $C_7H_8 + C_6Cl_4O_2 + HCl$). **Chl** is consumed along with the azoalkanes, and a white solid material of high molecular weight precipitates as the photolysis proceeds.

Chl sensitized photolysis of **Q** in acetonitrile solution to ca. 40% conversion afforded **N** (~20%) and a similar distribution of higher molecular weight products with low GC mass balance. Photolysis of acetonitrile solutions of **Chl** and **N** also resulted in the formation of the higher molecular weight species and an insoluble material.

Nuclear Spin Polarization. Irradiation (370 < λ < 600 nm) of acetonitrile-d_3 solutions of **Chl** and **Azo-Q** gave rise to a ^{1}H CIDNP spectrum showing enhanced absorption for the olefinic (H_{ol}; 6.74 ppm; strong) and bridgehead (H_{bh}; 3.56 ppm; very weak) protons of **N** (Figure 1). An emissive signal at 1.92 ppm, partially obscured by solvent resonances, is attributed to the

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Table 2. Oxidation potentials of **Azo-N**, **Azo-Q**, **N**, and **Q** and Rate Constants ($k_q/10^9$ M^{-1} s^{-1}) for Quenching of **DCA**, **TCA**, **Nap**, and **CN** Fluorescence and Quenching of ^{3}**Chl*** by These Donors in Acetonitrile Solution at 23 ± 2 °C[a]

compound	E_{ox} (V vs SCE)	DCA	TCA	Chl	Nap	CN
Azo-N	2.3[b]	1.87 ± 0.04	11.3 ± 0.4	4.4 ± 0.1	15 ± 2	36 ± 2
Azo-Q	2.1[b]	6.4 ± 0.1	14.5 ± 0.2	5.7 ± 0.4	15 ± 2	34 ± 3
N	1.56[c]	11.6 ± 0.1	21 ± 1	5.3 ± 0.6[d]	*f*	8.4 ± 0.1
Q	0.91[c]	20.1 ± 0.6	25 ± 1	11 ± 2[e]	*f*	14.4 ± 0.6

[a] Fluorescence quenching rate constants determined from Stern–Volmer plots (eq 4) and subsequent substitution of the literature fluorescence lifetimes (τ).[33] ^{3}**Chl*** quenching rate constants determined by LFP according to eq 5. Errors are reported as twice the standard deviation from the least squares analysis of the data according to eq 4 or 5. [b] Estimated from peak oxidation potentials in acetonitrile solution with 0.1 M n-Bu$_4$ClO$_4$ supporting electrolyte. [c] Data from ref 34. [d] Ishiguro, K.; Turro, N. J. Unpublished results. [e] Data from ref 15. [f] Not determined.

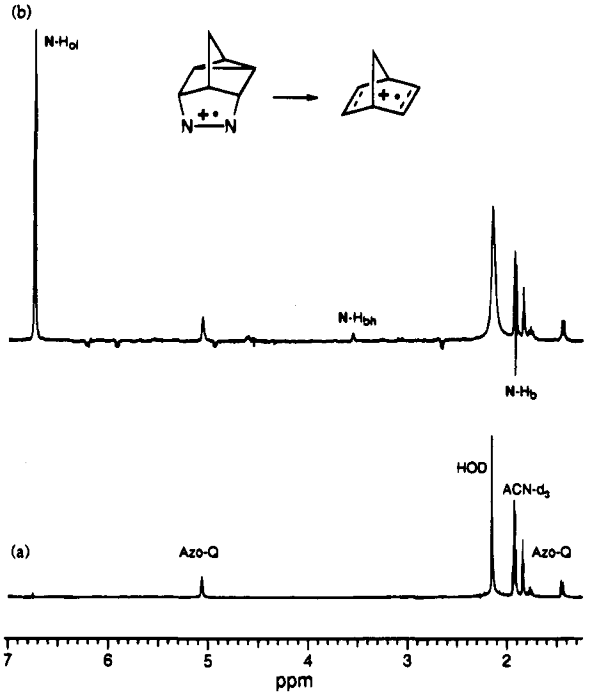

Figure 1. ^{1}H CIDNP spectrum recorded (a) before and (b) during photolysis of a deoxygenated acetonitrile-d_3 solution of **Chl** (0.02 M) and **Azo-Q** (0.02 M). The individual resonances of **Azo-Q** and **N** are labeled. Spectra recorded immediately following irradiation were identical to (a).

bridge protons (H$_b$). The starting material does not exhibit polarization; however, several weaker enhanced signals in emission (6.2, 5.9, 4.9, 2.7, 1.2 ppm) and absorption (4.6, 3.1 ppm) are detected. The signal of residual water (HOD) in the solvent is broadened during irradiation, possibly due to a protonation–deprotonation reaction between HOD and **Chl**$^{\bullet-}$.

Photolysis (370 < λ < 600 nm) of acetonitrile-d_3 solutions of **Chl** and **Azo-N** gave rise to a CIDNP spectrum which showed formation of polarized **N** and **Q** (Figure 2). The polarization pattern of **N** was essentially identical to that detected from **Azo-Q**. Polarized **Q** showed strongly enhanced absorption for the cyclobutane (H$_{cb}$; 1.48 ppm) and bridge protons (H$_b$; 1.98 ppm) and strong emission for the bridgehead protons (H$_{bh}$; 1.36 ppm). Again, the azo donor showed no polarization, whereas several weak signals in emission (5.9, 4.9, 4.35, 4.2, 4.15, 4.05, 3.1, 1.9, and 1.7 ppm) or absorption (2.3 and 1.6 ppm) were observed.

Direct irradiation of **Azo-N** and **Azo-Q** or reaction with photosensitizers (**DCA**, **CN**, or benzophenone) failed to give rise to any detectable CIDNP effects, although the azo donors are depleted; **N** and/or **Q** have been identified as major products in each case.[19]

Fluorescence Spectroscopy. Rate constants for reaction of **Azo-N** and **Azo-Q** with the singlet sensitizers have been determined by steady-state fluorescence quenching experiments (Table 2). The rate constants for reaction of **N** and **Q** with these sensitizers were also determined for comparison. The fluorescence quenching rate constants (k_q) were determined (eq 4) from the Stern–Volmer constants, $K_{SV} = k_q\tau$, and the known

$$I_0/I = 1 + k_q\tau[Q] \quad (4)$$

sensitizer fluorescence lifetimes (τ).[33] The Stern–Volmer plots were linear in the donor concentration ranges employed (<0.03 M); in no case was any exciplex emission observed.

The oxidation potentials of **Azo-N** (2.3 V vs SCE) and **Azo-Q** (2.1 V vs SCE) are significantly higher than those for **N** (1.56 V vs SCE) and **Q** (0.91 V vs SCE).[34] Conversely, **Q** and **N** are better quenchers than are their azo derivatives; the rate constants for quenching of **DCA** fluorescence by **Q** and **N** are 2.0 × 10^{10} and 1.2 × 10^{10} M^{-1} s^{-1}, respectively, compared to rate constants of 6.4 × 10^9 and 1.9 × 10^9 M^{-1} s^{-1} for **Azo-Q** and **Azo-N**, respectively.

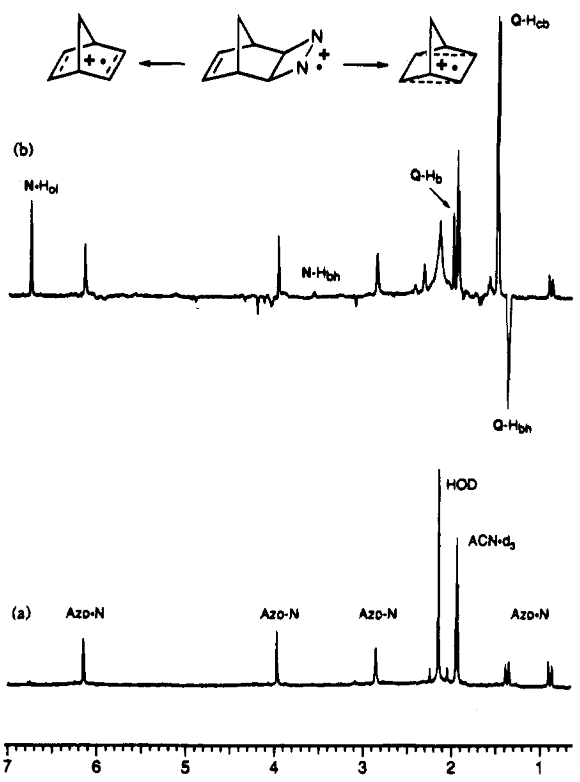

Figure 2. ^{1}H CIDNP spectrum recorded (a) before and (b) during photolysis of a deoxygenated acetonitrile-d_3 solution of **Chl** (0.02 M) and **Azo-N** (0.02 M). The individual resonances of **Azo-N**, **Q**, and **N** are labeled. Spectra recorded immediately following irradiation were identical to (a).

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The fluorescence of **Nap** and **CN** was quenched efficiently by **Azo-N** and **Azo-Q** with rate constants near the diffusion-controlled limit in acetonitrile. Steady increases in the lower energy azoalkane fluorescence emission with increasing azoalkane concentration confirmed singlet energy transfer quenching for these sensitizers. The fluorescence emissions of **Azo-N** (λ_{max} = 400 nm) and **Azo-Q** (λ_{max} = 350 nm)[35] overlap substantially with that of **CN** (λ_{max} = 344 nm), leading to potentially less accurate rate constants in this case.

Laser Flash Photolysis. Laser flash photolysis (308 nm excitation) of dilute acetonitrile solutions of **Chl** affords a transient absorption in the range 460−540 nm (λ_{max} = 510 nm) which decays on the microsecond time scale ($\tau \geq 3$ μs); this absorption has been assigned to the triplet excited state of **Chl** (^{3}**Chl***).[36] Addition of **Azo-N** or **Azo-Q** reduced the lifetime of ^{3}**Chl*** with clean pseudo-first-order decay kinetics. The decay of ^{3}**Chl*** was accompanied by the growth of **Chl**$^{\bullet -}$ (λ_{max} = 450 nm)[15] with matching kinetics. An extremely weak transient absorption centered at 630 nm, growing in at the same rate as **Chl**$^{\bullet -}$, is attributed to **N**$^{\bullet +}$.[15,37,38] Bimolecular rate constants (k_q) for quenching of ^{3}**Chl*** by the azoalkanes as well as **N** and **Q** were obtained from plots of the pseudo-first-order rate constants for decay of ^{3}**Chl*** (k_{decay}) versus the concentration of added quencher (eq 5). Here k_o represents the first-order

$$k_{decay} = k_o + k_q[Q] \tag{5}$$

rate constant for decay of ^{3}**Chl*** in the absence of added quencher (Table 2). All four donors quench ^{3}**Chl*** rapidly with rate constants in the range $4 \times 10^9 - 1 \times 10^{10}$ M^{-1} s^{-1}.

Laser flash photolysis (308 nm) of dilute acetonitrile solutions of **DCA** in the presence of **Azo-N** or **Azo-Q** (0.05 M) led to reduced **DCA** fluorescence but failed to reveal any significant transient absorption at 705 nm attributable to **DCA**$^{\bullet -}$ ($\epsilon \approx 7700$ M^{-1} cm^{-1}).[39,40]

Discussion

The decomposition of **Azo-N** and **Azo-Q** results in deazatization with formation of **N** and/or **Q**. However, the individual reactions may follow different pathways, depending on the nature of the sensitizer excited state and on the relative energies of key intermediates. Key questions concern the mechanism of interaction with the excited state sensitizer and the nature of the intermediate generated from the azo donor (**Azo-D**) as well as their lifetimes and reactivities. The aromatic hydrocarbons and cyano-substituted derivatives used as sensitizers in this study have long-lived excited singlet states; their reactions involve the singlet states exclusively. In contrast, the excited singlet state of **Chl** has a much shorter lifetime[31,36] so that only ^{3}**Chl*** is intercepted.

Potential reactions of a sensitizer with an azo donor include electron transfer, exciplex formation, or energy transfer. The prevailing pathway is determined by energetic principles. The free energy of electron transfer from a donor to an acceptor excited state is given by the excited state energy ($E_{0,0}$), the redox potentials of the acceptor ($E_{(A^-/A)}$), and donor, ($E_{(D/D^+)}$), and a term ($e^2/\epsilon a$) accounting for ion pairing (Rehm−Weller equation, eq 6).[41] The oxidative strength of an excited state is

$$-\Delta G = 23.06[E_{(0,0)} - E_{(D/D+)} + E_{(A^-/A)} + e^2/\epsilon a] \tag{6}$$

conveniently expressed by the excited-state reduction potential (eq 7),[42] We used singlet sensitizers in the range 2.45 V <

$$^*E_{(A^-/A)} = -E_{(0,0)} + E_{(A^-/A)} \tag{7}$$

$^*E_{(A^-/A)}$ < 1.5 V.[43] Given the oxidation potentials of **Azo-N** and **Azo-Q**, electron transfer to these sensitizers ranges from clearly exergonic to clearly endergonic.

Electron Transfer to Excited Singlet Sensitizers. Two of the singlet sensitizers employed, **DCA** and **TCA**, have substantial excited-state reduction potentials, $^*E_{(A^-/A)}$ = 2.0 and 2.45 V,[42,43] respectively. Even for the reluctant electron donors **Azo-N** and **Azo-Q** (**Azo-D**; $E_{(D/D^+)} \approx 2$ V), electron transfer to these excited-state electron acceptors is energetically feasible.

$$^1\mathbf{A^*} + \mathbf{Azo\text{-}D} \rightarrow \mathbf{A}^{\bullet -} + \mathbf{Azo\text{-}D}^{\bullet +} \tag{8}$$

The rate constants for quenching of **TCA** and **DCA** fluorescence by the azo donors **Azo-Q** and **Azo-N** and their deazatization products **Q** and **N** follow trends expected for electron transfer quenching; i.e., they increase with decreasing oxidation potential of the donor.[34] **Azo-N** and **Azo-Q** quench the fluorescence of the stronger acceptor **TCA** with rate constants approaching the diffusion-controlled limit in acetonitrile solution, whereas they quench the fluorescence of **DCA** with rate constants 2−8 times slower (Table 2), increasing in the order: **Azo-N** < **Azo-Q** < **N** < **Q**. The electron transfer nature of the quenching process is also supported by the observation that **Q** and **N** are ~1.5−2.5 times more efficient quenchers in acetonitrile than in methylene chloride.[12]

The mechanism for the photosensitized oxidation of the azoalkanes and subsequent generation of **N** and **Q** can be formulated as follows. Electron transfer from the azo donor to the electronically excited sensitizer (^{1}**sens***; eq 9) affords geminate radical ion pairs comprised of a sensitizer radical anion (**sens**$^{\bullet -}$) and an azoalkane radical cation (**Azo-D**$^{\bullet +}$; eq 10). The driving force of the reaction determines whether the electron transfer produces contact pairs or solvent-separated pairs. These pairs can undergo several competing processes: (i) back electron transfer (BET; eq 11), (ii) diffusive escape from the solvent cage, yielding free radical ions ^{2}**sens**$^{\bullet -}$ and ^{2}**Azo-D**$^{\bullet +}$ (eq 12), or (iii) deazatization to afford secondary radical ion pairs [**sens**$^{\bullet -}$/**N**$^{\bullet +}$] and/or [**sens**$^{\bullet -}$/**Q**$^{\bullet +}$] (eq 13). The secondary pairs also may undergo back electron transfer (eq 14) or cage escape (eq 15); free ^{2}**Q**$^{\bullet +}$ may have sufficiently long lifetimes to undergo valence isomerization to ^{2}**N**$^{\bullet +}$ (eq 16); the free radical cations ^{2}**N**$^{\bullet +}$, ^{2}**Q**$^{\bullet +}$, ^{2}**Azo-N**$^{\bullet +}$, and ^{2}**Azo-Q**$^{\bullet +}$ may also participate in side reactions with the sensitizer and/or the solvent. The

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potential electron transfer induced reactions of the azo donors are summarized in Scheme 2 (brackets signify radical ion pairs).

Scheme 2

$$\text{sens} \rightarrow {}^{1}\text{sens}^{*} \tag{9}$$

$${}^{1}\text{sens}^{*} + \text{Azo-D} \rightarrow [\text{sens}^{\bullet-} + \text{Azo-D}^{\bullet+}] \tag{10}$$

$$[\text{sens}^{\bullet-} + \text{Azo-D}^{\bullet+}] \rightarrow \text{sens} + \text{Azo-D} \tag{11}$$

$$[\text{sens}^{\bullet-} + \text{Azo-D}^{\bullet+}] \rightarrow {}^{2}\text{sens}^{\bullet-} + {}^{2}\text{Azo-D}^{\bullet+} \tag{12}$$

$$[\text{sens}^{\bullet-} + \text{Azo-D}^{\bullet+}] \rightarrow [\text{sens}^{\bullet-} + \text{D}^{\bullet+}] + \text{N}_2 \tag{13}$$

$$[\text{sens}^{\bullet-} + \text{D}^{\bullet+}] \rightarrow \text{sens} + \text{D} \tag{14}$$

$$[\text{sens}^{\bullet-} + \text{D}^{\bullet+}] \rightarrow {}^{2}\text{sens}^{\bullet-} + {}^{2}\text{D}^{\bullet+} \tag{15}$$

$${}^{2}\text{Q}^{\bullet+} \rightarrow {}^{2}\text{N}^{\bullet+} \tag{16}$$

The **DCA** and **TCA** photosensitized reactions (sens = **DCA**, **TCA**) of **Azo-N** and **Azo-Q** in acetonitrile are remarkably clean; the reaction of **Azo-Q** only generates **N** whereas **Azo-N** yields **Q** as the major product (82%; eq 3). The experimental evidence available for these reactions, including the analysis of product mixtures and the CIDNP and LFP results, is consistent with the mechanism outlined above; however, several of the potentially competing reactions are not observed. Although BET (eq 11) may be quite rapid, the deazatization of the **Azo-D**$^{\bullet+}$ species (eq 13) may be competitive; several azoalkane radical cations are known to undergo nitrogen loss with rate constants in the range $\sim 7 \times 10^{6}$ s^{-1}[27] $< k_{\text{deaz}} < 10^{10}$ s^{-1}.[30] In view of this precedent, rapid deazatization of **Azo-D**$^{\bullet+}$ within geminate pairs is reasonable, giving rise to secondary radical ion pairs **DCA**$^{\bullet-}$/**N**$^{\bullet+}$ and/or **DCA**$^{\bullet-}$/**Q**$^{\bullet+}$. Subsequent (rapid) BET in the secondary pairs (eq 14) will afford **N** and **Q**.

The lack of side reactions is notable given that some hydrocarbon radical cations are quite reactive toward unsaturated compounds and nucleophiles.[44-51] For example, the electron transfer induced dimerization of olefins has been studied in detail.[44,45] Also, several bifunctional organic radical cations have been trapped by nucleophiles as poor as acetonitrile.[27,50,52] On the other hand, the high yields of **N** and/or **Q** from **Azo-N** and **Azo-Q** are not surprising, considering that both **Q**$^{\bullet+}$ and **N**$^{\bullet+}$ have been found to be relatively unreactive both toward acetonitrile and with respect to dimer formation.[51]

The lack of polarization in CIDNP experiments with **DCA** sensitization is attributed to the fact that singlet radical ion pairs are short-lived and rapidly undergo BET, either in the geminate or the secondary deazatized pairs.[4] In keeping with this assignment, the LFP experiments failed to reveal more than insignificant yields of free **DCA**$^{\bullet-}$; thus, the formation of free radical ions is clearly inefficient under these conditions. Similar results have been reported for LFP studies of **DCA** photosensitized oxidation of amines.[53]

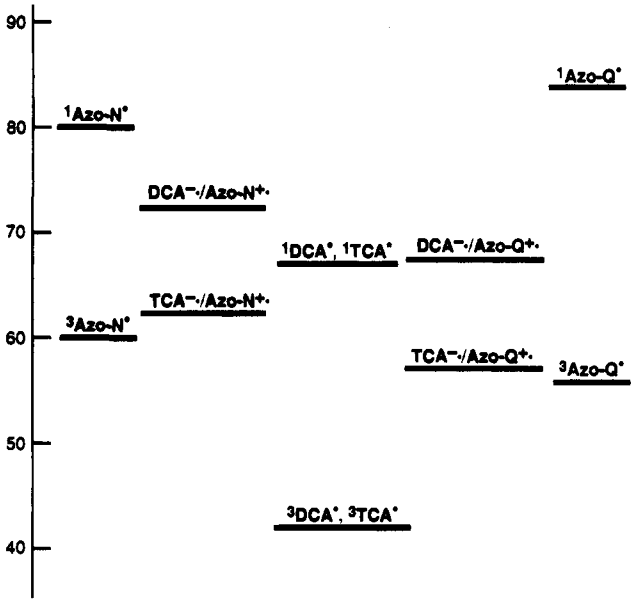

Figure 3. Energy levels (kcal/mol) of key intermediates in the **DCA**/**TCA** photosensitized oxidation of **Azo-N** and **Azo-Q**. The free energies of the radical ion pairs relative to the neutral parent molecules are calculated according to the Rehm–Weller equation. The free energies of **Azo-N**$^{\bullet+}$ and **Azo-Q**$^{\bullet+}$ are not known relative to each other or relative to **N**$^{\bullet+}$ and **Q**$^{\bullet+}$.

The formation of **N** in the electron transfer reaction of **Azo-N** may be ascribed to one of two mechanisms, either deazatization of **Azo-N**$^{\bullet+}$ to **N**$^{\bullet+}$ (e.g., eq 13) or conversion of **Q**$^{\bullet+}$ to **N**$^{\bullet+}$ (eq 16). In view of the known rate constant of valence isomerization, $k_{vi} \approx 10^{6}$ s^{-1},[15] and given the limited lifetime of the ion pairs, it is unlikely that isomerization of **Q**$^{\bullet+}$ plays a significant role in the conversion of **Azo-N**$^{\bullet+}$ to **N**. Accordingly, the yields of **N** and **Q** reflect the fragmentation pathways available to the two azoalkane radical cations. One species, **Azo-Q**$^{\bullet+}$, cleaves specifically to **N**$^{\bullet+}$, whereas **Azo-N**$^{\bullet+}$ forms **Q**$^{\bullet+}$ and **N**$^{\bullet+}$ in the ratio of ~4:1 via two competing fragmentation pathways.

The product distributions obtained from the two singlet sensitizers **TCA** and **DCA** are strikingly similar despite differences in the energetics of the forward (eq 6) and back electron transfer steps (eq 17; Figure 3). The excitation energies of **TCA**

$$-\Delta G = 23.06[-E_{(\text{D/D+})} + E_{(\text{A-/A})} + 0.06] \tag{17}$$

and **DCA** are essentially identical whereas ^{1}**TCA*** is a noticeably stronger oxidant than ^{1}**DCA***. Accordingly, electron transfer from **Azo-N** and **Azo-Q** to ^{1}**TCA*** is exergonic whereas electron transfer from **Azo-N** and **Azo-Q**, respectively, to ^{1}**DCA*** is either marginally exergonic or slightly endergonic.

The free energy of the BET process is given by the pair energy (eq 17).[41,54] Because of the lower reduction potential of **TCA**, BET in **DCA**$^{\bullet-}$/**Azo-D**$^{\bullet+}$ pairs is ~10 kcal/mol more strongly exergonic than in **TCA**$^{\bullet-}$/**Azo-D**$^{\bullet+}$ pairs. Also, the free energies (kcal/mol) of the **Q**$^{\bullet+}$- and **N**$^{\bullet+}$-containing pairs follow the order **DCA**$^{\bullet-}$/**N**$^{\bullet+}$ (55) > **TCA**$^{\bullet-}$/**N**$^{\bullet+}$ (45) > **DCA**$^{\bullet-}$/**Q**$^{\bullet+}$ (40) > **TCA**$^{\bullet-}$/**Q**$^{\bullet+}$ (30). However, these differences fail to manifest themselves in significantly different product yields for the two sensitizers.

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An alternative mechanism for singlet photosensitized reactions of the azoalkanes involves triplet recombination of geminate radical ion pairs, generating triplet states of the azoalkanes, ^{3}**Azo-N*** or ^{3}**Azo-Q*** (eq 18), or back electron transfer in secondary pairs, populating triplet states of the deazatized hydrocarbons, ^{3}**N*** or ^{3}**Q*** (eq 20), as intermediates on the pathway to **N** and **Q**.

$$^3[\mathbf{sens}^{\bullet-} + \mathbf{Azo\text{-}D}^{\bullet+}] \rightarrow \mathbf{sens} + {}^3\mathbf{Azo\text{-}D}^* \qquad (18)$$

$$^3\mathbf{Azo\text{-}D}^1 \rightarrow \mathbf{N} \text{ and/or } \mathbf{Q} + \mathrm{N}_2 \qquad (19)$$

$$^3[\mathbf{sens}^{\bullet-} + \mathbf{D}^{\bullet+}] \rightarrow \mathbf{sens} + {}^3\mathbf{D}^* \qquad (20)$$

$$^3\mathbf{D}^* \rightarrow \mathbf{N} \text{ and/or } \mathbf{Q} \qquad (21)$$

Three observations have a bearing on this mechanism: (1) deazatization of **Azo-N**$^{\bullet+}$ and **Azo-Q**$^{\bullet+}$, leading to **N**$^{\bullet+}$ and/or **Q**$^+$, is exothermic; (2) BET of triplet radical ion pairs, populating the corresponding azoalkane triplet excited states, is exothermic with **DCA** as the sensitizer and thermoneutral in the case of **TCA** (Figure 3); and (3) the triplet azoalkanes ^{3}**Azo-N*** and ^{3}**Azo-Q*** are known to cleave preferentially to **Q**.[19]

Given these facts, ^{3}**Azo-Q*** can be eliminated in the **DCA** or **TCA** photosensitized decomposition of **Azo-Q** since **Q** is not produced in detectable amounts at low conversion. On the other hand, the high yield of **Q** obtained upon **DCA** and **TCA** photosensitized decomposition of **Azo-N** is formally compatible with the involvement of ^{3}**Azo-N***. However, this mechanism is eliminated because it requires intersystem crossing in the **sens**$^{\bullet-}$/**Azo-N**$^{\bullet+}$ pairs, not very probable in view of their limited lifetimes. In summary, the **DCA** and **TCA** photosensitized decomposition of the azo donors **Azo-N** and **Azo-Q** is best formulated via rapid deazatization of their radical cations.

Electron Transfer to Triplet Sensitizers. Photosensitization with the triplet excited state acceptor ^{3}**Chl*** illustrates the effects of spin multiplicity on the reactivity of radical ion pairs.[53] If generated from a triplet precursor, radical ion pairs must undergo intersystem crossing prior to the BET step. The correspondingly longer lifetimes will allow separation by diffusion to a much greater extent than for radical ion pairs generated from a singlet precursor.[53] The yields of **N** and **Q** observed upon ^{3}**Chl*** sensitization are lower compared to those obtained in the reactions with **DCA** and **TCA**. The shortfall is ascribed to side reactions of the radical cations **N**$^{\bullet+}$ and **Q**$^{\bullet+}$ with **Chl**$^{\bullet-}$, for example, the formation of 1:1 adducts. Adducts between chloranil and donor systems have been observed, for example, in photoreactions of dimethylindene or 1,1-diphenyl-2-methylenecyclopropane.[31,32] Interestingly, the deazatization of **Azo-N** by **Chl** yields a higher ratio of **N**/**Q** than do the **DCA** and **TCA** sensitized reactions (Table 1); this result is attributed to valence isomerization of free ^{2}**Q**$^{\bullet+}$ to ^{2}**N**$^{\bullet+}$ prior to BET. The rearrangement may become competitive because of the increased lifetime of the ion pairs (Scheme 3).

The nuclear spin polarization effects observed during the **Chl** sensitized decomposition of **Azo-N** and **Azo-Q** indicate the formation of polarized **N** and **Q**. In general, these data provide a basis for evaluating the spin density distribution in the paramagnetic intermediate(s) in which the polarization is generated. In the specific case of **Azo-N** and **Azo-Q**, the observed polarization might be induced solely in (deazatized) hydrocarbon radical cations **Q**$^{\bullet+}$ and/or **N**$^{\bullet+}$, or it may reflect the fleeting intermediacy of **Azo-N**$^{\bullet+}$ and/or **Azo-Q**$^{\bullet+}$ and, thereby, possibly hold information about their lifetimes.

Scheme 3[a]

$$^3\mathbf{Chl}^* + \mathbf{Azo\text{-}D} \rightarrow {}^3[\mathbf{Chl}^{\bullet-} + \mathbf{Azo\text{-}D}^{\bullet+}] \qquad (22)$$
$$(\mathbf{D} = \mathbf{N}, \mathbf{Q})$$

$$^3[\mathbf{Chl}^{\bullet-} + \mathbf{Azo\text{-}D}^{\bullet+}] \rightarrow {}^1[\mathbf{Chl}^{\bullet-} + \mathbf{Azo\text{-}D}^{\bullet+}] \qquad (23)$$

$$^{1,3}[\mathbf{Chl}^{\bullet-} + \mathbf{Azo\text{-}D}^{\bullet+}] \rightarrow {}^{1,3}[\mathbf{Chl}^{\bullet-} + \mathbf{D}^{\bullet+}] + \mathrm{N}_2 \qquad (24)$$
$$\mathbf{D} = \mathbf{N}, \mathbf{Q}$$

$$^1[\mathbf{Chl}^{\bullet-} + \mathbf{D}^{\bullet+}] \rightarrow \mathbf{Chl} + \mathbf{D}\uparrow \qquad (25)$$

$$[\mathbf{Chl}^{\bullet-} + \mathbf{N}^{\bullet+}] \rightarrow \mathbf{Chl\text{-}N}\downarrow \qquad (26)$$

$$^{1,3}[\mathbf{Chl}^{\bullet-} + \mathbf{D}^{\bullet+}] \rightarrow {}^2\mathbf{Chl}^{\bullet-} + {}^2\mathbf{D}^{\bullet+} \qquad (27)$$

$$^2\mathbf{Q}^{\bullet+} \rightarrow {}^2\mathbf{N}^{\bullet+} \qquad (28)$$

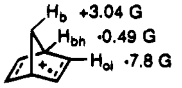
[a] Vertical arrows designate products carrying nuclear spin polarization.

According to the radical pair theory of CIDNP,[55-58] the net polarization patterns (Γ_{net}, emission or absorption) are determined by four parameters (eq 29): the initial spin multiplicity

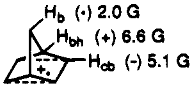
$$\Gamma_{\mathrm{net}} = \mu \epsilon \Delta g a \qquad (29)$$

of the radical (or radical ion) pair (μ), the mode of product formation (ϵ), the relative magnitude of the g factors of the individual radicals (Δg), and the signs of the hyperfine couplings (hfc) for the nuclei whose polarization is observed (a).

With **Chl** as the sensitizer, several of the polarization-determining parameters can be assigned unambiguously: the radical ion pairs are generated from a triplet precursor ($\mu > 0$); the g factors of the hydrocarbon radical cations **N**$^{\bullet+}$ ($g \approx 2.0026$)[59] and **Q**$^{\bullet+}$ ($g \approx 2.0035$)[15] are significantly lower than the g factor of **Chl**$^{\bullet-}$ ($g = 2.0057$;[59] $\Delta g < 0$); in addition, the signs and magnitudes of the individual hfcs for **N**$^{\bullet+}$ and **Q**$^{\bullet+}$ are known.[14,15,60,61] Accordingly, the observed signal directions will identify the mode of product formation (ϵ), and the polarization patterns will reveal any significant involvement of either **Azo-N**$^{\bullet+}$ or **Azo-Q**$^{\bullet+}$.



N$^{+\bullet}$



Q$^{+\bullet}$

In the CIDNP spectrum of the **Chl** photosensitized oxidation of **Azo-Q** (Figure 1), the olefinic protons (H$_{ol}$) of polarized **N** show absorption ($\Gamma_{\mathrm{net}} > 0$). Since their hfc in the radical cation is negative (-7.8 G),[14,61] this result indicates that **N** is generated by recombination of singlet radical ion pairs ($\epsilon > 0$). The remaining protons of **N** exhibit net polarization consistent with this assignment: H$_{bh}$ has a negative hfc (-0.5 G) and is (very weakly) absorptive ($\Gamma_{\mathrm{net}} > 0$); H$_b$ has a positive hfc ($+3.0$ G)

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and is emissive ($\Gamma_{net} < 0$). This polarization pattern is virtually identical to the pattern observed during the reaction of **Chl** with **N**.[10,11] Thus, any significant contribution of **Azo-Q**$^{\bullet+}$ to the observed polarization can be ruled out; **Azo-Q**$^{\bullet+}$ must have a shorter lifetime than is required for the induction of nuclear spin polarization.

The **Chl** photosensitized oxidation of **Azo-N** generates a CIDNP spectrum with polarized **N** and **Q** resonances (Figure 2). The polarization pattern for **N** is similar to that obtained with either **Azo-Q** or **N** as the starting material, suggesting that the polarization is generated in **Chl**$^{\bullet-}$$-$**N**$^{\bullet+}$ radical ion pairs and that polarized **N** is generated by recombination of singlet pairs ($\epsilon > 0$). Similarly, the polarization of **Q** is compatible with the intermediacy of **Chl**$^{\bullet-}$$-$**Q**$^{\bullet+}$ radical ion pairs; the signal directions suggest that polarized **Q** also is generated by recombination of singlet pairs ($\epsilon > 0$). Apparently, the two radical cations are generated and depleted by similar mechanisms.

Neither the polarization pattern of **N** nor that of **Q**, show any contribution of **Azo-N**$^{\bullet+}$. However, this species is a necessary intermediate. The observed polarization requires two different species, **N**$^{\bullet+}$ and **Q**$^{\bullet+}$, with different hyperfine coupling patterns. This unique result is explained by two competing retro-cycloadditions of **Azo-N**$^{\bullet+}$, both formally of the [3+2] type, giving rise to the three-electron radical cations **N**$^{\bullet+}$ and **Q**$^{\bullet+}$, respectively. In contrast to the pronounced escape polarization induced during the electron transfer reaction of **Q**,[10,11] the reaction of **Azo-N** fails to show any such polarization. This failure is ascribed to the very low concentration of **Q** in the early phase of the reaction. Although **Q**$^{\bullet+}$ rearranges to **N**$^{\bullet+}$ (vide supra), any escape polarization must be fully relaxed before this radical cation is reduced to **N**.

The potential recombination of triplet radical ion pairs has been considered in these reactions as well. Such a mechanism has been documented in the electron transfer photosensitized isomerization of **N** to **Q**[10,11] in radical ion pairs whose free energy exceeds the triplet energy of **N** ($E_T \approx 70$ kcal/mol).[62] However, the pair energies of **Chl**$^{\bullet-}$/**N**$^{\bullet+}$ (~35 kcal/mol) and **Chl**$^{\bullet-}$/**Q**$^{\bullet+}$ (~42 kcal/mol) lie well below the triplet energies of **N** and **Q**, rendering triplet recombination energetically unfavorable. Geminate radical ion pairs which do not undergo BET may undergo one of two alternative reactions: (1) they may diffuse apart and lose their polarization by spin–lattice relaxation, or (2) they may undergo slow coupling reactions, generating a weakly polarized oxetane. The formation of chloranil adducts in general[31,32] and a benzoquinone adduct to norbornadiene has precedence.[63] The lack of polarization for **Azo-N** and **Azo-Q** is attributed to fast fragmentation of the azoalkane radical cations relative to intersystem crossing and BET.

The observed CIDNP spectra are compatible with a mechanism involving electron transfer quenching of ^{3}**Chl*** by the azoalkanes (eq 22), followed by deazatization to **N**$^{\bullet+}$ and/or **Q**$^{\bullet+}$ (eq 24), and BET (eq 25) after intersystem crossing (Scheme 3). The formation of polarized **N** and **Q** as cage products from photosensitized oxidation of **Azo-N** indicates that **Azo-N**$^{\bullet+}$ undergoes two competitive formal retro-[3+2]-cycloaddition reactions, yielding **Q**$^{\bullet+}$ and **N**$^{\bullet+}$, respectively. On the other hand, the oxidation of **Azo-Q** affords polarized **N** exclusively, implying that the deazatization of **Azo-Q**$^{\bullet+}$ occurs via a single pathway, formally a retro-[3+2]-cycloaddition affording **N**$^{\bullet+}$. So far, our results do not allow us to determine whether the deazatization is concerted, or proceeds via short-lived diazenyl radical cations.[23,26] This problem is being pursued as are approaches to several alternative azo derivatives of **N** or **Q**.

Energy Transfer to Excited Singlet Sensitizers. Two of the sensitizers employed, **CN**[33] and **Nap**, are relatively weak excited state oxidants. Their excited-state reduction potentials, $^*E_{(A^-/A)} = 1.9$ V for **CN**, $^*E_{(A^-/A)} = 1.5$ V for **Nap**, are significantly lower than those of **TCA** and **DCA**. Electron transfer to these sensitizers is substantially endergonic. Nevertheless, the fluorescence emission of **CN** in acetonitrile is quenched by **Azo-N** and **Azo-Q** at the diffusion-controlled limit. Indeed, the singlet energies of these sensitizers, $E_{0,0} = 89$ kcal/mol[33] for **CN**, $E_{0,0} = 92$ kcal/mol for **Nap**, lie well above those of both ^{1}**Azo-N*** ($E_{0,0} = 80$ kcal/mol) and ^{1}**Azo-Q*** ($E_{0,0} = 84$ kcal/mol). Accordingly, singlet energy transfer to these sensitizers, generating the azo donor excited states (eq 30), is highly probable. The resulting excited states are known to fluoresce (eq 31) as well as suffer deazatization (eq 32).[19]

$$^1\mathbf{A}^* + \mathbf{Azo\text{-}D} \rightarrow \mathbf{A} + {}^1\mathbf{Azo\text{-}D}^* \qquad (30)$$

$$^1\mathbf{Azo\text{-}D}^* \rightarrow \mathbf{Azo\text{-}D} + h\nu \qquad (31)$$

$$^1\mathbf{Azo\text{-}D}^* \rightarrow \mathbf{N} \text{ and/or } \mathbf{Q} + \mathrm{N_2} \qquad (32)$$

Indeed, the yields of **N** and **Q** obtained upon **CN** and **Nap** sensitized irradiations of **Azo-N** and **Azo-Q** are very similar to those obtained upon direct irradiation.[19] The suggested involvement of energy transfer is further supported by the observation of **Azo-N** and **Azo-Q** fluorescence in the quenching experiments.

Summary and Conclusions

The photoinduced oxidation of **Azo-Q** and **Azo-N** results in rapid and efficient deazatization, producing mixtures of **N** and **Q**. The reactions with singlet electron transfer sensitizers (**DCA** and **TCA**) are clean. On the other hand, the reaction with the triplet photosensitizer **Chl** produces lower yields of **N** and **Q** due to side reactions of the radical ions. CIDNP experiments with **Chl** provide indirect evidence for the fleeting intermediacy of **Azo-Q**$^{\bullet+}$ and **Azo-N**$^{\bullet+}$ and for their subsequent rapid deazatization. The azoalkane species undergo different fragmentation reactions: **Azo-Q**$^{\bullet+}$ exclusively affords **N**$^{\bullet+}$ whereas **Azo-N**$^{\bullet+}$ yields both **N**$^{\bullet+}$ and **Q**$^{\bullet+}$; accordingly, both **N** and **Q** are formed as cage products.

The rate constants for the quenching of **TCA** and **DCA** fluorescence by **Azo-Q** and **Azo-N** correlate roughly with the calculated free energies for electron transfer. Similarly, LFP experiments revealed rapid reaction of the azoalkanes with ^{3}**Chl*** and subsequent production of **Chl**$^{\bullet-}$. These experiments provide an example of photoinduced electron transfer from azoalkanes as an alternate route to similar products although in chemical yields different from those typically obtained via more direct thermal or photochemical methods. Further studies of the photoinduced electron transfer chemistry of azoalkanes are in progress.

Experimental Section

Materials and Solvents. Norbornadiene was passed through activated alumina prior to use; quadricyclane (Aldrich) was used as received. 3,4-Diazatricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**Azo-N**)[64] and 3,4-diazaquadricyclo[6.1.0.0^{2,6}.0^{5,9}]non-3-ene (**Azo-Q**)[65,66] were synthesized

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following a slight modification of the published procedures; they exhibited spectral properties and melting points in agreement with the literature values. 9,10-Dicyanoanthracene (Eastman Kodak) and naphthalene (Aldrich scintillation grade) were used as received, chloranil (Aldrich) was recrystallized from chloroform/acetonitrile, 1-cyanonaphthalene (Aldrich) was recrystallized twice from ethanol, and 2,6,9,-10-tetracyanoanthracene was prepared from 2,6,9,10-tetrabromoanthracene and cuprous cyanide according to the published procedure.[67] Acetonitrile (Aldrich spectrophotometric grade) was distilled from calcium hydride immediately before use. Acetonitrile-d_3 (Aldrich, 99% D) was used as received.

Product Analysis and Characterization. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3392A integrator, and an HP-1 capillary column (25 m × 0.2 mm; Hewlett-Packard, Inc.). The GC injector port temperature was maintained at or below 175 °C to avoid thermal decomposition of the azoalkanes. GC/MS analyses were carried out using a Hewlett-Packard 5988A GC/MS system and a Hewlett-Packard 5890 gas chromatograph equipped with an HP-1 capillary column and interfaced to a Hewlett-Packard 9133 data station.

Ultraviolet absorption spectra were recorded on a Hewlett-Packard HP8452A UV spectrometer. Fluorescence emission spectra were recorded on a SPEX 1680 0.22 m double spectrometer.

CIDNP Experiments. CIDNP experiments were carried out by irradiation of the sample in the probe (equipped with a light pipe) of a Bruker AF 250 (250 MHz) NMR spectrometer. The collimated beam of a Hanovia 1000 W high-pressure Hg−Xe lamp was passed through water and the appropriate combination of filter solutions and cutoff filters: **Chl**, **DCA** sensitization (aqueous $CuSO_4$ solution and $\lambda > 370$ nm cutoff filter); direct photolysis (aqueous $CuSO_4$ solution); **CN** and benzophenone sensitization (aqueous K_2CrO_4/K_2CO_3 solution, $\lambda_{max} \approx 313$ nm).

Steady-State Photolyses. For the **DCA**, **TCA**, and **Chl** sensitized steady-state photolysis experiments a 150 W Xe lamp was used with a cutoff filter ($\lambda > 370$ nm) to avoid irradiation of the azoalkanes. The **Nap** and **CN** sensitized experiments were carried out in a Rayonet photochemical reactor equipped with four RPR-300 (300 nm) lamps. Solutions containing 0.02 M substrate, 0.001−0.02 M sensitizer, and 0.003 M *m*-tolunitrile (internal GC standard) in acetonitrile in 1 × 1 cm quartz cells were deoxygenated prior to photolysis with a stream of dry argon for 15 min and sealed with rubber septa. The progress of the reaction was monitored by GC. Products were identified by GC/MS and by co-injection.

Stern−Volmer Fluorescence Quenching Experiments. Sensitizer solutions were prepared at concentrations (10^{-4}−10^{-5} M) such that the optical density was ≤0.05 at the excitation wavelength. The relative intensities of sensitizer fluorescence emission were recorded at 6−10 different quencher concentrations. The following excitation and emission wavelengths (λ_{ex}, λ_{em}) were employed: **DCA** (420, 460 nm), **TCA** (404, 438 nm), **CN** (300, 326 nm), **Nap** (276, 334). The sensitizer solutions were measured in 1 × 1 cm quartz cells and deoxygenated as described above. Quenchers were added to the sensitizer solutions via a microliter syringe as stock solutions in acetonitrile.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments employed the pulses (308 nm, ca. 80 mJ/pulse, 20 ns) from a Lambda-Physik Lextra excimer laser and a computer-controlled system which has been described elsewhere.[68] Solutions of **Chl** were prepared at concentrations (0.003−0.005 M) such that the absorbance at the excitation wavelength (308 nm) was ca. 0.3−0.5. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) and a flow system to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured using argon-saturated static samples contained in 1 × 1 cm Suprasil quartz cells. Fresh samples were prepared at each quencher concentration.

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Supporting Information Available: Stern−Volmer plots for fluorescence quenching by **Azo-N**, **Azo-Q**, **N**, and **Q** and table giving thermodynamic parameters pertinent to the electron transfer photochemistry of **Azo-Q** and **Azo-N** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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