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Substituent Effects on Photochemistry of Anthracene-Phenol-Pyridine Triads Revealed by Multireference Calculations

Elvira R. Sayfutyarova, Sharon Hammes-Schiffer*

Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520

Abstract

Inverted region behavior for concerted proton-coupled electron transfer (PCET) was recently demonstrated for biomimetic anthracene–phenol–pyridine molecular triads. Photoexcitation of the anthracene to a locally excited state (LES) is followed by concerted electron transfer from the phenol to the anthracene and proton transfer from the phenol to the pyridine, forming a relatively long-lived charge separated state (CSS). The long-lived CSS and the inverted region behavior associated with the decay from the CSS to the ground state through charge recombination were experimentally observed only for triads with certain substituents on the anthracene and the pyridine. To explain this distinction, we computed the proton potential energy curves in four substituted triads using the complete active space self-consistent-field method and multireference perturbation theory, including solvent effects with a dielectric continuum model. The calculations revealed a local electron-proton transfer (LEPT) state, in which both the electron and proton transfer from the phenol to the pyridine. When the LEPT state is lower in energy than the CSS, it may provide an alternative pathway for fast decay from the LES to the ground state and thereby preclude detection of the CSS and the inverted region behavior. These calculations predict that substituents stabilizing negative charge on the pyridine and destabilizing negative charge on the anthracene will favor the LEPT pathway, while substituents with the reverse effects will favor the CSS pathway, which could exhibit inverted region behavior. These insights about the stabilization of energy-storing charge-separated states have implications for designing and controlling PCET reactions in artificial photosynthetic systems and other energy conversion processes.

Graphical Abstract

*Corresponding author: sharon.hammes-schiffer@yale.edu.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Optimized Cartesian coordinates for the molecular triads, details of electronic state identification, computed CASSCF electronic states, NEVPT2 energy corrections for dynamic correlation, solvation free energies, partial atomic charges for selected calculations, SVD analysis for active space consistency evaluation.

Introduction

Proton coupled electron transfer (PCET) is ubiquitous in organic molecules and enzymatic reactions.^{1–9} A well-known example of a system that exhibits multi-site PCET is photosystem II, where the oxidation of tyrosine is accompanied by proton transfer from tyrosine to the hydrogen-bonded histidine.^{10–15} To understand and emulate the PCET reactivity in the tyrosine-histidine pair of photosystem II and other biological systems, a wide range of artificial model systems containing phenols as tyrosine mimics in proximity to various proton acceptors, which are often nitrogen-based, have been synthesized and characterized.^{5, 16–28} These model systems have provided fundamental insights into PCET processes and are guiding the design of advanced biomimetic systems.

Recently designed biomimetic anthracene–phenol–pyridine molecular triads have attracted special attention because they exhibit Marcus inverted region behavior.²⁹ In particular, the rate constant for PCET charge recombination decreases with increasing driving force in the inverted region, where the driving force is greater than the reorganization energy. In these anthracene–phenol–pyridine triads, An–PhOH–py, an anthracene unit is linked to the planar hydrogen-bonded phenol-pyridine dyad via a CH₂ bridge (Figure 1). Photoexcitation of anthracene to its locally excited state (LES) transforms it into a strong oxidant and initiates PCET reactions within the triad.^{29–30} Electron transfer from the phenol to the locally-excited anthracene concerted with proton transfer from the phenol to the pyridine results in the charge separated state (CSS), An^{•+}–PhO[•]–pyH⁺, which has been characterized by transient absorption spectroscopy in the visible and mid-infrared regions.

The experimentally observed inverted region behavior is associated with the decay from the CSS to the ground state (GS) by charge recombination.²⁹ However, this decay from the CSS to the GS was observed for only some of the triads studied, depending on the pyridine and anthracene substituents.²⁹ Specifically, the triads denoted **1–3** in Ref. 29 exhibited an experimentally observable long-lived transient CSS intermediate and demonstrated inverted region behavior. The triads denoted **4–8** in Ref. 29 decayed from the LES to the GS without observation of the CSS intermediate and therefore did not demonstrate inverted region behavior. Note that all of these triads are thought to undergo some type of PCET process because the lifetime of the LES is much shorter than the lifetime of the LES in isolated anthracene molecules. Moreover, this fast quenching of the LES is absent upon substitution of the transferring hydrogen with a methyl group for triad **6**,³⁰ and triads **1–3** and **6** exhibit

kinetic isotope effects,^{29–30} implicating proton transfer. The decay pathway for triads **4–8** from the LES to the GS, inferred to involve some type of PCET, is not clear.

Herein, we examine the electronic structure of four different triads from Ref. 29 (Figure 1). Triads **1** and **3** exhibited the relatively long-lived CSS and the inverted region behavior for charge recombination from the CSS to the GS, while triads **4** and **6** did not exhibit this long-lived CSS or the associated inverted region behavior. Our objective is to use high-level *ab initio* multireference calculations to characterize the photochemistry and the PCET reactions within these triads and to provide an explanation for the different behavior observed experimentally for these two types of triads. These calculations provide general design principles that have implications for the development of more effective energy-conversion catalysts.

Computational Methods

We used the GS geometries obtained from Ref. 29 for our multireference calculations. These GS geometries were optimized in the gas phase using density functional theory (DFT) with the 6–31+G** basis set^{31–33} and the B3LYP functional^{34–35} using the Q-Chem software package.³⁶ The one-dimensional proton coordinate axis was defined to be the line connecting the positions of the hydrogen atom bonded to the donor oxygen atom and to the acceptor nitrogen atom for the GS structure. The position of the hydrogen atom bonded to the donor oxygen atom was determined by its position in the optimized GS geometry. The position of the hydrogen atom bonded to the acceptor nitrogen atom for the GS geometry was determined using the bond length and angles for this hydrogen in the CSS structure optimized with constrained DFT.^{37–38} The calculations used to generate the proton potential energy curves were performed with the nuclei other than the transferring hydrogen fixed at the optimized GS equilibrium geometry. The optimized GS and CSS geometries are similar, except for the angle between the anthracene and the phenol-pyridine dyad and the hydrogen position. The root-mean-square deviation of atomic positions for the four triads studied, excluding the transferring hydrogen, ranges from 0.775 to 1.445 Å for the entire triad and ranges from 0.050 to 0.156 Å for the phenol-pyridine dyad (Table S5). For comparison, we also performed single-point calculations at the optimized CSS geometries (Table S25).

To obtain a balanced description of the electronic states, we used the state-averaged complete active space self-consistent-field (CASSCF)^{39–40} method with N-electron valence state perturbation theory (NEVPT2)^{41–43} to include both static and dynamical correlation. To characterize the most relevant electronic states, we computed seven electronic states for triads **1**, **3**, and **6** and eight electronic states for triad **4** in a state-averaged manner with CASSCF, followed by strongly contracted NEVPT2 calculations for each grid point (see the Supporting Information for details). These calculations were performed for 24 points along the one-dimensional proton coordinate axis. The RHF calculation for the singlet ground state, as well as the subsequent CASSCF and NEVPT2 calculations, were performed using the 6–31++G** basis set^{31–33} using the PYSCF quantum chemistry package.⁴⁴

To construct the active spaces for the multireference calculations, we used the automated π -orbital space (PiOS) method,⁴⁵ which is well-suited for treating molecular complexes with

multiple π -systems, such as these anthracene–phenol–pyridine triads. In the case of phenol, the oxygen atom was included in the set of atoms forming the π -system, as it can participate in conjugation when the hydrogen moves toward the acceptor nitrogen atom. The PiOS algorithm built 14 (7 occupied + 7 virtual) π -orbitals for the anthracene fragment, 7 (4 occupied + 3 virtual) π -orbitals for the phenol segment, and 6 (3 occupied + 3 virtual) π -orbitals for the pyridine. Here we set the algorithm to select only two HOMOs and two LUMOs for each of the three conjugated fragments. This procedure resulted in a (12o, 12e) active space (Figure S5), which is computationally affordable. To confirm that the active space remained consistent (i.e., the same set of orbitals) along the proton transfer coordinate, we performed the singular value decomposition analysis for 1) the overlap between the initial active space constructed from the atomic orbitals and the overlap-optimized active space at a given grid point (see Ref. ⁴⁶), and 2) the overlap between the optimized active spaces at consecutive (i.e., ($N-1$)th and N th) points on the grid. For benchmarking purposes, we performed density matrix renormalization group (DMRG)⁴⁷ CASSCF calculations with a (28o, 27e) active space for certain geometries (Table S29).

To include the effects of dichloromethane solvent, we used the frequency resolved cavity model (FRCM),⁴⁸ which is a dielectric continuum model with molecular-shaped cavities. The solute charge densities for the electronic states of interest were modeled with partial charges on the atoms of the solute molecule at a given geometry. The atomic charges for each electronic state at each position of the transferring proton were obtained from the gas phase CASSCF calculations with a modified Löwdin/Mulliken procedure⁴⁹ using the atomic natural orbitals (see page S40 of SI and Table S28 for a comparison to atomic charges obtained using the intrinsic atomic orbitals). For dichloromethane CH₂Cl₂, we used the static dielectric constant $\epsilon_0 = 8.93$ and the optical dielectric constant $\epsilon_\infty = 2.028346$. This model provides the equilibrium solvation free energy for each electronic state at each geometry, leading to proton potential energy curves that include solvent effects. Note that this approach does not include the effect of the solvent on the solute charge density and provides only qualitatively accurate solvation free energies. Nevertheless, inclusion of these solvent effects at even a qualitative level is important for the analysis herein because the CSS is significantly more stabilized by solvent than the other states studied.

Results and Discussion

We studied the singlet electronic states of four different anthracene–phenol–pyridine triads (Figure 1) to understand the interplay among the relevant electronic states during the PCET process. According to our calculations, three types of excited states are observed in these triads: 1) locally excited states (LESSs), which exhibit negligible change in the electronic charge distribution with respect to the GS; 2) charge separated states (CSSs) associated with the An^{•-}–PhO[•]–pyH⁺ diradical resulting from electron transfer from the phenol to the anthracene and proton transfer from the phenol to the pyridine; and 3) local electron-proton transfer (LEPT) states associated with the An–PhO[•]–pyH[•] diradical resulting from electron and proton transfer from the phenol to the pyridine. The CSS was observed experimentally for triads **1** and **3** but not for triads **4** and **6**. The LEPT state is local in the sense that both electron and proton transfer occur within the hydrogen-bonded phenol-pyridine dyad region, in contrast to the CSS, which involves long-range electron transfer from the phenol to the

anthracene. The degree of charge separation is much smaller in the LEPT state than in the CSS due to a shorter electron transfer distance and delocalization of the electron density over both the phenol and the pyridine through the conjugated π system in the LEPT state. The details of the state identification procedure, as well as the partial atomic charges of the relevant states (Tables S15–18), are given in the Supporting Information.

To elucidate the characters of the electronic states, we performed a partial atomic charge analysis for each of these states before and after proton transfer for triads **1** and **6** (Tables S14–S17, Figure 2). Prior to proton transfer, the GS and LES have negligible charge transfer character, while the LEPT state has a small degree of charge separation between the phenol and the pyridine (0.15 on the phenol and –0.16 on the pyridine for triad **1**) and the CSS has a significant amount of charge transfer to the anthracene (0.84 on the phenol-pyridine and –0.88 on the anthracene for triad **1**). As the proton transfers from the donor oxygen atom to the acceptor nitrogen atom, the GS structure can be stabilized via conjugation and delocalization of the π -electrons within the phenol-pyridine dyad. The GS exhibits some charge separation between the phenol and pyridine after proton transfer (–0.71 on the phenol and 0.70 on the pyridine for triad **1**). The LEPT state is a diradical excited state with partial electron transfer from the phenol to the pyridine with respect to the GS (–0.18 on the phenol and 0.15 on the pyridine for triad **1**) after proton transfer. In contrast, the CSS has a significant amount of charge transfer to the anthracene (0.88 on the phenol-pyridine and –0.92 on the anthracene for triad **1**) after proton transfer, similar to its charge separation prior to proton transfer.

We tracked five states along the one-dimensional proton coordinate axis: the GS, two LESs, the lowest CSS, and the lowest LEPT state. These five states constitute the lowest energy states prior to proton transfer for all triads except triad **6**. Note that we observe two LESs that are always lower than the CSS when the hydrogen is on the donor oxygen atom in the CASSCF calculations. The ordering of these states, however, changes after dynamic correlation and solvent effects are included. We continued to track these same five states along the proton coordinate, although these states did not remain the lowest five states for all positions of the transferring hydrogen. Figures 3 and 4 show these five states computed along the proton transfer coordinate at two different level of theory. Figure 3 was obtained from CASSCF calculations with solvation free energies included using the FRCM method based on the CASSCF state charge distributions. Figure 4 was obtained by adding a correction for dynamic correlation to the energies in Figure 3 using the NEVPT2 method. The solvent effects have negligible impact on the LESs and the LEPT states, as shown by the CASSCF energies without inclusion of solvent effects given in Tables S6–S9 and Figure S1. However, we observe significant solvent stabilization of the CSS due to the long-range charge separation and associated dipole moment. This solvent stabilization decreases the energy gap between the GS and the CSS in solvent compared to gas phase.

On the basis of spectroscopic measurements, the excitation energy E_0-0 from the GS to the LES was estimated to be 2.97 eV for triads **1**, **3**, and **4** and 3.20 eV for triad **6**.²⁹ Our theoretical estimates at the optimized GS structure are 3.57–3.58 eV for triads **1** and **3**, 3.92 eV for triad **4**, and 3.48 eV for triad **6** (Tables S23–S24). Note that these GS structures were optimized at the DFT level, and the GS minima are located at slightly different geometries at

the CASCCF+NEVPT level. We have determined that the differences between the computed and experimental excitation energies can be attributed to the state averaging over multiple states with different character. The state-averaging procedure using the same set of molecular orbitals for all electronic states and variationally optimizing an average energy ensures orthogonality of the electronic states but can lead to inaccuracies in the description of individual excited states. For comparison, we also performed these multireference calculations at the optimized GS structure averaging over only the lowest two states. In this case, the excitation energy to the LES decreased to 3.18–3.20 eV for triads **1**, **3**, and **4** and to 3.44 eV for triad **6** (Table S23), leading to much better agreement with the experimental values. Note that these excitation energies correspond to the lowest LES after inclusion of all energy corrections.

When the hydrogen is on the acceptor nitrogen atom, the CSS is lower than the LEPT state for triads **1** and **3**, whereas the LEPT state is lower than the CSS for triads **4** and **6**. Note that additional LEPT states become lower than the CSS for triads **4** and **6** but are not shown in the figures. The presence of the CN group on the pyridine or the absence of the CN group on the anthracene lowers the energy of the LEPT state relative to the energy of the CSS. Specifically, the CN group on the anthracene for triads **1**, **3**, and **4** stabilizes the electron on the anthracene and therefore stabilizes the CSS for these triads compared to triad **6**, which does not have a CN group on the anthracene. For triad **4**, however, the CN group on the pyridine counteracts this effect by stabilizing the electron on the pyridine, thereby stabilizing the LEPT state compared to the CSS.

Thus, the lowest excited state when the hydrogen is on its acceptor nitrogen is the CSS for triads **1** and **3** and the LEPT state for triads **4** and **6** (Figure 5). Interestingly, the long-lived transient CSS is observed experimentally for triads **1** and **3** but not for triads **4** and **6**. Moreover, charge recombination from the CSS to the GS leads to inverted region behavior for triads **1** and **3**, but such behavior cannot be observed for triads **4** and **6**. Note that the LEPT state is an excited state of the GS proton-transferred tautomer (Figure 5) and is thought to relax via the GS proton-transferred tautomer in most related dyads.⁵⁰ Our calculations show that the energetically more favorable LEPT state could provide an alternative pathway for fast decay to the GS for triads **4** and **6** because of the larger electronic coupling and smaller reorganization energy expected for the transition from the LEPT state to the GS compared to charge recombination from the CSS. This alternative decay pathway provides an explanation for why the CSS, as well as the inverted region behavior, is not observed experimentally for triads **4** and **6**.

The formation of LEPT structures via excited state intramolecular proton transfer has been investigated in hydrogen-bonded phenol-pyridines^{51–52} and similar phenol-N-base dyads.^{53–65} For molecules similar to the phenol-pyridine dyad, the excited diradical LEPT state can undergo ultrafast radiationless decay to the GS,^{52, 55, 62} and the rates of this decay depend on the polarity of the solvent. The exact mechanism of this ultrafast radiationless decay in such phenol-base systems is not clear, but it has been proposed to occur through conjugation and π -electron delocalization in the phenol-pyridine dyad and/or conformational relaxation.^{52, 55, 62} The LEPT state for 2-(2'-hydroxyphenyl)pyridine, which is the dyad most closely related to the triads studied herein, is non-fluorescent at room

temperature.⁵² However, in non-polar, frozen solvent at 77 K, very weak emission from the proton-transferred tautomer of this dyad is observed at ~500 nm (2.48 eV).⁵² This emission energy is consistent with our calculated energy difference between the LEPT state and the GS after proton transfer in the gas phase: 2.35 – 2.42 and 2.77 – 2.86 eV for triads **4** and **6**, respectively, depending on the geometry (Table S25). This consistency provides experimental corroboration for the proposed LEPT state in the triads.

To test the dependence of the state ordering on the molecular geometry, we also performed the CASSCF/NEVPT2 calculations at the optimized CSS geometry, which favors the CSS more than any other geometry, for all four triads. We found that the state ordering is the same as that observed at the optimized GS geometry with the proton transferred in the gas phase for all four triads (Table S25). The inclusion of solvation effects changes the state ordering only for triad **4**, where the CSS state becomes slightly lower in energy than the LEPT state with the proton transferred (Table S25, Figure S4). Given the approximations inherent to the FRCM approach with fixed partial atomic charges obtained from gas phase CASSCF calculations, this energy difference between the CSS and LEPT state for triad **4** is smaller than the accuracy of the calculated solvation free energies. Moreover, the timescale for the solvent relaxation to fully stabilize the CSS may be slower than the decay from the LEPT state to the GS for triads **4** and **6**. Nevertheless, the LEPT state is still lower in energy than the CSS for triad **6** and is much more energetically accessible in triad **4** compared to triads **1** and **3** at the optimized CSS geometries. These results indicate that the qualitative conclusions regarding the LEPT and CSS states for the four triads are valid at the optimized CSS geometry as well as the optimized GS geometry.

Conclusion

We studied the electronic structure of four anthracene-phenol-pyridine triads to understand the impact of the substituents on the decay pathway from the LES to the GS. Specifically, our goal was to explain the experimental observation of the long-lived CSS, as well as the inverted region behavior associated with the charge recombination to the GS, for triads **1** and **3** but not for triads **4** and **6**. To address this issue, we computed the ground and excited electronic states in the anthracene-phenol-pyridine triads using multireference methods including both static and dynamic correlation and including solvent effects with a dielectric continuum model. These calculations identified a local electron-proton transfer state, denoted the LEPT state, in which both the electron and proton transfer from the phenol to the pyridine, in contrast to the CSS, in which the electron transfers from the phenol to the anthracene. The LEPT state has a substantially smaller degree of charge separation than does the CSS state and is expected to decay more rapidly to the GS due to the presumably larger electronic coupling and smaller reorganization energy. Nonadiabatic dynamics simulations would be required to fully elucidate the photochemical mechanism.

Our calculations indicate that the combined substituent effects on pyridine and anthracene determine whether the CSS or the LEPT state is lower in energy after proton transfer from the phenol to the pyridine. For triads **1** and **3**, which have a CN substituent on the anthracene, the CSS is lower in energy than the LEPT state after proton transfer due to stabilization of the electron on the anthracene. For triad **6**, which does not have any CN

substituents, and triad **4**, which has a CN substituent on the pyridine to counteract the effect of the CN substituent on the anthracene, the LEPT state is lower in energy than the CSS after proton transfer. These differences provide an explanation as to why the relatively long-lived CSS is observable for triads **1** and **3** but not for triads **4** and **6**. In particular, the lower-lying LEPT state for triads **4** and **6** may provide an alternative pathway for fast decay from the LES to the GS and thereby prevent detection of the CSS intermediate and the inverted region behavior. These calculations predict that substituents stabilizing negative charge density on the pyridine and destabilizing negative charge density on the anthracene will bypass the CSS and inhibit inverted region behavior, while substituents with the reverse effects will stabilize the CSS and allow the possibility of inverted region behavior. These design principles may guide the development of photoinduced PCET systems with a sufficiently stable CSS to allow the experimental observation of inverted region behavior. Moreover, the stabilization of energy-storing charge-separated states has implications for a wide range of energy conversion processes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Chemical structures of the studied triads with the notation used in Ref. 29.

Figure 2.

Charges on the anthracene, phenol, and pyridine fragments for the GS, CSS, and LEPT state before (left) and after (right) proton transfer obtained from CASSCF calculations for triad **1**. The small deviation of the sum of the charges of the fragments from zero for each electronic state is the partial charge on the bridging CH₂ group.

Figure 3.

Electronic states obtained for the four different triads from CASSCF calculations with solvation free energies included using the FRCM approach. The excited states are colored according to their character, as determined from analysis of the electronic charge distribution for each state at each proton coordinate. The apparent discontinuities occur when the adiabatic states change character (Figure S3), and they are influenced by minor numerical errors in the solvation free energies due to mixing of the states in these regions.

Figure 4.

Electronic states obtained for the four different triads from CASSCF+NEVPT2 calculations with solvation free energies included using the FRCM approach. The excited states are colored according to their character, as determined from analysis of the electronic charge distribution for each state at each proton coordinate. The apparent discontinuities occur when the adiabatic states change character (Figure S3), and they are influenced by minor numerical errors in the solvation free energies and NEVPT2 corrections due to mixing of the states in these regions.

Figure 5.

Schematic representation of the ground state and the lowest excited state when the transferring hydrogen is on its acceptor atom as a function of the proton coordinate for the four different triads. For the LEPT state of Triads 4 and 6, both the phenol and pyridine rings are slightly negatively charged, and the transferring proton contributes a slightly positive partial charge, leading to the overall transfer of positive charge from the phenol to the pyridine upon proton transfer (Table S18).