

Theoretical Investigation of the Directional Electron Transfer in 4-Aminonaphthalimide Compounds[†]

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Photoinduced electron-transfer reactions in small supramolecular systems, such as the 4-aminonaphthalimide compounds, are interesting in that there are two alternative directions for the electron transfer to occur. Nevertheless, the electron transfer occurs only along one path, as deduced from pH-dependent fluorescence quenching studies of selected compounds. The role of the electronic coupling matrix element and the effect of the charges accompanying protonation are considered so as to explain the directionality of the electron transfer and other results. A related mechanism is suggested for interpreting the behavior of similar molecules, which serve as fluorescent sensors of metal ions.

I. Introduction

In recent years, the 4-aminonaphthalimide compounds have been the subject of many studies,^{1–8} in part because of their fluorescence properties and their use as sensors. Recently, the photoinduced electron-transfer reactions in synthesized supramolecular systems consisting of various 4-aminonaphthalimide compounds were studied by de Silva and co-workers.^{1,2} The pH-dependent fluorescence spectrum was investigated for the compounds depicted in Figure 1. Each of these molecules contains a fluorescent 4-aminonaphthalimide as the core, and different amino groups in the side chains serve as the electron donors. The electronic absorption and fluorescence emission spectra were measured as a function of the pH of the solution, the solvent being water/methanol in a ratio of 1:1. Some of the observed optical properties^{1,2} are given in Table 1. A strong pH dependence of the fluorescence quantum yield is displayed by **3**,¹ **4**,² and **5**,² but not by **1** or **2**:¹ the fluorescence quantum yield of **1** and **2** remains relatively low (~ 0.2) in the pH range of the experiments (4–11), while the fluorescence quantum yield for **3**, **4**, and **5** is very low under basic conditions (< 0.1) but high under acidic conditions (> 0.5). The recovery of the fluorescence of **3**,¹ **4**,² and **5**² occurs at a pH that corresponds to the pK_a of the distal nitrogen of the 4-substituent.

Of particular interest is the pH-dependent fluorescence experiment for **4** and **5**.² Each of these two compounds consists of a fluorophore with two side chains, each containing an amino electron donor. With the pH-dependent fluorescence spectroscopy studies, two possible electron-transfer directions responsible for the fluorescence quenching could be investigated. In their experiments,² de Silva and Rice made the striking discovery that the electron transfer is directional: the fluorescence is recovered only when the distal nitrogen on the 4-substituent is protonated, while the protonation of the distal nitrogen on the 9-substituent has negligible influence on the fluorescence quantum yield. Thus, the electron transfer occurs only from the distal nitrogen in the 4-substituent. In their explanation of their striking observations on the directional behavior of **4** and **5**, de Silva and Rice suggested² that the excitation first produces a

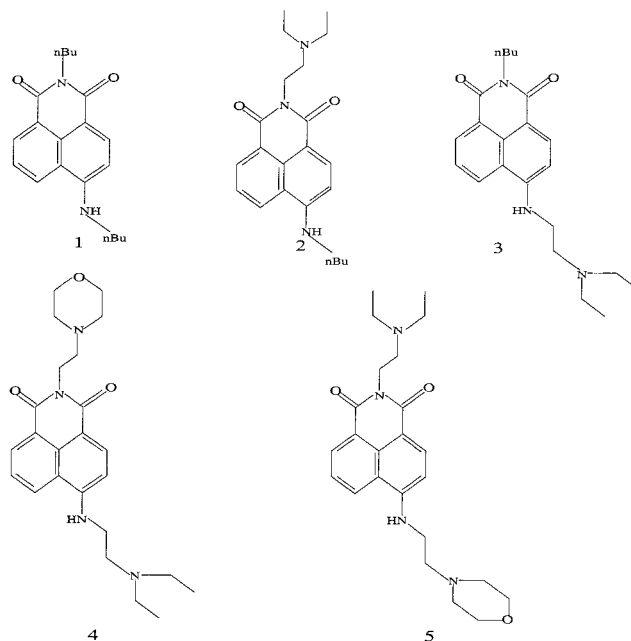


Figure 1. The structures of the five molecules, **1–5** studied by the pH-dependent fluorescence spectroscopy.^{1,2}

charge-separated state, namely, a charge $+\delta$ on the 4-N and a charge $-\delta$ on the dicarboximide ($-\text{CO}-\text{N}-\text{CO}-$) group, the 4-N being the amino group at the 4-position. The resulting internal electric field then directs the hole to the distal nitrogen in the 4-substituent. A similar mechanism was assumed later by Tian et al. to explain the pH-dependence of the fluorescence of a 4-amino-1,8-naphthalimide compound.⁹

Indeed, as de Silva et al. noted, there is an effect of a ground-state dipole on the direction of electron transfer in an α -helical polypeptide.¹⁰ However, there is a striking contrast in the two phenomena: in the 4-aminonaphthalimide, the creation of a hole-electron pair in the excited state causes the dipolar field, rather than its being a dipole undergoing further separation under the influence of an external field. The concept was not developed further in the form of an actual calculation. In the present paper, a different but simple explanation of the results is proposed,

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TABLE 1: Optical Properties^a for Compounds 1–5

	1	2	3	4	5
$\lambda_{\text{abs}}^{\text{max}}$ (base ^b), nm	454	455	449	450	452
$\lambda_{\text{abs}}^{\text{max}}$ (acid ^b), nm	454	455	431	432	433
λ_{shift} , nm	0	0	18	18	19
$\lambda_{\text{abs}}^{\text{max}}$ (pH = 7.0), nm				432	452
$\lambda_{\text{flu}}^{\text{max}}$ (base ^b), nm	555	557	549	526 ^c	524 ^c
$\lambda_{\text{flu}}^{\text{max}}$ (acid ^b), nm	555	559	538		
Φ_{flu} (base ^b), nm	0.23	0.15	0.030	0.030	0.070
Φ_{flu} (pH = 7.0), nm	0.23	0.12	0.57	0.66	0.062
Φ_{flu} (acid ^b), nm	0.23	0.12	0.76	0.53	0.52

^a The properties for **1**, **2**, and **3** are taken from ref 1, and those for **4** and **5** are taken from ref 2. ^b pH was only specified for **4** and **5**. Here, the pH was 3.0 in acidic solution and 10.8 in basic solution. ^c Value changes very little with the pH.

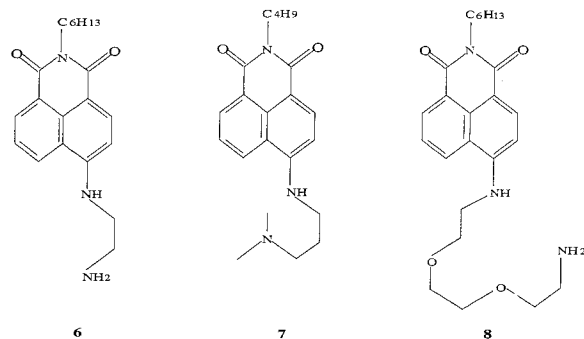


Figure 2. The structures of the fluorescent sensors **6**, **7**, and **8** studied by Mitchell et al.^{6,7}

one based on the calculations of the relevant electronic coupling matrix elements between the orbitals.

The paper is organized as follows: Further experimental results are described in section II. The electronic states involved in the present mechanism are given in section III. In section IV, a crude estimate of the electronic coupling matrix elements is given for the two electron-transfer directions. The electronic coupling matrix elements for the two pathways are calculated and used to interpret the directionality of the electron transfer in section V. A reorganizational factor is also considered. Explanations of various other experimental results are given in section VI and VII, and the discussion concludes in section VIII.

II. Further Experimental Results

In the experiments,^{1,2} a noticeable difference was observed between the pH-dependence of the wavelength of the absorption maxima, $\lambda_{\text{abs}}^{\text{max}}$, for **1** and **2** and that for **3**, **4**, and **5** (Table 1): the $\lambda_{\text{abs}}^{\text{max}}$ undergoes very little change with pH for compounds **1** and **2**, while there was about a 20 nm blue shift of the absorption spectra of **3**, **4**, and **5** when measured in acid relative to the spectra in base.¹¹ These changes of the $\lambda_{\text{abs}}^{\text{max}}$'s of **3**, **4**, and **5** occur at pH's corresponding to the pK_a 's of the distal nitrogens in the 4-substituent.

In a related study, other 4-aminonaphthalimide compounds (**6** and **7** in Figure 2) were investigated by Mitchell et al. as fluorescent sensors for metal ions,^{6,12} in which the compounds are again believed to undergo intramolecular quenching by the distal nitrogen of the 4-substituent. For comparison, the fluorescence of **8**, a molecule similar to **6** and **7** but with a much longer 4-substituent side chain, was also studied in the presence of metal ions.⁶ This quenching of **6** and **7** disappeared with the complexation of the metal ions with the distal nitrogen of the 4-substituent. The electron transfer from this distal nitrogen is thus again believed to be responsible for the fluorescence

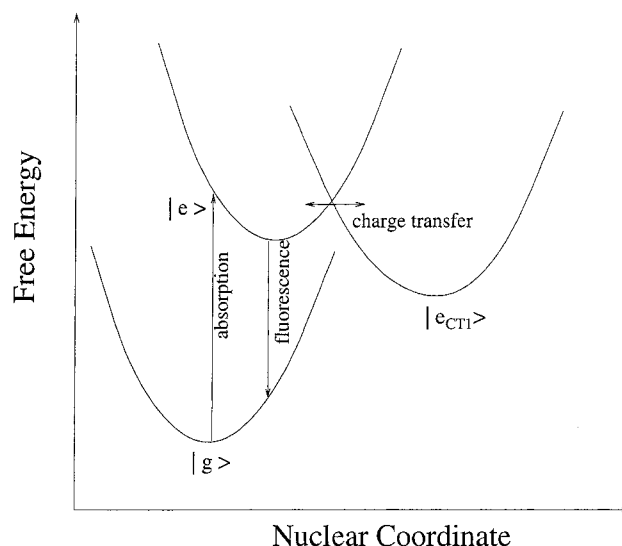


Figure 3. Schematic diagram of the free energy vs nuclear coordinate for the ground and excited states for the fluorophore. $|g\rangle$ is the ground state, $|e\rangle$ is the fluorescence excited state, $|e_{\text{CT1}}\rangle$ is the charge-separated, nonfluorescent state due to the electron transfer from the distal nitrogen. When the distal nitrogen in the 4-substituent is protonated, the energy of the fluorescent state $|e\rangle$, which is slightly charge-separated, is increased and there is a blue shift of the absorption. The $|e_{\text{CT1}}\rangle$ does not exist in **1** or **2**.

quenching of **6** and **7**. The fluorescence decay profile of **6** and **7** shows that the addition of metal ions that form amino complexes increases both the intensity and the lifetime of the fluorescence, while such effects have not been observed for **8**.

Experiments also confirmed that when a 4-substituent is moved to the 9-position it has, Mitchell et al. noted,⁶ much less influence on the fluorescence quenching and on the fluorescence recovery mechanism of **6** and **7**.^{7,13} It was also observed that the addition of metal ions that can readily form complexes with the 4-distal nitrogen of **6**, **7**, and **8** causes the absorption maxima of **6** and **7** to undergo a 10–30 nm blue shift. The addition of the same metal ions to the solution of **8** has no effect on absorption wavelength. The addition of metal ions that do not form amino complexes causes no change in the spectrum of any of the three molecules, **6**, **7**, and **8**.

III. The Electronic States

We consider a mechanism for the fluorescence quenching and for its recovery for the 4-aminonaphthalimide compounds in which there are the ground state, $|g\rangle$, and at least two excited states, one of which, $|e\rangle$, is less charge-separated and is fluorescent. The other, labeled $|e_{\text{CT1}}\rangle$ in Figure 3, is more charge-separated and relatively nonfluorescent. The state $|e\rangle$ is created by the excitation of a HOMO of the fluorophore and contains one electron in the HOMO and one in the LUMO of the fluorophore (Figure 4). The $|e_{\text{CT1}}\rangle$ is coupled to $|e\rangle$ and arises from the electron transfer from the distal nitrogen. It has a positive charge on that nitrogen, and the electron transfer quenches the fluorescence. This quenching mechanism is removed if this electron transfer is inhibited, and then, the fluorescence increases. For the present systems, the attached amino groups act as electron donors and the ring system acts as an electron acceptor. The assumption of having a locally excited state, such as $|e\rangle$, and a charge-separated state is common for similar systems.¹⁴ A state $|e_{\text{CT2}}\rangle$ defined in the legend of Figure 4 is higher in energy than $|e_{\text{CT1}}\rangle$ because of the relative energies of the N4 and ND orbitals. Its possible role is discussed later.

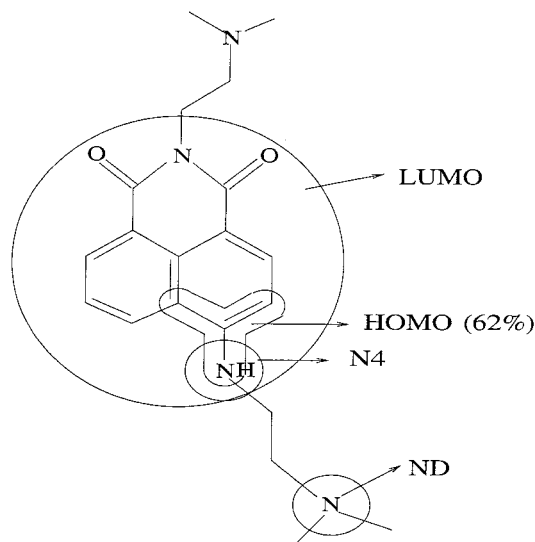
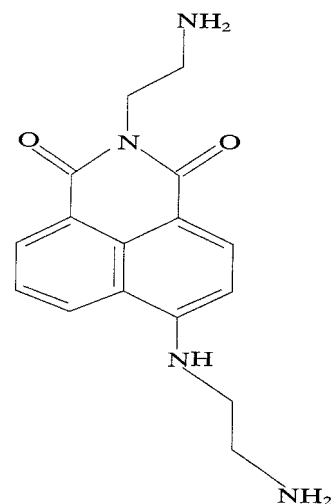


Figure 4. The various diabatic states and the relevant orbitals: $|g\rangle$, $(\text{HOMO})^0(\text{LUMO})^0(\text{N4})^2(\text{ND})^2$; $|e\rangle$, $(\text{HOMO})^1(\text{LUMO})^1(\text{N4})^2(\text{ND})^2$; $|e_{\text{CT1}}\rangle$, $(\text{HOMO})^2(\text{LUMO})^1(\text{N4})^2(\text{ND})^1$; $|e_{\text{CT2}}\rangle$, $(\text{HOMO})^2(\text{LUMO})^1(\text{N4})^1(\text{ND})^2$. About 70% of the relevant orbital of $|e\rangle$, which is the HOMO of the system, is localized at the 4-N (40%), 3-C, 4-C, and 10-C.

IV. Crude Theoretical Estimate of the Electronic Coupling Matrix Elements

We first consider a very approximate estimate of the difference in coupling of the fluorophore to the two distal nitrogens by noting that the distal N on the 4-substituent is three bonds removed from the 4-N, which is found in the calculations given later to make a significant contribution to the HOMO of the system and is part of the initial acceptor state $|e\rangle$ for the electron-transfer reactions (Figure 4). With the use of a decrease of the square of the coupling matrix element V of a factor of 3 per bond of an alkyl chain as an approximate figure,¹⁵ this $|V|^2$ is about $1/27$ of the contact value. If the contact value is of the order of 2 eV, the V then would be of the order of $2/\sqrt{27}$, i.e., ~ 0.4 eV. On the other hand, the distal nitrogen in the 9-substituent is three single bonds and six double bonds away from that 4-N. If one takes the decay of the coupling matrix element for electron transfer via double bonds as $e^{-\beta R}$, where β is a distance decay parameter and R is the total length of the double bonds, about 8.5 Å in this case, the coupling matrix element for the electron transfer from the distal nitrogen of the 9-substituent would be $(2/\sqrt{27})e^{-8.5\beta/2}$. If β is taken as 0.36 Å^{-1} (although strictly speaking this β refers to a direct distance),¹⁶ this coupling matrix element would be about 0.08 eV, and if β is instead 0.57 Å^{-1} ,¹⁷ it would be about 0.03 eV. Thus, the electronic coupling to the distal N on the 9-substituent is expected to be much weaker than that to the distal N on the 4-substituent.

At the intersection of the two diabatic states in a plot versus a reaction coordinate, their energies, denoted by E_x , are, of course, equal. When the electronic coupling between the two states is calculated, there is a splitting of these degenerate levels at the intersection and the lower adiabatic curve has an energy $E_x - |V|$, where V is the electronic coupling matrix element. The activation energy for the electron transfer from the distal N of the 4-substituent would be significantly less than that for the electron transfer from the distal N of the 9-substituent, other factors being equal. If these crude "back of the envelope" figures were taken literally, the electron transfer from the distal N on the 9-substituent would be $\sim e^{0.37/0.025}$ (0.025 being $k_B T$ in eV) or 10^7 times slower than the electron transfer from the distal N on the 4-substituent.



Compound 9

Figure 5. The structure of the model system used in the calculations of electronic coupling matrix elements.

However, a reorganizational factor also needs to be considered. There is a reorganizational free energy barrier, $(\lambda/4)(1 + \Delta G^0/\lambda)^2$ in the usual terminology.¹⁸ Changing the ΔG^0 by transposing the distal N's of the 4- and 9- substituent did not noticeably affect the dominance of the path associated with the distal N on the 4-substituent.² The λ for the 4-N distal substituent is expected to be somewhat larger than that for the 9-N one, because of a larger charge-separation distance. Only if the reaction were in the deep "inverted region", would this larger λ favor the path to the 4-distal N. It seems highly unlikely that the $|e\rangle$ to $|e_{\text{CT1}}\rangle$ transfer in Figure 3 would be in the deep inverted region. Experiments in which the ΔG^0 for reaction is varied could test this aspect. Further, if the system were in the deep inverted region, a larger V would actually retard electron transfer, unlike its effect in the normal region. The experiments are used later to show that the rate constant for $|e\rangle \rightarrow |e_{\text{CT1}}\rangle$ is expected to be relatively insensitive to λ and ΔG^0 , and we focus on the electronic coupling, V .

In the following section, we give a more detailed estimate of $|V|$, using an extended Hückel theory.

V. Calculations: Directionality and $|e_{\text{CT1}}\rangle$

We focus first on a comparison between the electron transfer from the distal nitrogens in the 4- and 9-substituents of **4** and **5**, where $|e\rangle$ and $|e_{\text{CT1}}\rangle$ are the principal states involved. Extended Hückel calculations for the electronic coupling matrix elements between $|e\rangle$ and $|e_{\text{CT1}}\rangle$ were performed using a model compound, **9** in Figure 5, instead of **4** and **5**, to reduce the computational time. The two distal amino groups of **9** were then both chosen to be an NH_2 group. In the calculations, the acceptor level was chosen to be the HOMO of the molecule and the donor states were identified as the levels having electrons localized at the distal amino groups. The coordinates¹⁹ are given in the Supporting Information in Table 1 Supplement. Interaction parameters were taken from a standard program²⁰ and were not further modified.

In the extended Hückel calculations, the relative energies of the two diabatic states, $|e\rangle$ and $|e_{\text{CT1}}\rangle$, in Figure 3 were changed by placing an F^- anion at different distances from the nitrogen of the donor group under consideration. The F^- was moved along the axis of the lone pair electrons of the distal N. The energies of the two states $|e\rangle$ and $|e_{\text{CT1}}\rangle$ are plotted in Figure 6 versus the distance between the F^- and the distal N. In this

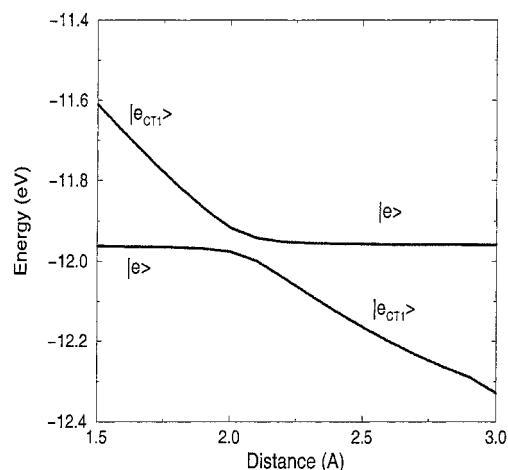


Figure 6. The calculated adiabatic curves used to obtain the electronic coupling matrix element for the electron-transfer reaction from the 9-distal N to the fluorophore.

way, two adiabatic curves are obtained, and the coupling matrix element is one-half of the least splitting of the adiabatic curves at their avoided crossing. That avoided crossing occurred when the distance between the distal group in the 9-substituent and the F^- was about 2 Å.

The calculated $|V|$ is 0.25 and 0.030 eV for the electron transfer from the 4- and 9-substituents, respectively. Both values are large enough for the reactions to be considered as adiabatic. This difference in the electronic coupling matrix elements would make the energy barrier about $10k_B T$ smaller at the avoided crossing for the electron transfer from the 4-distal nitrogen compared with that from the 9-distal nitrogen. On this basis, the electron transfer from the 4-distal nitrogen would be much faster ($\sim e^{10}$ or 10^4 , if the calculations were literally correct) than that via the competing pathway, from the 9-distal nitrogen. The fluorescence of the fluorophore would then be mainly quenched by the electron transfer from the distal amino group in the 4-substituent.

When the 4-distal nitrogen is protonated, the electron-transfer reaction is inhibited because the protonation of that nitrogen should considerably stabilize electrons on it and lower the energy of the ND orbital relative to that of the HOMO in Figure 4 and lower the energy of the fluorescent excited state $|e\rangle$ relative to the charge-separated state $|e_{CT1}\rangle$. This inhibition of the electron transfer then leads to the fluorescence recovery observed at pH's equal to and lower than the pK_a values of the distal nitrogen in the 4-substituent.

VI. Fluorescence Quenching in 1 and 2 and the Role of 4-N

We turn next to the differences between the pH-dependence of the fluorescence of 1 and 2 and that of 3, 4, and 5. As noted earlier, the experimental^{1,2} fluorescence quantum yields of molecules 1 and 2 are relatively low at all pH values, compared to those of 3, 4, and 5 in acid (Table 1). The main structural difference between them is that there exists a distal nitrogen in the 4-substituent of 3, 4, and 5 but not in that of 1 or 2.

The fluorescence of the 4-aminonaphthalimide due to an $|e\rangle \rightarrow |g\rangle$ transition is in competition with a radiationless transition, even in the absence of any distal amino group. The quantum yield of the fluorescence is low (~ 0.2) for 1 and 2 because of that competition. This radiationless transition rate is enhanced when the (HOMO)₁(LUMO)₁ and (HOMO)₂(LUMO)₀ surfaces are more displaced in coordinate space from each other. The

presence of the 4-amino substituent on the ring presumably enhances this displacement by concentrating the charge in a smaller region near the 4-N. It thereby enhances the radiationless transition rate and decreases the fluorescence quantum yield.

As discussed in the preceding section, protonation lowers the energy of $|g\rangle$ relative to $|e\rangle$ and leads to a larger energy gap. The latter in turn decreases the radiationless transition rate and enhances the fluorescence quantum yield. Accordingly, the protonation of the 4-distal nitrogen increases the fluorescence quantum yields of 3, 4, and 5 to values (>0.5) greater than that of 1 or 2 (~ 0.2), which does not contain a distal nitrogen in the 4-substituent.

This discussion also applies to the pH-dependence of the absorption spectra of 1–5. Compounds 1 and 2 cannot be protonated in the pH range of the experiments, because of the absence of the distal nitrogen in the amino position and the low pK_a of the 4-N. Correspondingly, their λ_{abs}^{max} should be pH-independent. For compounds 3, 4, and 5, however, lowering of $|g\rangle$ relative to $|e\rangle$ by the protonation of the distal nitrogen leads to a blue shift of the λ_{abs}^{max} in acid compared with that in base, in agreement with the experimental results in Table 1.

The energy of a state $|e_{CT2}\rangle$ is expected to be appreciably higher than that of $|e_{CT1}\rangle$ (see legend to Figure 4). The pK_a of the 4-N is -0.5 , a very low value, which indicates that the lone pair electrons on the 4-N are bound so tightly that an added H^+ binds only weakly to it. The pK_a of the distal N group is between 6 and 8, depending on its nature, indicating a much weaker binding of the lone pair to the N. The difference in pK_a corresponds to an energy difference of 0.39 eV in proton binding affinities. Thus, the creation of a hole is expected to be energetically much more favorable at the distal N than at the 4-N, and the $|e_{CT2}\rangle$ state is expected to be in a higher energy than $|e_{CT1}\rangle$. While the state $|e_{CT2}\rangle$ may therefore not be directly involved in the present electron transfer, its presence could only enhance the pathway to the 4-distal nitrogen via a superexchange mechanism. The pathway from the distal nitrogen in the 9-substituent cannot be similarly enhanced.

VII. Fluorescence of 6, 7, and 8 in the Presence of Metal Ions

The spectra of systems 6, 7, and 8⁶ can be interpreted in a similar way. The electron transfer is faster from the distal nitrogen of the 4-substituent than that from the distal nitrogen of the 9-substituent, for the reason discussed above. The fluorescence is quenched by the distal amino group on the 4-substituent, and recovery occurs when a complex between this nitrogen and some metal ion or a chelation among this nitrogen, the 4-N, and the metal ion is formed. Both the intensity and the lifetime are increased with the increase of the ion concentration.⁶ This complexation between the distal nitrogen and metal ions, which has a charge effect on the fluorophore, also provides a possible explanation of the blue shift of the absorption spectra²¹ of 6 and 7 occurring in the presence of metal ions that can form an amino complex. The molecule 8, however, has a much longer side chain at the 4-substituent position and the distal nitrogen and 4-N are separated by eight other atoms and are less likely to chelate. The negligible influence of the metal ions on the observed absorption and fluorescence wavelength of 8²² can be understood in these terms.

VIII. Concluding Discussion

To summarize the calculations, the fast electron transfer from the distal nitrogen in the 4-substituent, versus slow charge

transfer from the 9-substituent, is mainly due to the difference in the electronic coupling matrix elements $|V|$ for the two reactions. The extended Hückel calculation yielded a much larger electronic coupling matrix element for the electron transfer from the distal nitrogen attached to the 4-position than that from the distal nitrogen attached to the 9-position. This result is consistent with the "back of the envelope" argument given in section IV.

We have given a reason that we suppose that possible differences in ΔG° play only a minor role. We also know from the experiments² that the different free energies for the two distal amino groups (with pK_a 's of 6 and 8) did not change the direction of the electron-transfer reaction. This pK_a difference corresponds to a free energy difference of about 0.1 eV for the two reactions and, depending on the value of $\lambda + \Delta G^\circ$, will cause a difference in the free energy barrier typically between 0.05 and 0 eV, using an expression in section IV and considering the limits of the case that $|\Delta G^\circ| \leq \lambda$. This difference is small compared to the difference in energy barrier caused by the difference in the electronic coupling matrix elements, $|V|$ (the calculated difference is about ~ 0.2 eV). We note that the energy barrier at the transition state is lowered by an amount $|V|$ when the reaction is adiabatic. Accordingly, the electron transfer from the 4-substituent can still dominate over that from the 9-substituent even when it has a less favorable ΔG° . The low yield of the fluorescence for **4** and **5** in Table 1, ~ 0.05 , corresponds to an intramolecular electron-transfer rate on the order of 10^{10} s^{-1} , if the natural fluorescence lifetime is on the order of 5 ns.

The proposed mechanism provides an explanation of the various observations.^{1,2,6} Further experiments, particularly real-time observations of the absorption and fluorescence spectra, would be of interest. Direct measurement of a charge-transfer fluorescence spectrum of $|e_{CT1}\rangle$ would be of particular help in establishing the ΔG^0 of the $|e\rangle \rightarrow |e_{CT1}\rangle$ electron transfer.

Acknowledgment. We are pleased to acknowledge the support of this research by the Office of Naval Research and the National Science Foundation. It is a real pleasure to dedicate this article to Professor Norboru Mataga, whom one of us (R.A.M.) has had the pleasure of knowing for many years and of appreciating his incisive research in photophysics and in electron-transfer processes.

Appendix A: Calculations for the Coupling Matrix Element

To obtain the coupling matrix element, a two-state picture is used for each of the two electron-transfer reactions. In the two-state model, the Hamiltonian is written as²³

$$H = \begin{pmatrix} H_{DD} & V \\ V & H_{AA} \end{pmatrix} \quad (\text{A1})$$

where H_{DD} and H_{AA} are the energies of the donor and acceptor diabatic states, respectively, and V is the coupling between the two states. When the donor and acceptor states are chosen to be orthonormal to each other, as in the extended Hückel and Hartree–Fock calculations in this study, the energies of adiabatic states, denoted by E_1 and E_2 , are obtained directly from the diagonalization of the Hamiltonian matrix as

$$E_1 = H_{DD} + V \tan \eta, \quad E_2 = H_{DD} - V \tan \eta \quad (\text{A2})$$

where $\tan 2\eta = 2V/(H_{DD} - H_{AA})$. It then immediately follows that

$$V = (1/2)(E_1 - E_2) \sin 2\eta \quad (\text{A3})$$

As indicated by eq A3, $E_1 - E_2$ has a minimum when $\sin 2\eta = 1$, and $E_1 - E_2 = 2V$. Equation A3 then provides a way of calculating the coupling matrix element V , if the energies of two adiabatic states can be changed continuously in the neighborhood of $H_{DD} = H_{AA}$ to give the two adiabatic curves. The coupling matrix element is one-half of the minimum splitting of the two adiabatic curves.

Supporting Information Available: A table of the coordinates for the atoms in compound **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Note Added after ASAP Posting

This article was released ASAP on 11/08/2001 with a minor error in the Concluding Discussion section. The correct version was posted on 11/14/2001.

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- (22) In their published paper, only data of **7** are presented. It was noted that the experimental results for **6** are similar.
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