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Fluorescence Quenching of n,π*-Excited Azoalkanes by Amines: What Is a Sterically Hindered Amine?

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Abstract: The fluorescence quenching of two azoalkanes, the weak acceptor 2,3-diazabicyclo[2.2.2]oct-2-ene and its less reactive derivative 4-methyl-1-isopropyl-2,3-diazabicyclo[2.2.2]oct-2-ene, by a series of aliphatic amine donors was examined by time-resolved spectroscopy in benzene. The fluorescence quenching rate constants ranged from 0.13×10^7 to 25×10^7 M^{-1} s^{-1}, while the activation energies were found to be 1.3 and 3.0 kcal mol^{-1} for the best (*N*-ethyldicyclohexylamine) and the poorest (*N,N*-diisopropyl-3-pentylamine) donor. The oxidation potentials of the amines and the reduction potentials of the azoalkanes were measured. Deviations from the expected dependence of the quenching rate constants on the energetics of electron transfer were observed. Steric effects on the kinetics of quenching, namely a reduction by up to a factor of 50, became significant for amines with three secondary alkyl substituents, triisopropylamine, and *N,N*-diisopropyl-3-pentylamine, while a stereoelectronic effect was found for 1,4-diazabicyclo[2.2.2]octane (reduction by a factor of 2). The experimental data are interpreted within a general kinetic scheme, which involves both exciplex formation and electron transfer, by assuming a steady-state kinetics for quenching. The steric effects are attributed to the hindrance toward exciplex formation, based on the experimental results and semiempirical calculations (PM3). Factors governing steric hindrance by amines, differences between ketone and azoalkane acceptors, and the persistence of the corresponding amine radical cations are discussed.

Introduction

Since the pioneering work of Rehm and Weller[1] and Marcus,[2] the energetic aspects of the kinetics of charge-transfer (CT) induced photoreactions have received much attention. Steric hindrance has also moved into the focal point[3−5] to allow a more comprehensive understanding of the factors governing CT processes. Significant steric effects on the kinetics of CT-induced quenching of ketones and quinones were observed for aromatic donors as quenchers.[3,5] It has been suggested, based on the comparison with structural data for the electron-donor−acceptor ground-state complexes of these donors,[6] that steric effects on the kinetics are manifested in the hindrance toward formation of intermediate π-type sandwich exciplexes with aromatic quenchers. In earlier studies the steric demand of fluorescent acceptors was varied.[7−9]

In the present study, aliphatic amines were examined as sterically congested donors in CT-induced quenching. The donor properties of amines are of considerable practical interest for photoreduction of ketones,[10−13] azoalkanes,[14−16] and dyes,[17] as well as in polymer technology, where amines serve both as photoinitiators and light stabilizers.[18,19] In addition, fluorescence quenching by amines has been the subject of numerous mechanistic investigations.[1,7,9,20−24] Obviously, aliphatic amines donate electrons through their lone pair orbital and are expected

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to interact with excited states in a different manner than aromatic donors. The absence of steric effects on quenching of benzophenone by amines was previously attributed to diffusion-controlled quenching,[25] which could mask subtle steric effects. Hence, the use of an alternative n,π^* chromophore with significantly weaker acceptor properties became first choice to gain further insight into steric control of amine quenching.

Ia   **Ib**
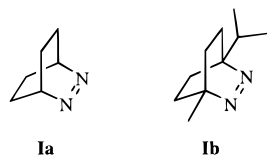
Toward this end, we have examined the fluorescence quenching of 2,3-diazabicyclo[2.2.2]oct-2-ene (**Ia**) and its bridgehead-alkylated derivative **Ib**. Both azoalkanes have long-lived singlet-excited states (up to 1 μs) with pure n,π^*-character.[26] More importantly, azoalkanes **I** are prototypes for "weak" acceptors due to their low reduction potential (ca. -2.8 V), **Ib** being the least reactive one. This causes an endergonic thermodynamics for electron transfer, which favors quenching through the formation of exciplexes with partial CT character.[27,28] Since exciplex formation should be particularly sensitive toward steric effects,[3,5,8] significant differences were expected and observed for the following amines: *N*-ethyldicyclohexylamine (**1**), triisopropylamine (**2**), *N,N*-diisopropyl-3-pentylamine (**3**), tri-*n*-propylamine (**4**), *N*-ethyldiisopropylamine (**5**), *N,N*-diisopropylisobutylamine (**6**), 1,2,2,6,6-pentamethylpiperidine (**7**), and 1,4-diazabicyclo[2.2.2]octane (**8**).

1   **2**   **3**   **4**

5   **6**   **7**   **8**
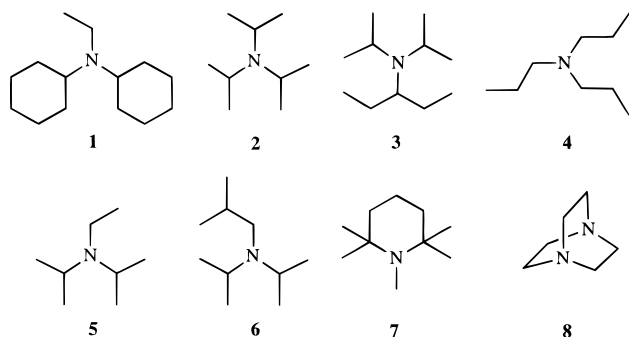
Experimental Section

Materials. The azoalkanes **I** were synthesized according to known procedures.[29,30] The amines were either commercially (Fluka) or synthetically (only amine **2**[31]) accessible. Benzene and absolute *N,N*-dimethylformamide (DMF) over molecular sieve (3 Å) were UV-spectroscopic grade (Merck, Uvasol quality). Acetonitrile (Scharlau, Multisolvent grade) was dried over molecular sieve (3 Å) before use. Electrolyte salts were used as received (Fluka). Measurements were performed at ambient temperature (24 °C).

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Table 1. Photophysical and Electrochemical Data for Azoalkanes **I** and Benzophenone

	Ia	**Ib**	benzophenone
$E_{\mathrm{p}}^{\mathrm{Red}}$/V	-2.8^a	-2.8^a	-1.83^b
E^*/eV	3.3^c	3.2^c	3^b
ΔG_{et} (**2**)/eV^d	$>0.12^e$	$>0.22^e$	-0.55

^{a} Irreversible reduction potential vs. SCE in acetonitrile, measured with a HMDE electrode, cf. ref 27. ^{b} Half-wave reduction potential and triplet energy from ref 36. ^{c} Singlet excitation energy estimated from the absorption maximum in benzene, i.e., 379 nm for **Ia** and 385 nm for **Ib**. ^{d} Estimated for amine **2** from eq 1, $C = -0.06$ eV in acetonitrile. ^{e} Lower limits due to the use of the (irreversible) peak potentials.

Time-Resolved Experiments. Samples were prepared by dissolving the azoalkanes (ca. 0.1–1 mM) in benzene and administering the appropriate amounts of amines with a GC syringe. The samples were degassed by 3 freeze–pump–thaw cycles. Homemade quartz cells (4 × 1 × 1 cm) with high-vacuum Teflon stopcocks were used for degassing. Thermostated versions of these cells were employed for temperature-dependent experiments and in these cases the degassed solutions were flushed with dry, oxygen-free nitrogen to avoid boiling of the solvent at elevated temperatures.

A XeF excimer laser pulse from a COMPex 205 laser (351 nm, fwhm ca. 20 ns, pulse energy 70–90 mJ) was used for excitation. The time-resolved fluorescence decays were monitored with a monochromator–photomultiplier setup at 430–530 nm. The kinetic traces were registered by means of a transient digitizer and analyzed by nonlinear least-squares fitting of monoexponential functions. For the kinetic quenching plots usually four different amine concentrations were chosen. Temperature effects on the kinetics of quenching were studied in benzene with ±0.2 °C temperature control.

Cyclovoltammetric Measurements. The reduction potentials for azoalkanes **I** were measured in dry acetonitrile (absolute DMF gave consistent results) by using a hanging mercury drop electrode (HMDE) setup[32] with tetrabutylammonium perchlorate (0.1 M) as electrolyte. The oxidation potentials of the amines were measured in dry acetonitrile with tetrabutylammonium hexafluorophosphate or tetrabutylammonium perchlorate (0.1 M) as supporting electrolytes. The two electrolytes gave consistent results. The experimental setup consisted of a platinum working electrode, a graphite counter electrode, and a silver reference electrode. Irreversible peak potentials were measured at different scan rates (0.02–1 V s^{-1}) and extrapolated to zero scan rate as recommended by Heinze.[32] All values are reported relative to ferrocene as internal standard ($E_{1/2}^{\mathrm{Ox}}$ vs. SCE = 0.380 V in acetonitrile and 0.455 V in DMF).[33] All samples were deaerated by bubbling with nitrogen for ca. 5 min.

Computational Studies. The semiempirical PM3 method[34] included in the Hyperchem program package[35] was employed to assess the energetics of exciplex formation. The PM3 geometries were optimized for the ground states of amines **1**–**8** as well as azoalkane **Ia** and for the triplet state of the exciplexes.[27] The geometries corresponding to the exciplexes are dissociative on the singlet ground-state surface. The energies of singlet-excited **Ia**, the amines, and the corresponding singlet exciplexes were then obtained by single-point CI-PM3 calculations, including the lone pairs and closest π and π^* as active orbitals.

Results

Acceptor Properties of the Azoalkanes. The photophysical properties and the (irreversible) reduction potentials of azoalkanes **I** are given in Table 1.[27] The data for n,π^* triplet-excited benzophenone are shown for comparison. The driving force (ΔG_{et}) for photoinduced electron transfer can be estimated according to Rehm and Weller[1]

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$$\Delta G_{et} = E^{Ox}(D) - E^{Red}(A) - E^* + C \qquad (1)$$

with the oxidation potential of the donor $E^{Ox}(D)$, the reduction potential of the acceptor $E^{Red}(A)$, and the excitation energy of the acceptor E^*. C is the Coulomb term which describes the electrostatic attraction within the contact ion pair and has a value of ca. -0.06 eV in acetonitrile. The driving force was calculated for amine **2** as a representative donor ($E_{1/2}^{Ox} = 0.68$ V, Table 2) to reveal the endergonic thermodynamics for the acceptors **I**, cf. ΔG_{et} values in Table 1. In contrast, electron transfer to benzophenone as acceptor is strongly exergonic.

The acceptor **Ib** possesses a lower singlet excitation energy (Table 1) than **Ia**, which reduces the driving force for CT. The irreversibility of the azoalkane reductions tends to result in peak potentials which are less negative than the "true" (reversible) peak potentials.[32] Hence, the driving force for electron transfer with amines in Table 1 should be considered as a *lower* limit. Moreover, the difference in driving force between the acceptors **Ia** and **Ib** is probably a conservative estimate. A more negative reduction potential is expected for **Ib** due to the electron-donating bridgehead alkyl groups,[36] which should tend to destabilize the resulting azo radical anion. The fact that this intuitive presupposition is not manifested in the experimental peak potentials (Table 1) is presumably related to the irreversibility of azo reduction.

The electrochemical and thermodynamic considerations, along with the measured rate constants for quenching by amines, lead us to qualify these azoalkanes as *weak* acceptors. **Ib** is somewhat weaker than **Ia**.

Donor Properties of the Amines. Gas-phase ionization potentials provide a measure for the donor strength of amines **1**−**8**. Subject to a typical uncertainty of ± 0.1 eV[24] in the adiabatic ionization potential, the examined amines can be divided in two groups (Table 2): one with an adiabatic ionization potential (IP$_a$) around 6.9 eV and the other ca. 7.2 eV.[37] The vertical ionization potentials[25,38] follow a very similar trend.

Oxidation potentials in solution (E^{Ox}), which are required in eq 1, should correlate well with the gas-phase IP values, although the slopes of such plots may fall below unity,[39−42] i.e., variations in E^{Ox} are less pronounced than for IP.[43] Cyclovoltammetric measurements for amines **1**−**8** (Table 2) revealed reversible oxidation behavior only for amines **2**, **3**, and **8**. The half-wave oxidation potentials ($E_{1/2}^{Ox}$) of amine **2** (0.68 V) and amine **8** (0.66 V) compare favorably with previous measurements of 0.71 V[31] and 0.70 V.[41] The irreversible oxidation for the other amines renders the measured peak potentials strongly dependent on the rates of the follow-up

Table 2. Rate Constants (k_q) for Fluorescence Quenching of Azoalkanes by Amines in Benzene

amine	E_p^{Ox}/V^a	IP$_a$/eV^b	$k_q/(10^7\ M^{-1}\ s^{-1})^c$ Ia	Ib	$\Delta E_{Ex}/(\text{kcal mol}^{-1})^d$
1	0.61	6.85^e	25	6.6	1.1
2	0.71^f	6.95^e	1.1	0.23	9.0
3	0.72^f	6.85^e	0.76	0.13	6.3
4	0.71	7.18^g	8.5	1.8	3.2
5	0.68	7.20^e	13	3.1	5.1
6	0.71	7.09^h	14	2.5	2.2
7	0.73	7.23^i	8.9	2.1	0.3
8	0.69^f	7.20^j	4.2	0.68	−1.1

^{a} Values vs. SCE in acetonitrile; irreversible peak potentials unless stated. ^{b} Adiabatic values are provided. ^{c} Obtained from time-resolved fluorescence measurements at 24 °C, 4−5 data points, 5−10% error. ^{d} Relative exciplex energies calculated with the CI-PM3 method for singlet-excited **Ia**; not corrected for zero-point energy and thermal translational, vibrational, and rotational enthalpic contributions. ^{e} Reference 25. ^{f} Oxidation is reversible, $E_{1/2}^{Ox} = 0.68$ V for **2**, 0.69 V for **3**, and 0.66 V for **8**. ^{g} Reference 87. ^{h} This work, from photoelectron spectroscopy as described in ref 24. ^{i} Reference 38. ^{j} Reference 41.

reactions of the amine radical cations;[32,44] the latter are unknown. Hence, a direct comparison with the ionization potentials and a quantitative use in eq 1 is not reliable. However, the deviations between the experimental oxidation potentials of amines **1**−**8** and those "expected" from the ionization potentials, i.e., **1**−**3** < **4**−**8**, are well accounted for. In particular, the higher E^{Ox} values for **2** and **3** compared to **1** are unquestionably related to the reversibility for oxidation of **2** and **3**, which tends to result in higher peak potentials than for irreversible oxidations.[32]

Bimolecular Quenching Rate Constants. Photoexcitation of azoalkanes **I** in benzene at 351 nm results in the formation of the singlet-excited n,π* states, which are strongly fluorescent. The fluorescence lifetimes of **Ia** and **Ib** in the absence of quencher (τ_0) are solvent dependent.[14,45−47] Values of 490 and 790 ns, respectively, are characteristic for benzene, which was preferred in the present study due to the insufficient solubility of some amines in acetonitrile, e.g., **3**.

$$\tau_0/\tau = 1 + \tau_0 k_q[\text{amine}] \qquad (2)$$

The fluorescence lifetime (τ) is shortened by the successive addition of the amines (Figure 1). Kinetic plots according to eq 2 were accurately linear in all cases (inset of Figure 1) and afforded the quenching rate constants in Table 2, which refer to benzene as solvent. The values in acetonitrile as solvent display a similar trend as in benzene, but they are somewhat lower (e.g., 1.9 versus $2.5 \times 10^8\ M^{-1}\ s^{-1}$ for amine **1** and 1.0 versus $1.1 \times 10^7\ M^{-1}\ s^{-1}$ for amine **2**, both for **Ia**). This is a consequence of the recently discussed "inverted" solvent effect.[27] Saturation effects, i.e., downward curvature in the kinetic plots,[3,48] were not observed at high amine concentrations (up to 0.3 M). The quenching rate constants of the different azoalkane/amine combinations display significant variation, which can be interpreted in terms of thermochemical and steric effects (cf. Discussion).

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(43) The slope for this correlation was found to be 0.83 for aliphatic amines (ref 41), indicating that a difference of 1 eV in the ionization potential corresponds to an effect of only 0.83 V in the oxidation potential.
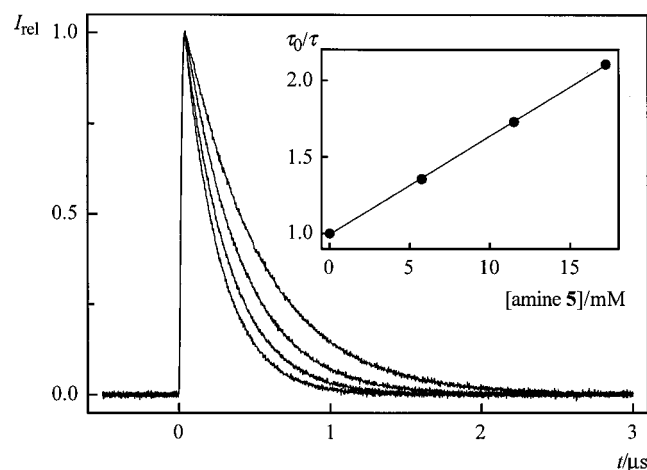
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Figure 1. Fluorescence decay kinetics for **Ia** (ca. 0.1 mM) in degassed benzene in the absence (upper traces) and presence (lower traces) of different concentrations of amine **5** (5.7, 11.5, and 17.2 mM). Shown in the inset is the corresponding kinetic plot according to eq 2.
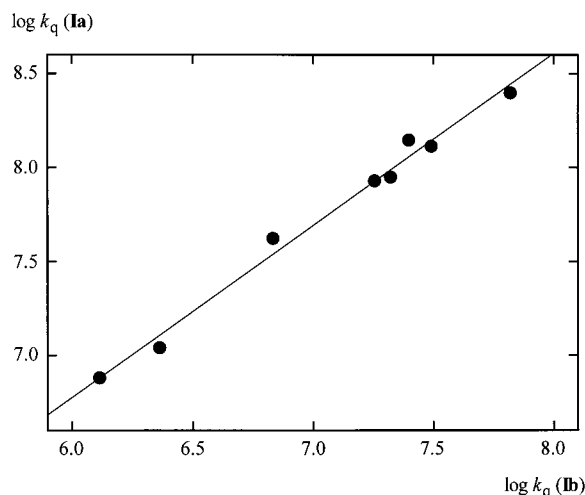

Figure 2. Gettler correlation of the logarithmic rate constants for the quenching of azoalkanes **I** by amines **1**−**8**.

Temperature Dependence of Quenching. The temperature dependence of the bimolecular quenching rate constants was representatively evaluated for the best (amine **1**) and the poorest (amine **3**) quenchers of azoalkane **Ia** fluorescence. For this purpose, the fluorescence lifetimes of **Ia** (τ) were measured in benzene between 10 and 50 °C in 5 deg C intervals. The amine concentrations were chosen sufficiently high to produce significant (ca. 30−40%) quenching, while maintaining relatively long fluorescence lifetimes (>200 ns) at all temperatures. The latter was essential to allow accurate deconvolution from the laser pulse (ca. 20 ns). The fluorescence lifetimes of **Ia** in the absence of quenchers (τ_0) were independently obtained for the same temperatures; they followed accurately the previously established temperature dependence.[49] The corresponding quenching rate constants (k_q) were obtained according to eq 2 by using the experimental τ and τ_0 values measured for each temperature. The resulting Arrhenius plots [$\ln(k_q)$ versus T^{-1}] were linear over the examined temperature range ($r > 0.99$, $n = 9$, Figure 3). They provided a preexponential factor [$\log A/(M^{-1}\ s^{-1})$] of 9.4 ± 0.1 and an activation energy (E_A) of 1.3 ± 0.1 kcal mol^{-1} for amine **1**. A slightly lower $\log A$ factor of 9.0 ± 0.1 and a
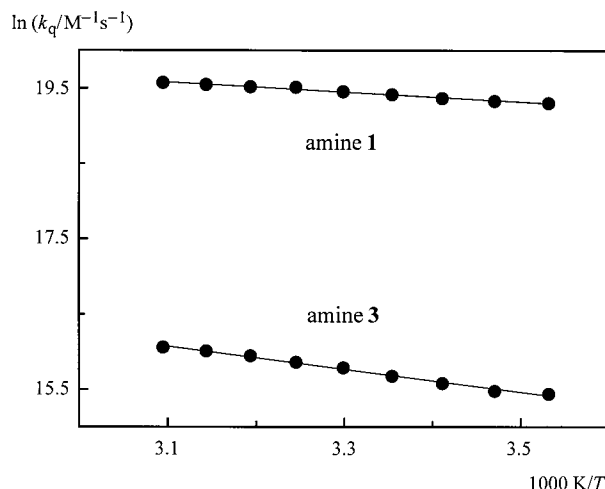

Figure 3. Arrhenius plots of the bimolecular rate constants for fluorescence quenching of azoalkane **Ia** by amines **1** and **3**.

significantly higher E_A of 3.0 ± 0.2 kcal mol^{-1} were obtained for amine **3**.

Computational Studies. UHF-PM3 calculations[34] have recently been found to produce reasonable geometries for the triplet exciplexes.[27] For the present study of steric effects, it was important to reassure the performance of the PM3 method to reproduce structural properties. The calculated geometries of ground-state **Ia**,[50,51] triisopropylamine (**2**),[31,52−54] *N,N*-diisopropyl-3-pentylamine (**3**),[53] and 1,4-diazabicyclo[2.2.2]octane (**8**)[55] were in good agreement with experimental data. Most importantly, the conformational orientation of the alkyl groups in the sterically demanding amines and their nearly-planar arrangement was reproduced (calculated sum of C−N−C angles for **2** is 349°, exptl[31,52] 350−358°). The propensity of the PM3 method to somewhat overestimate the degree of pyramidalization of the amino substituents is known.[52]

CT interaction entails molecular orbital overlap between the donor-HOMO and the acceptor-LUMO or, in the case of an excited acceptor, its lowest SOMO. In the case of n,π*-excited azoalkanes and amines, CT interaction should take place between the lone pair of the amine and the electron-deficient, singly occupied lone pair orbital (n$_-$ combination),[56] as confirmed by the calculated geometries, e.g., the triplet exciplex between azoalkane **Ia** and triisopropylamine **2** (Figure 4).

The nuclear charges revealed only partial, but significant CT from the amine to the azoalkane (ca. 40%), which is reflected in the relatively small calculated exciplex dipole moments (ca. 4 D).[27] A plot of $\log k_q$ versus IP$_a$ has been recommended to obtain experimental information on the degree of CT character in the quenching of excited states.[57−59] The use of the data for

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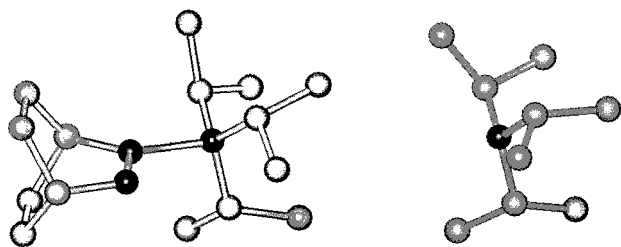
Figure 4. Calculated geometry (UHF−PM3 method) of the triplet exciplex between azoalkane **Ia** and triisopropylamine **2** (left) and the minimum geometry of uncomplexed triisopropylamine **2** (right) for comparison. Hydrogen atoms are not shown for clarity.

amines **1**−**8**, excluding the sterically hindered derivatives **2** and **3**, as well as the quenching rate constants for 9 additional tertiary amines,[60] provided a linear correlation ($n = 15$, $r = 0.917$) with a slope of -1.56 eV^{-1} for azoalkane **Ia**. This slope falls far below the value expected for full electron transfer (-17 eV^{-1}).[1] This confirms partial CT in the exciplex, which has been previously established for other systems.[36,59,61−64]
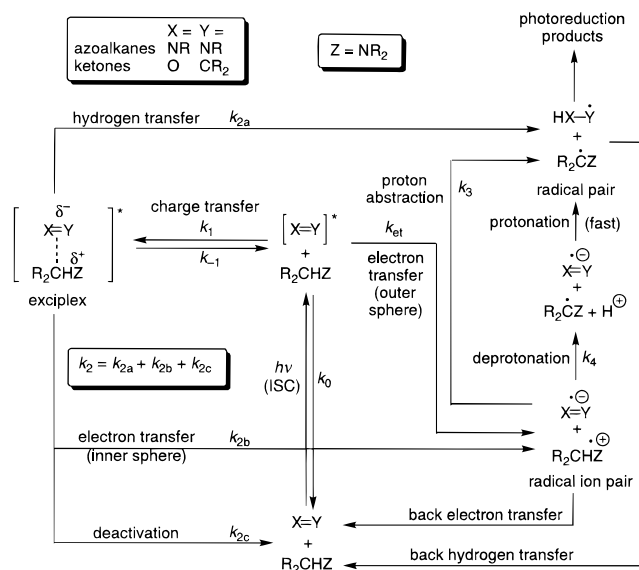
Interestingly, the steric crowding and destabilization in the exciplexes of amines **2** and **3** manifests itself less in a lengthening of the CT bond (e.g., 1.88 Å for **2** versus 1.87 Å for **4**) or a reduced amount of CT (all ca. 40%) but rather in a conformational reorganization of the alkyl chains, i.e., the conformation of the amine in the exciplexes differs significantly from the ground state conformation of the amines as shown for amine **2** in Figure 4. For example, the sum of C−N−C angles in the amine decreases by ca. 7° in the exciplex, corresponding to an increased pyramidalization.

The energetics for exciplex formation (ΔE_{Ex}) between singlet-excited **Ia** and the amines **1**−**8** (single point CI−PM3 calculations) was found to be mostly endothermic and varied from -1.1 to $+9.0$ kcal mol^{-1} (Table 2). Obviously, some of the calculated values are too high in view of the measured activation energies for quenching and the relatively high quenching rate constants (see above). There is also a significant scatter in the calculated energetics (Table 2), which may be related to the simplicity of the semiempirical method. Nevertheless, the exciplex energies for amines **2** and **3** clearly stand out from the remaining data by ca. 3−6 kcal mol^{-1}. It is this calculated discrepancy that is considered significant.

Discussion

The quenching of n,π*-excited ketones[10−12] and azoalkanes[16,27] by amines, which usually leads to the formation of photoreduction products, is a representative case of a CT-induced photoreaction. This photoreaction involves either electron transfer or exciplex formation in the primary step (Scheme 1).[65]

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(65) A direct hydrogen abstraction pathway can also be included in Scheme 1, cf. ref 13, although for good donors such as amines the CT pathways are presumed to be the most important ones (ref 10−16). This conclusion can be drawn from the examination of quenchers with poor electron donor properties and similar C−H bond strengths. Their rate constants fall far short of the values measured for amines, indicating that direct hydrogen abstraction, which should be primarily dependent on the C−H bond strength, does not compete for amines (see, for example, refs 14−16).

Scheme 1

Energetics of Electron Transfer. Rate constants for CT-induced photoreactions, regardless of whether free ions (k_{et}) or exciplexes (k_1) are formed as primary intermediates, should be strongly dependent on the driving force for electron transfer (ΔG_{et}).[1,28,61] For example, Marcus' cross rate theory predicts k_{et} to be proportional to the square root of the equilibrium constant for electron transfer.[2,66−68] The electrochemical data imply endergonic ΔG_{et} values for the excited azoalkanes and all amines (ΔG_{et} values from eq 1 in Table 1). The absolute quenching rate constants, which fall 2−3 orders of magnitude below the diffusion-controlled limit (ca. 10^{10} M^{-1} s^{-1} in benzene), and the failure to observe free ions in the quenching of azoalkane **Ia** by aliphatic amines[69] provide experimental support for an endergonic ΔG_{et}.

It is expected for the endergonic region[28] that exciplex-induced quenching predominates by far over quenching by outer-sphere electron transfer (k_{et}), i.e., $k_1 \gg k_{\mathrm{et}}$. In fact, the involvement of exciplexes has been previously established in the quenching of excited azoalkanes by amines[16,27] and olefins.[70,71] The photoreduction of azoalkane **I** derivatives by tertiary amines leads to the formation of the corresponding hydrazines.[27,72] However, the reaction quantum yields are very low (3−5%),[27,72] which suggests that exciplex-induced deactivation (k_{2c}) predominates over the hydrogen transfer (k_{2a}).

Kinetics of Quenching. The integrated rate law for excited-state quenching according to Scheme 1 can only be analytically solved for limiting situations (cf. Appendix). Such limiting behavior is experimentally indicated by the observation of monoexponential decay kinetics of the excited state as observed in the fluorescence quenching of azoalkanes **I** by amines. The observed linearity and consistency of the time-resolved and steady-state quenching plots is indicative of a *steady-state* situation (eq I.1, Appendix).[48] The measured "regular" Arrhenius

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temperature dependence (Figure 3) supports this notion. These experimental observations are distinct from those made in a recent study of steric effects on the quenching of quinones by aromatic donors,[3] for which a preequilibrium non-steady-state situation applied (eq I.2, Appendix).

Further neglect of outer-sphere electron transfer in the steady-state kinetic scheme due to the endergonic ΔG_{et} for azoalkanes **I** (see above) yields eq 3 as an analytical expression of the quenching rate constant (k_q). Accordingly, k_q should increase with the rate constant of exciplex formation (k_1) and the exciplex binding constant ($K = k_1/k_{-1}$). These two related kinetic and thermodynamic properties should be sensitive not only to the driving force for electron transfer but also to steric hindrance.

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (3)$$

Driving Force Dependence. In the endergonic region for electron transfer, the rate constant for exciplex formation (k_1) should increase with the driving force for electron transfer.[1,28] This is reflected by the bimolecular quenching rate constants in Table 2 and has been previously confirmed for this and related azoalkanes.[27,70,71] The driving force for electron transfer can be reduced by employing a weaker acceptor, i.e., one with a lower excitation energy and a more negative reduction potential. Consequently, amine quenching of the weaker acceptor **Ib** is 4−6 times slower than that for **Ia** (Table 2) while the rate constants for the stronger acceptor benzophenone are much larger.[18,25]

There is a surprisingly accurate ($r = 0.994$, $n = 8$) linear correlation (Gettler correlation)[73] between the logarithmic quenching rate constants of **Ia** and **Ib** by amines.[74] This is in accordance with the reactivity−selectivity principle since **Ib** is less reactive, but more selective than **Ia**. Note that the smaller-than-unity slope (0.92) of the plot in Figure 2 provides a quantitative measure of the higher selectivity of **Ib** compared to **Ia**. In essence, the rate constants for **Ib** can be quite reliably predicted by knowing only the values for **Ia**.

The driving force for electron transfer is also affected by employing a stronger donor, i.e., one with a lower oxidation or ionization potential. Higher rate constants are expected in this case. Indeed, amine **1**, which has the lowest ionization and oxidation potential of all examined amines, is the best quencher for both azoalkanes (Table 2). Second, amines **4−7** show very similar quenching rate constants for each azoalkane, in line with their very similar ionization potentials.

Steric Effects. For the amines **2** and **3** with three secondary alkyl groups attached, other factors besides the driving force for electron transfer must become important, since the quenching rate constants fall far from expectation: Although amines **2** and **3** should be excellent donors as judged by their low ionization and oxidation potentials, they are the poorest quenchers. Amine **3** is a better electron donor than amine **5** (ca. 0.4 eV difference in IP$_a$, Table 2), but it quenches **Ia** nevertheless more than 10 times slower. Most striking, although amine **3** has the same ionization potential as **1**, its quenching rate constant is 50 times

lower for **Ib**. We attribute the drop in reactivity of amines **2** and **3** (observed in benzene and/or acetonitrile) to steric hindrance toward exciplex formation: k_1 and K are reduced and lower k_q according to eq 3. In essence, exciplexes require the formation of "charge-transfer bonds" between the acceptor and the donor,[22] and such bonding should be sensitive to steric effects as previously proposed.[3]

What Is a Sterically Hindered Amine? Three secondary alkyl substituents as in amines **2** and **3** are essential to produce significant steric effects on the fluorescence quenching of azoalkanes **I**. While the so-called HALS amines,[18,19] i.e., 2,2,6,6-tetramethylpiperidine derivatives such as **7**, are considered to be sterically demanding for use as polymer stabilizers (HALS = hindered amine light stabilizer), their steric demand is insufficient to manifest itself in the present kinetics for CT-induced quenching. Amine **5**, which has been deemed sterically hindered in the exciplex quenching by amines[22] and fluorescence quenching of benzo[*b*]thiophenes,[75] behaves as an unhindered donor in the present study. In view of these contrasting appraisals of steric hindrance, it may be trivial but nonetheless timely to note that the steric demand of an amine depends strongly on the process one is looking at. This makes generalizations difficult and emphasizes the need for case-to-case studies to evaluate steric effects on CT reactions involving exciplexes,[3,5,7] electron transfer,[4] and back electron transfer.[76]

Stereoelectronic Effects. The amine 1,4-diazabicyclo[2.2.2]octane (**8**) is an exceptional case, since it is known to exert a stereoelectronic effect on the quenching mechanism of n,π*-excited states by amines.[12] This amine possesses C−H bonds, which are conformationally frozen into a 60° orientation with respect to the amine lone pair. This stereoelectronic effect, which is known to render exciplex-induced hydrogen abstraction (k_{2a}) virtually impossible, should also lower the observed quenching rate constant according to eq 3. Indeed, a factor of ca. 2 decrease is observed for amine **8** versus tri-*n*-propylamine (**4**) as reference. While this appears to be the first *kinetic* manifestation of the stereoelectronic effect of amine **8** on excited-state quenching, the difference is too small to account for the dramatic drop in reactivity of amines **2** and **3**. Hence, steric effects upon exciplex formation are involved.

Exciplex Structures. In the previously examined cases of aromatic donors,[3,5] e.g., the hexamethylbenzene−hexaethylbenzene couple, structural data of the electron-donor−acceptor ground-state complexes could be consulted to assess the impact of steric effects on exciplex formation and, thus, on CT-induced quenching. Experimental structures of the ground-state complexes of ketones or azoalkanes with amines are not available. Such complexes are expected to be weak, e.g., ca. 5 M^{-1} for benzophenone−amine complexes,[77,78] and should involve different orbital interactions, since the LUMO of the ground-state acceptor is π* in nature.[78]

Alternatively, the structure of azoalkane/amine exciplexes can be computationally assessed with the UHF-PM3 method.[27] CT interaction takes place between the amine lone pair and one azo nitrogen as illustrated for the triisopropylamine exciplex in Figure 4. The approach occurs in the C−N=N−C plane of the azoalkane, which has been referred to as an "edge" attack in the case of the related n,π*-excited ketones.[8] Note that the CT

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(74) Such excellent structure−reactivity correlations, while common in thermal chemistry, are scarce in the photochemistry of n,π*-excited states. Structural variations, in particular for ketones, often affect the electronic configuration (n,π*−π,π* mixing or state switching), which renders definite structure−reactivity relationships difficult. In this respect, the examination of such azoalkanes presents a novel mechanistic tool, since the properties of an n,π*-excited acceptor can be fine-tuned by substituents without admixing any sizable character of the very high-lying (ref 26) π,π* state.

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interaction results in the formation of a weak three-electron σ bond[22,79,80] (bond length ca. 1.9 Å) and takes place in an unsymmetrical fashion at one azo nitrogen, akin to the protonation behavior of azoalkanes.[81] The well-defined geometry of these exciplexes and the formation of a "real" charge-transfer bond qualify these exciplexes as "tight" ones.

The observed trend in the experimental preexponential factors [$\log A/(M^{-1}\ s^{-1}) = 9.4$ for **1** and 9.0 for **3**] may not be experimentally significant, but agrees with the formation of a "tight" exciplex. In such cases, a larger decrease in entropy is expected for the sterically congested complex.[82] This differs from the situation for the quenching of pyrene fluorescence by anilines,[83] for which the formation of the sterically congested exciplex has been suggested to be entropically *favored* (decrease in the preexponential factor for exciplex dissociation). Looser exciplex structures or different types of exciplexes have been held responsible for the contrary effects in the latter study.

Exciplex Energies. Fluorescence from singlet exciplexes of n,π*-excited states has remained elusive. This precludes one to obtain direct evidence for their involvement and to estimate the energies for exciplex formation. These energies can be alternatively evaluated by the computational method. Although the absolute values (ΔE_{Ex} values in Table 2) are clearly too endothermic and show significant scatter (cf. Results) there is a marked increase (ca. 3−6 kcal mol^{-1}) in exciplex formation energy for the sterically congested amines **2** and **3**. A less favorable energetics of exciplex formation for amines **2** and **3** is expected to reduce the quenching rate constant according to eq 3 by lowering the exciplex formation rate constant (k_1) and the exciplex binding constant (K). This agrees with the experimental findings.

Moreover, a less favorable energetics for exciplex formation for these amines is also experimentally indicated by the observation of a significantly higher activation energy for quenching, namely, it is nearly 2 kcal mol^{-1} higher for amine **3** than for amine **1**, while the ionization potentials are the same. The difference in experimental activation energies (1.3 versus 3.0 kcal mol^{-1}) is mechanistically important since the activation energy for amine **1** is actually that expected for diffusion, i.e., solvent viscous flow.[84] In contrast, the activation barrier for amine **3** clearly exceeds this lower limit, i.e., quenching is thermally activated. The fact that the quenching rate constant of amine **1** falls below the diffusion-controlled limit of ca. 10^{10} M^{-1} s^{-1}, although it displays an activation energy characteristic for diffusion, must be related to the reversibility of exciplex formation (Scheme 1), which reduces the preexponential factor for the overall quenching process.

Comparison with Ketones. In contrast to the examined azoalkanes, quenching of triplet benzophenone (as well as other acceptors)[22] by a series of closely related aliphatic amines occurs with rate constants close to the diffusion-controlled limit ($k_q > 10^9$ M^{-1} s^{-1}).[25] This can be reconciled in terms of the stronger acceptor properties of triplet benzophenone (Table 1), which result in exergonic energies of electron transfer for all examined amines. As has been previously suggested,[25] the high rate constants may render the detection of subtle structural effects as those imposed by steric hindrance difficult.

Scheme 2
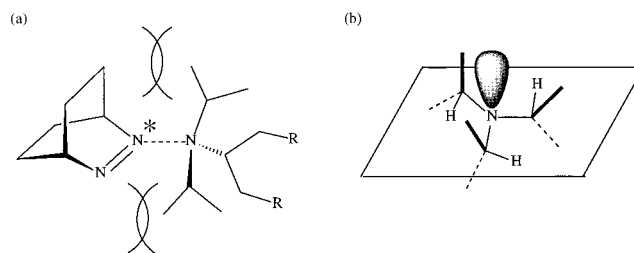
In contrast to the quenching of singlet-excited azoalkanes by amines, where no formation of free ions was detected,[69] quenching of triplet benzophenone results in the formation of free ions.[85] This contrast is a direct manifestation of the endergonic electron transfer for azoalkanes and an exergonic one for benzophenone. Kochi and co-workers have suggested a switch-over from inner-sphere (exciplex formation) to outer-sphere electron transfer for sterically demanding donors.[3] This might well take place for benzophenone as well, but does not manifest itself in the kinetics of quenching since the reaction is diffusion-controlled. Transferring this argument to Scheme 1 means that k_1 may well become significantly smaller than k_{et} due to steric hindrance, but as long as both are faster than the rate of diffusion, no net effect on the kinetics is seen. For azoalkanes **I** outer-sphere electron transfer (k_{et}) is unlikely to compete due to the endergonic ΔG_{et}. Consequently, steric effects manifest themselves in the quenching rate constant through exciplex formation (k_1).

Persistence of Amine Radical Cations. We observed an interesting correlation between steric effects on the kinetics of excited-state quenching by amines (k_q) and the persistence of the amine radical cations in the cyclovoltammetric measurements. Namely, while amines **2** and **3** are the only amines which display large steric effects on the quenching rate constants, they are also the only amines, together with the bicyclic amine **8**, which persist as radical cations in solution. This high persistence is experimentally indicated by (a) the reversibility of the electrochemical oxidation of these three amines (Table 2) and (b) the observation of free ions in the quenching of triplet benzophenone by these three amines, but not for the other examined amines.[85]

While it is tempting to attribute all these observations to the steric demand by these two amines, we suggest that they are not directly related and, in fact, originate from different effects. In the case of the quenching of the singlet-excited azoalkanes, steric effects manifest themselves in the difficulty toward formation of exciplexes (Scheme 2a, R = H, Me), i.e., they affect k_1. In contrast, the persistence of the amine radical cations is presumably related to a stereoelectronic rather than a steric effect. Both the deprotonation of the amine radical cations (k_4), the presumed follow-up reaction and reason for irreversibility in electrochemical measurements,[86] and the proton transfer in the radical ion pair (k_3), a possible follow-up reaction in the quenching of excited states (Scheme 1), are obstructed by an unfavorable arrangement of the C−H bonds and the lone pair orbital in the radical cations of amines **2** and **3** (Scheme 2b).[54] Such an unfavorable conformation is suggested by experimental and computed structural data for these amines.[31,52,53]

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Conclusions

This work presented evidence for steric effects of aliphatic amine donors on the kinetics of quenching of n,π*-excited states. This finding is important in view of the extensively studied photoreduction and fluorescence quenching by amines and their use in polymer technology. The following conclusions can be drawn: (1) Weak acceptors such as azoalkanes **I** are required to reveal steric and stereoelectronic effects on the kinetics of excited-state quenching by aliphatic amines. (2) Significant steric effects of donors are most likely to be observable when exciplexes are involved, as expected for the present acceptors. (3) Semiempirical calculations can be employed to evaluate structural and energetic trends for exciplex formation of n,π*-excited states with amines. (4) The rarely observed reversibility of amine oxidation in solution provides an empirical indicator for steric or stereoelectronic effects on the kinetics of quenching. (5) Amines need to be substituted with *three secondary alkyl groups* (isopropyl and higher) to exhibit significant (up to factor 50) steric effects on the quenching kinetics.

Appendix: Quenching Kinetics

When exciplex formation competes with electron transfer in Scheme 1, the kinetics of quenching depends sensitively on the relative magnitude of the rate constants of exciplex formation ($k_1[Q]$), exciplex dissociation (k_{-1}), and the exciplex follow-up reactions (k_2). When the unimolecular rate constant of exciplex dissociation *exceeds* the bimolecular rate constant of exciplex formation ($k_{-1} \gg k_1[Q]$) a *steady-state* kinetics applies. This situation is experimentally indicated by the linearity and consistency of the quenching plots in both time-resolved and steady-state experiments. Smaller-than-unity binding constants ($K = k_1/k_{-1}$), i.e., endergonic exciplex formation, always result in steady-state kinetics, since the condition $k_{-1} \gg k_1[Q]$ is fulfilled even at high quencher concentrations (up to 1 M). The observed rate constant (k_{obs}) of fluorescence decay is then first order in quencher concentration (eq I.1):

$$k_{obs} = k_0 + \left(k_{et} + \frac{k_1 k_2}{k_{-1} + k_2}\right)[Q] \text{ and } k_q = k_{et} + \frac{k_1 k_2}{k_{-1} + k_2}$$

(I.1)

When the rate constant of exciplex dissociation exceeds the rate constant of the exciplex follow-up reactions ($k_{-1} \gg k_2$), a *preequilibrium* kinetics applies, which is a priori unrelated to the exciplex concentration and its binding constant. Experimentally, nonlinear kinetic quenching plots, inverse temperature effects, and deviations between the results from time-resolved and steady-state experiments are expected.[3,48] A simple first-order kinetics no longer applies and eq I.2 holds:

$$k_{obs} = \frac{k_0 + k_{et}[Q] + k_2 K[Q]}{1 + K[Q]}$$

(I.2)

When both of the above conditions are fulfilled simultaneously ($k_{-1} \gg k_1[Q] \cup k_2$), the simplest case of a preequilibrium *and* steady-state kinetics results (eq I.3):

$$k_{obs} = k_0 + (k_{et} + k_2 K)[Q] \text{ and } k_q = k_{et} + k_2 K \quad \text{(I.3)}$$

For larger-than-unity binding constants, i.e., exergonic exciplex formation, the "admixture" of steady-state character to the kinetics depends on the examined concentration range, since k_{-1} can become larger than $k_1[Q]$ at sufficiently low quencher concentrations. This presents an important experimental tool for kinetic analysis, since steady-state behavior can be imposed upon a preequilibrium kinetics by working at low quencher concentration. The same net effect can be achieved by monitoring the quenching with stationary rather than time-resolved techniques.