# Amide Conformation-Dependent Intramolecular Photoinduced Electron Transfer

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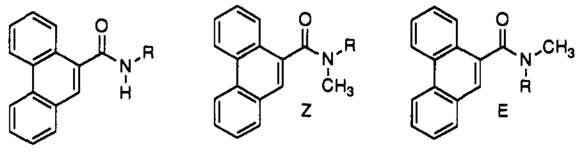
Secondary amides exist predominantly in the *Z* conformation, whereas tertiary amides with nonidentical substituents exist as mixtures of *Z* and *E* conformers with barriers of 13–20 kcal/mol for amide rotation.[1] In tertiary aromatic carboxamides such as *N*,*N*-dimethyl-9-phenanthrenecarboxamide, the dihedral angle between the aromatic ring and the amide group is large in both the ground and the excited singlet states.[2] Thus a conformationally mobile *N*-(2-aminoethyl) or *N*-(3-aminopropyl) substituent should have access to the face of the phenanthrene ring when it is in the *E* conformation but not in the *Z* conformation. We report here the results of our investigation of the photophysical behavior of several secondary (**1–3**) and tertiary (**4–8**) phenanthrenecarboxamides. These results serve to establish that rate constants for intramolecular electron-transfer quenching can be highly dependent upon amide conformation.



**1**: R = $CH_3$
**2**: R = $CH_2CH_2N(CH_3)_2$
**3**: R = $CH_2CH_2N(CH_3)Ph$

**4**: R = $CH_3$
**5**: R = $CH_2CH_2CH_2CH_3$
**6**: R = $CH_2CH_2N(CH_3)_2$
**7**: R = $CH_2CH_2CH_2N(CH_3)_2$
**8**: R = $CH_2CH_2N(CH_3)Ph$

The fluorescence of *N*-methyl- and *N*,*N*-dimethylphenanthrenecarboxamide (**1** and **4**) is quenched by added triethylamine (TEA) and *N*,*N*-dimethylaniline (DMA) in hexane or acetonitrile solution. Quenching constants obtained from the slopes of linear Stern–Volmer plots[3] for fluorescence intensity quenching and the measured singlet lifetimes ($k_{SV}$ = slope/$\tau_S$) are reported in Table 1. Quenching constants for DMA are equal to the rate of diffusion, indicative of irreversible quenching, whereas quenching constants for TEA are an order of magnitude slower, indicative of slower or reversible quenching. Also reported in Table 1 are the singlet energies, reduction potentials, and free energies for intermolecular photoinduced electron transfer in hexane and acetonitrile solution estimated using Weller's equation[4a] (eq 1, const = 0.38 eV in hexane and 0.17 in acetonitrile solution) and

$$\Delta G_{ex} = E_D^{ox} - E_A^{red} - E_S + \text{const} \qquad (1)$$

the oxidation potentials of TEA (1.42 V) and DMA (1.16 V).[4b] Exciplex fluorescence accompanies quenching by DMA but not TEA. The smaller quenching constants for quenching by TEA vs DMA and the absence of exciplex fluorescence for TEA are consistent with endergonic electron transfer for TEA. Increasing the driving force for electron transfer by increasing the solvent polarity does not result in a large increase in rate constant for quenching of **1** or **4** by TEA.

**Table 1.** Singlet Lifetimes and Intermolecular Quenching Data for Phenanthrenecarboxamides **1** and **4**[a]

| amide | **1** | **4** | **5** |
|---|---|---|---|
| $\tau_S$, ns | 23.7 | 13.8 (22.4) | 15.8 (22.5) |
| $10^{-9}\ k_{SV}$, $M^{-1}\ s^{-1}$ ($Et_3N$) | 1.8 (5.4) | 2.8 (2.6) | |
| $10^{-10}\ k_{SV}$, $M^{-1}\ s^{-1}$ ($PhNMe_2$) | 2.3 | 1.8 | |
| $E_s$, eV[b] | 3.42 | 3.52 | |
| $E_A^{red}$, V[c] | −1.90 | −2.04 | |
| $\Delta G_{et}$, eV ($Et_3N$) | 0.28 (0.07) | 0.33 (0.12) | |
| $\Delta G_{et}$, eV ($PhNMe_2$) | 0.02 | 0.06 | |

[a] Data for deoxygenated hexane solutions except as indicated. Values in parentheses are for acetonitrile solution. [b] Singlet energies estimated from highest energy fluorescence maxima. [c] Reduction potential measured in acetonitrile solution.[4]

**Table 2.** Fluorescence Decay Times and Intramolecular Quenching Data for Linked (Aminoalkyl)phenanthrenecarboxamides[a]

| amide | $\tau$, ns | $10^8\ k_{et}$, $s^{-1}$ (*Z*) | $10^8\ k_{et}$, $s^{-1}$ (*E*) |
|---|---|---|---|
| **2** | 14.1 | 0.3 | |
| **3** | 0.22 | 50 | |
| **6** | 15.0, 3.1 | 0.03 | 2.8 |
| **6** (MeCN) | 12.8, <0.2 | 0.3 | >50 |
| **7** | 14.7, 8.7 | 0.05 | 0.6 |
| **8** | 0.37 | >25 | >25 |

[a] Data for deoxygenated hexane solutions except where indicated.

Fluorescence lifetimes for the phenanthrenecarboxamides **1**, **4**, and **5** and decay times for the residual phenanthrene fluorescence from the *N*-(aminoalkyl)phenanthrenecarboxamides **2**, **3**, and **6–8** in hexane solution are reported in Tables 1 and 2. Single exponential decay is observed for **1–5** and **8**. The decay of **6** and **7** is best fit by a double exponential with comparable contributions to the total fluorescence from the fast and slow decaying components. Whereas the lifetimes of **4** and **5** are longer in acetonitrile vs hexane solution, both of the decay times for **6** are shorter. The decay times of **3** and **8** are close to the 0.2-ns time resolution of our instrumentation, and thus a second, shorter-lived component might not have been resolved. Exciplex fluorescence is observed only in the cases of **3** and **8**. $^1H$ NMR spectral analysis establishes that **1–3** exist predominantly as the *Z* conformer, whereas **5–8** exist as approximately equal mixtures of *Z* and *E* conformers in the ground state. The observation of single exponential decay for **5** indicates that *Z* and *E* conformers can have the same fluorescence decay times when no quenching group is appended.

Rate constants for intramolecular electron-transfer quenching can be estimated from the observed lifetimes for the phenanthrenecarboxamides **1** and **5** ($\tau_S$) and the decay times for the *N*-(aminoalkyl)phenanthrenecarboxamides ($\tau$) using eq 2. The

$$k_{et} = \tau^{-1} - \tau_S^{-1} \qquad (2)$$

resulting values of $k_{et}$ for **2** and **3** indicate that intramolecular quenching is inefficient for a *Z* tertiary aliphatic amine but highly efficient for a *Z* tertiary aromatic amine. We attribute the slow and fast fluorescence decay from **6** and **7** to the *Z* and *E* amide conformers, respectively, based on the observation of slow fluorescence decay for **2**.[5] Evidently, the barrier to amide rotation remains sufficiently high in the excited singlet state to prevent

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(4) (a) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *133*, 93. (b) Redox potentials were measured in nitrogen-purged acetonitrile solution using a Ag/AgI reference electrode and $Et_4NBF_4$ as the electrolyte. The half-wave potential of ferrocene is 0.668 ± 0.002 V under these conditions.

(5) Replacement of the *N*-methyl group with an *N*-isopropyl group results in a decrease in the population of the *E* aminoalkyl conformer and a concomitant decrease in the preexponential for the short-lived component of the fluorescence decay.

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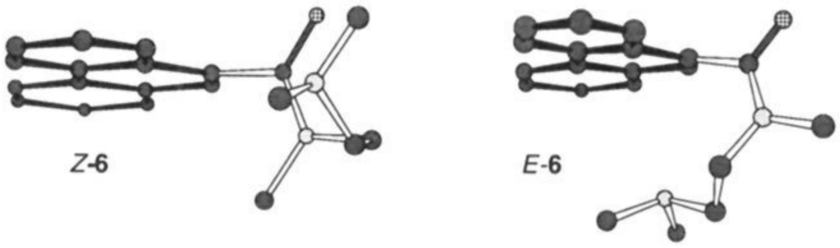
interconversion of conformers.[6] The calculated value of $k_{et}$ for the *E* conformer of **6** is larger than that for its homologue **7**. Values of $k_{et}$ for both conformers of **6** are larger in acetonitrile than in hexane solution. Since only one short-lived fluorescence decay is resolved for **8**, the values of $k_{et}$ for both the *Z* and *E* conformers must be large.

Intramolecular photoinduced electron transfer between donor–acceptor pairs separated by a flexible polymethylene chain has been extensively investigated.[7-12] In nonpolar solvents, arene–trialkylamine exciplexes are proposed to adopt specific folded conformations which maximize orbital overlap and Coulombic attraction while avoiding high-energy conformations of the polymethylene chain. Arene–aniline exciplexes adopt sandwich-type geometries when possible. In spite of the apparent entropic advantage for intra- vs intermolecular electron transfer,[13] intramolecular exciplexes typically have fluorescence maxima at higher energy than intermolecular exciplexes, and rate constants for intramolecular electron transfer are slower than those for solvent relaxation or conformational isomerization. These phenomena have been attributed to the conformational limitations on orbital overlap and Coulombic attraction introduced by the connecting polymethylene chain.[7-12]

Inefficient quenching by *Z* aminoalkyl groups in **2**, **6**, and **7** plausibly reflects the absence of spatial overlap between the phenanthrene singlet and amine lone pair, coupled with the small driving force for photoinduced electron transfer. Chain folding of the *Z* aminoalkyl group in **6** can position it above the face of the amide group but not the phenanthrene (Scheme 1). Spatial overlap of the amine and phenanthrene is possible for *E* aminoalkyl groups. The folded conformations for the *Z* and *E* conformers of **6** (Scheme 1) are calculated by MM2 to lie ca. 2 kcal/mol above the global ground-state energy minima.[14] Whereas a conformational energy of this magnitude can be overcome by Coulombic attraction in the singlet exciplex when the driving force for intramolecular electron transfer is large, it may be responsible for the relatively small rate constants for intramolecular quenching by both the *E* and *Z* trialkyl aminoalkyl groups. Extending the linking polymethylene chain does not improve the spatial overlap and should increase the entropy of exciplex formation, in accord with the decrease in rate constant for the *E* conformer of **7** vs **6**.

**Scheme 1**



Increasing the driving force for intramolecular electron transfer is known to reduce its dependence on spatial overlap between donor and acceptor.[10] The driving force can be increased either by increasing the solvent polarity or changing the redox potentials of the donor or acceptor (eq 1).[3] Changing the solvent from hexane to acetonitrile results in an increase in the driving force for electron transfer of ca. 0.21 eV (eq 1), a large increase in $k_{et}$ for the *E* conformer of **6**, a smaller increase in $k_{et}$ for the *Z* conformer of **6**, and little change in the rate constant for intermolecular electron transfer (Tables 1 and 2). Replacing the tertiary aliphatic amine by a tertiary aniline decreases the amine oxidation potential by ca. 0.26 eV and results in diffusion-controlled intermolecular quenching and highly efficient intramolecular quenching by the *Z* conformers of **3** and **8** as well as the *E* conformers of **8**. Exciplex fluorescence is also observed for the *Z* conformer of **3**, which cannot form a sandwich-type exciplex.[15] Whether the exciplex fluorescence observed from **8** is from the *Z* and/or *E* conformer remains to be established.

In view of the frequent use of amides as linkers for donor and acceptor groups in studies of intramolecular electron transfer,[16] the different behavior of *Z* vs *E* conformers and tertiary amine vs aniline donors merits further investigation. Additional studies of the effect of solvent polarity on the photophysical behavior of the phenanthrenecarboxamides and conformationally rigid analogues are in progress.

**Acknowledgment.** Financial support for this research has been provided by the National Science Foundation.

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