JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

Hydrolytic Stability of *N*-Methyl-2,6-dimesityl-4,4′-Pyrylogen Bis-tetrafluoroborate

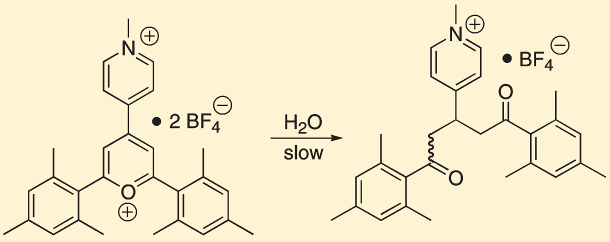
Tamer T. El-Idreesy*[,§] and Edward L. Clennan*[,†]

[§]Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

[†]Department of Chemistry, University of Wyoming, 1000 East University Avenue, Laramie, Wyoming, United States

Supporting Information

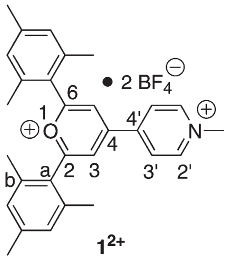
ABSTRACT: The synthesis and characterization of a new mesityl ring-substituted pyrylogen with a substantially decreased rate of reaction with water is reported. Computational and experimental data are presented that suggest that addition of water to the pyrylium ring of this highly sterically shielded pyrylogen is reversible. On the other hand, experimental data suggest that the overall hydrolysis of this new sterically shielded pyrylogen, but not the parent pyrylogen, is irreversible. Two potential explanations for this behavior are presented and discussed. These results provide important new information that can be used to design and synthesize new electron transfer sensitizers that can be used even in highly aqueous environments.



INTRODUCTION

In 2008 we introduced pyrylogens, **PY**$^{2+}$, as a new type of electron-transfer sensitizer.[1−7] These new materials incorporated a pyrylium ring that endowed them with ideal optical and electrochemical properties and a pyridinium ring that together ensured formation, upon reaction with a substrate (**S**), of a repulsive cation-radical/cation-radical pair whose rapid separation (k_{SEP}) competitively inhibited return electron transfer (RET in Scheme 1).

These pyrylogens were shown to behave as electron-transfer sensitizers; unfortunately, however, they also slowly reacted with adventitious water even in scrupulously dried acetonitrile.[1] Previous studies of pyrylium cation reactions with water suggested that the reaction was initiated by nucleophilic attack at position 2.[8−10] Consequently, we postulated that introducing mesityl (2,4,6-trimethylphenyl) groups in positions 2 and 6 in the pyrylium ring would increase hydrolytic stability. The *o*-methyl groups would force the aryl rings to adopt a near-perpendicular geometry relative to the pyrylium core and afford steric hindrance to nucleophilic attack at these positions. In this paper, we describe the synthesis and properties of this target molecule, **1**$^{2+}$, and preliminary results on its hydrolytic stability.



1^{2+}

RESULTS AND DISCUSSION

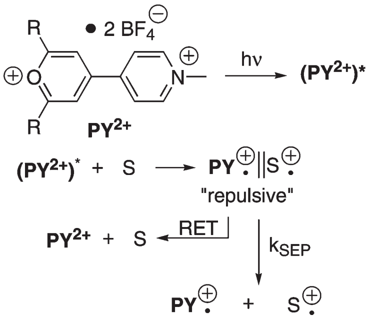
The synthesis of **1**$^{2+}$ followed the route that was previously utilized to make other 2,6-diaryl pyrylogens as shown in Scheme 2.[1−7] However, the steric bulk associated with the 2,4,6-trimethylphenyl (mesityl) groups reduced the rates of both the condensation reaction to form the 1,5-diketone and the oxidative cyclization step and required extended reaction times and harsher reaction conditions than used for the formation of the analogues in which the mesityl are replaced by phenyl groups.[1,6] For example, the final oxidative cyclization step in the reaction sequence shown in Scheme 2 required refluxing at an elevated temperature of 95 °C for 2 days to give a 57% yield of **1**$^{2+}$. In contrast, *N*-allyl-2,6-diphenyl-4,4′-pyrylogen bis-tetrafluoroborate[6] formed by oxidative cyclization in 73% yield by just stirring the reaction mixture at 80 °C for 30 min.

The electrochemical and photophysical properties for **1**$^{2+}$ are compared to those for the parent compound, *N*-methyl-2,6-diphenyl-4,4′-pyrylogen bis-tetrafluoroborate, **2**$^{2+}$, and to 2,4,6-triphenylpyrylium cation, **TPP**$^+$, in Table 1. Remarkably, despite the substantially increased electron-donating ability of mesityl in comparison to phenyl, the electrochemical and photophysical behaviors are very similar for these two pyrylogens. For example, the two one-electron reductions of **1**$^{2+}$ to its radical cation and neutral redox partners only differ by 40 mV from those observed in **2**$^{2+}$. However, counterintuitively, despite the greater electron donating ability of the mesityl in comparison to the phenyl rings, the reduction to the radical cation in **1**$^{2+}$ is easier than in **2**$^{2+}$. On the other hand, as anticipated, the second reduction to form the neutral redox state is more difficult in **1**$^{2+}$ than in **2**$^{2+}$.

The structure of **1**$^{2+}$, its radical cation, **1**$^{\bullet+}$, and neutral redox, **1**^{0} partners were explored with the B3LPY/6-31+G(d,p)

Received: June 13, 2011
Published: July 15, 2011

Scheme 1. Pyrylogen Electron Transfer



Scheme 2. Synthesis of 1^{2+}

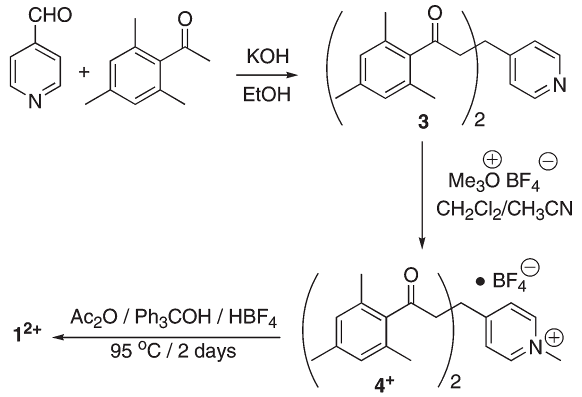


Table 1. Photophysical and Electrochemical Data for 1^{2+}, 2^{2+}, and TPP^+

	1^{2+}	2^{2+}	TPP^+
$E_{1/2}(1)$[a]	0.21	0.17	−0.35
$E_{1/2}(2)$[a]	−0.39	−0.35	−1.53
λmax (ε)[b]	274 (22000)	281 (28000)	277 (18000)
	432 (8000)	328 (10900)	355 (32000)
		440 (20800)	401 (25000)
λ_F[c]	570 (512)	533	465
λ_P[d]	563	565	520
τ_P[e]	22.7 ± 2	35.6 ± 0.2	225 ± 3
$E(S_1)$[f]	57	59	65[g]
$E(T_1)$[ϕ]	56	54	53[g]

[a] In volts versus SCE. [b] Nanometers (L $mol^{-1}cm^{-1}$). [c] In nanometers (nm) at 298 K (77 K in EtOH/HCl(g). [d] In nm at 77 K in EtOH/HCl(g). [e] In milliseconds (ms) at 77 K in EtOH/HCl(g). [f] In kcal/mol. [g] See ref 11.

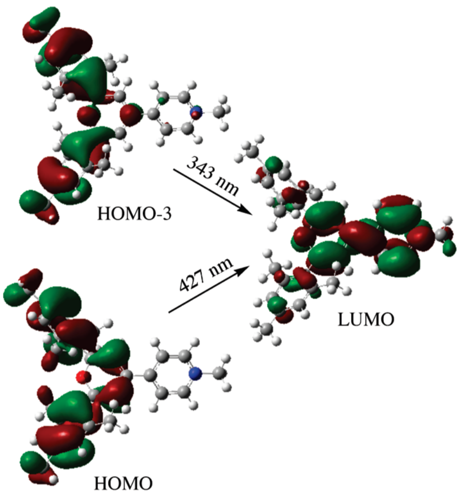


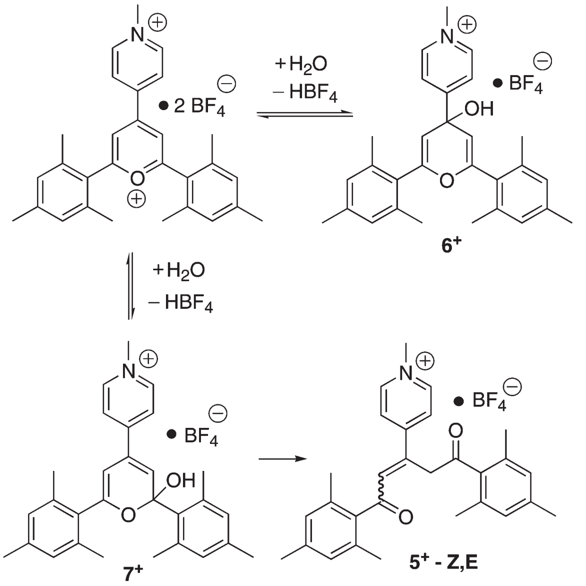
Figure 1. CAM-B3LYP/6-31+G(d,p) low energy transistion in 1^{2+}.

computational model.[12] The interpyrylium-pyridinium ring dihedral angle (>344′3′) is very similar for 1^{2+} (40°) and 2^{2+} (43°) and rather insensitive to the computational level (1^{2+} dihedral angle 41° at B3LYP/6-31G(d) and 40° at B3LYP/6-311+G(2d,p)). In contrast, the intermesityl−pyrylium dihedral angle in 1^{2+} is significantly larger (43°) than the interphenyl−pyrylium ring dihedral angle (16°) in 2^{2+}. In addition, examination of space-filling models indicate that the *o*-methyls in the mesityl rings significantly shield and should protect the 2,6-positions on the pyrylium ring from nucleophilic attack. In comparison to 1^{2+} the radical cation, $1^{\bullet+}$, and neutral, 1^0, redox partners are characterized by nearly coplanar pyrylium and pyridinium rings (>344′3; 40°, 0.25°, and 0.37°), significantly shorter pyrylium−pyridinium inter-ring distances ($d_{44'}$; 1.486, 1.434, and 1.386 Å) but larger mesityl−pyrylium ring dihedral angles (>12ab; 42°, 59°, and 64°), respectively.

The two lowest energy bands in the UV−vis spectrum for **TPP**$^+$ at 401 and 355 nm have been assigned to two perpendicular chromophores polarized in the *X* and *Y* directions, respectively.[13] In 1^{2+}, on the other hand, TD-DFT calculations[14] with the 6-31+G(d,p) basis set suggest that the two lowest energy bands are both primarily charge-transfer bands from the mesityl rings to the pyrylogen core. Excitation energies of charge transfer bands have been reported to be poorly reproduced with time-dependent density functional calculations as a result of their incorrect long-range form of the exchange potential.[15] That was certainly the case here with the computed low energy bands 90 and 167 nm bathochromic of the observed bands at 432 and 274 nm, respectively. (Table 1) In contrast, the Coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP)[16] does a much better job predicting excitation energies of 427 and 343 nm. The major contributors to the two lowest energy absorbances in this calculation were also primarily charge-transfer excitations from the mesityl rings to the pyrylogen core as shown in Figure 1.

Hydrolysis of 1^{2+} in dilute acetonitrile was followed by NMR and resulted in ring cleavage to give a 4:1 mixture of two geometric isomers of 1,5-dimesityl-3-(1-methylpyridinium-4-yl)-2-pentene-1,5-dione, 5^+**-Z,E** in Scheme 3. At the B3LYP/6-31G(d) level, the *Z* isomer is approximately 1.9 kcal/mol more stable than the *E* isomer. A reasonable/economical pathway to these 1,5-diketones is also shown in Scheme 3. The unproductive nucleophilic addition of water to C_4 in 1^{2+} to give 6^+, which cannot lead to a hydrolysis product, is also included in Scheme 3 because the Mulliken charge at C_4, in 1^{2+} at both the B3LYP/6-31+G(d,p) and B3LYP/6-311+G(2d,p) computational levels is substantially greater than at either C_2 or C_6. In addition, 6^+ is 4.5 kcal/mol more stable than 7^+ at the B3LYP/6-31(G) computational level. On the other hand, only 5^+**-Z,E** is observed by NMR in hydrolysis reaction mixtures. Consequently, if 6^+ is formed faster than 7^+, which seems likely given both the greater charge at C_4 than at $C_{2,6}$ in 1^{2+} and the greater stability of 6^+ than 7^+, it must be formed reversibly.

Scheme 3. Mechanism of Hydrolysis of 1^{2+}



The hydrolysis of 1^{2+} can be accurately followed at pH's up to 4.5 at 432 nm. At pH 4.5 1^{2+} and 2,4,6-triphenylpyrylium tetrafluoroborate, **TPP**$^{+}$ disappear at comparable rates despite the greater positive charge on the pyrylogen. The relative hydrolytic stability of 1^{2+} and 2^{2+} are compared at pH 2.5 in Figure 2. The reaction of 2^{2+} is clearly too fast even at pH 2.5 to be followed by conventional UV—vis spectrometry. Nevertheless, a qualitative analysis of the data reveals two interesting observations: (1) the mesityl pyrylogen, 1^{2+}, disappears approximately 20 time more slowly than the parent pyrylogen, 2^{2+}, and (2) the mesityl pyrylogen, 1^{2+} but not the parent pyrylogen, 2^{2+}, is completely consumed at long reaction times. This suggests the intriguing possibility that the hydrolysis of 2^{2+} but not mesityl pyrylogen, 1^{2+}, is reversible. The reversibility of the hydrolysis of simple pyrylium cations have been noted previously.[1−7] The irreversible hydrolysis of 1^{2+} must be due to the inability of 5^{+} to close to regenerate 7^{+} since as argued above the addition of water to generate 7^{+} from 1^{2+} is reversible. There are two possible reasons for the reluctance of 5^{+} to cyclize; (1) the population of 5^{+}**E**, the isomer needed for closure, is too low, or (2) the increased size of the mesityl ring in comparison to the phenyl ring sterically destabilizes the transition state for the formation of 7^{+}. Possibility 1 can be ruled out by comparing the *Z*—*E* energy difference in 5^{+} to the *Z*—*E* energy difference in 5^{+} in which the mesityl rings have been replaced by phenyl rings. At the B3LYP/6-31G(d) computational level the replacement of mesityl by phenyl actually decreases the population of the "closure-ready" *E*-isomer[17] despite the fact that hydrolysis of phenyl-substituted pyrylogen, 2^{2+}, is far more reversible than the hydrolysis of 1^{2+}. Parenthetically, this result also suggests that it is likely that the slow rate of cyclization of the diketone precursor rather than a steric impediment to hydride abstraction plays a dominant role in dramatically slowing down the rate of formation of 1^{2+} (vide supra) in comparison to the rate of formation of 2^{2+} (Scheme 2).

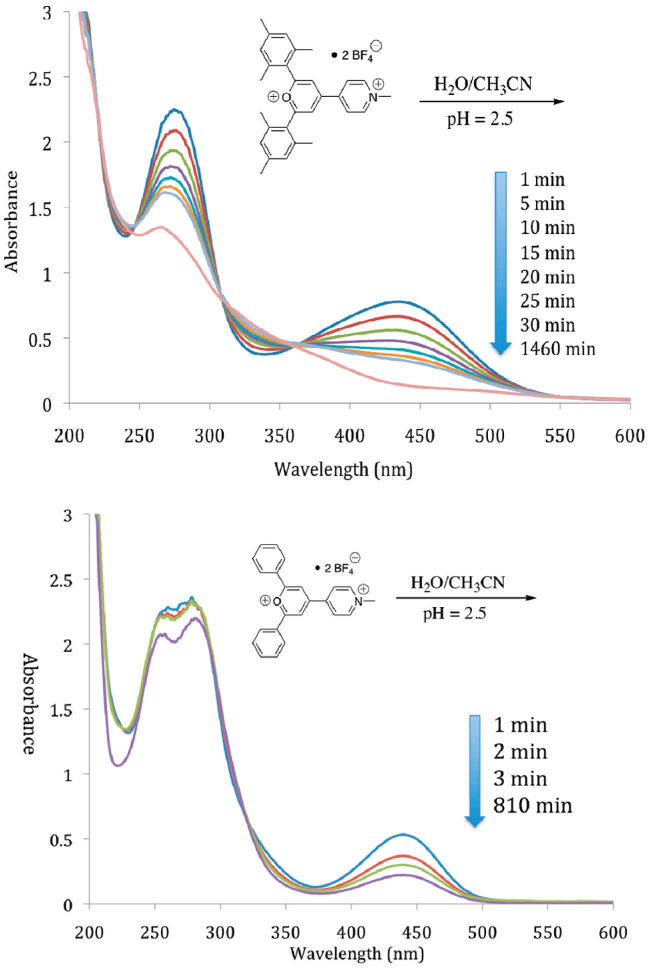


Figure 2. UV—vis hydrolysis data for 1^{2+} (top) and 2^{2+} (bottom).

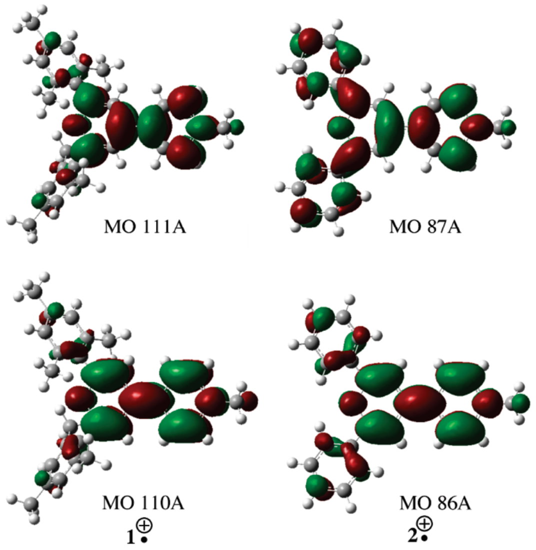


Figure 3. B3LYP/6-31+G(d,p) molecular orbitals involved in the transition responsible for the lowest energy absoeption in the radical cations of 1^{2+} and 2^{2+}.

The mesityl substituted pyrylogen, 1^{2+}, can also be reduced with zinc dust to the radical cation with a λ_{max} at approximately 570 nm. For comparison, *N*-benzyl-2,6-diphenyl-4,4′-pyrylogen radical cation absorbs at 619 nm[7] and the radical cation of 2^{2+} at 614 nm. The molecular orbitals primarily involved in this low energy transition for the radical cations of 1^{2+} and 2^{2+} are shown in Figure 3. They look topographically similar for the two pyrylogen radical cations, but both MOs 110 and 111 in the mesityl-substituted compound are more localized on the pyrylogen core. The hypsochromic shift in the mesityl in comparison to the phenyl pyrylogen radical cation is reproduced by both TD-DFT and CAM calculations. (With the B3LYP/6-31+G(d,p) geometries: TD-DFT **1**$^{\bullet+}$ 546 nm and **2**$^{\bullet+}$ 596 nm; CAM-B3LYP **1**$^{\bullet+}$ 540 nm and **2**$^{\bullet+}$ 579 nm.) This result is consistent with the anticipated increase in the MO energies of the aromatic ring by the inductively donating methyl groups. In fact, in the case of the phenyl-substituted pyrylogen radical cation the transition 86 → 87 appears to be associated with a modest amount of charge transfer from the pyrylogen core out to the phenyl rings. This does not occur in the mesityl-substituted radical cation presumably because of the greater twist out of the plane of the pyrylogen core of the mesityl in comparison to the phenyl rings. The slightly greater predicted hypsochromic shift as the computation method is changed from TD-DFT to CAM for **2**$^{\bullet+}$ (596 nm →579 nm) than for **1**$^{\bullet+}$ (546 nm →540 nm) might also be indicative of the greater charge transfer character of the transition in the phenyl-substituted pyrylogen radical cation.

■ CONCLUSION

In summary, we have successfully synthesized a new pyrylogen with a substantially reduced rate of reaction with water. The reactivity of this pyrylogen with water is approximately equal to that of **TPP**$^+$, suggesting that it can be used successfully under many of the conditions developed for TPP$^+$ reactions. On the other hand, we believe that many of the reactions with **TPP**$^+$ reported in water rely on the substantial amount of pyrylium cation that is in equilibrium with the diketone hydrolysis product.[18] Unfortunately, in the case of **1**$^{2+}$ ring-opening is irreversible which will restrict the use of this pyrylogen in highly aqueous environments. Future studies are focused on increasing the water resistance of pyrylogens without simultaneously preventing ring closure of the hydrolysis product. Of course, the ideal pyrylogen, which will be difficult to design and synthesize, will not react at all with water and will open up the possibility of using dicationic sensitizers, and the advantages they offer, in this valuable environmentally green solvent.

■ EXPERIMENTAL SECTION

Proton and carbon NMR were obtained on a 400 MHz NMR and are referenced to TMS. Pyridine-4-carboxaldehyde (97%), triphenylmethanol (97%), trimethyloxonium tetrafluoroborate, tetrafluoroboric acid (48% by weight in water), 2′,4′,6′-trimethylacetophenone, ferrocene, trifluoroacetic acid, and tetrabutyl ammonium perchlorate were used without further purification. HPLC grade acetonitrile (99.9%) was distilled and stored over activated 3 Å molecular sieves.

Synthesis of 1,5-Dimesityl-3-(4-pyridyl)pentane-1,5-dione, 3. 2′,4′,6′-Trimethylacetophenone (18.96 g; 117.04 mmol) was added to 2.48 g (44.29 mmol) of potassium hydroxide in dilute ethanol followed by 4.18 mL (44.42 mmol) of pyridine-4-carboxaldehyde. The mixture was refluxed for 45 h, cooled, poured on water, and extracted with chloroform. The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Crystallization of the crude residue from dilute ethanol afforded the pure product as a yellowish-white solid (12.60 g, 30.51 mmol, 69%). IR (KBr; cm^{-1}): 3382, 3069, 3024, 2908, 2734, 1934, 1700, 1610, 1597, 1408, 1364, 988, 985, 853, 812, m.p. 114−116. ^{1}H NMR (CDCl$_3$): δ 2.05 (s, 12H, 4 CH$_3$), 2.28 (s, 6H, 2 CH$_3$), 3.11 (dd, *J* = 7.6, 18.8 Hz, 2H, CH$_2$), 3.26 (dd, *J* = 6.0, 18.8 Hz, 2H, CH$_2$), 4.08 (tt, *J* = 6.0, 7.6, Hz, 1H, CH), 6.82 (s, 4H, mesityl CH), 7.28−7.30 (m, 2H, pyridinium CH), 8.53−8.55 (m, 2H, pyridinium CH). ^{13}C NMR (CDCl$_3$): δ = 18.9, 21.0, 34.6, 49.6, 123.5, 128.6, 132.6, 138.7, 149.9, 152.8, 207.7.

Synthesis of *N*-3-(1-Methylpyridinium-4-yl)-1,5-dimesitylpentane-1,5-dione Tetrafluoroborate, 4$^+$. Trimethyloxonium tetrafluoroborate (1.82 g, 12.30 mmol) was added to a solution of 1,5-dimesityl-3-(4-pyridyl)pentane-1,5-dione (4.52 g, 10.94 mmol) in dichloromethane/acetonitrile mixture, and the mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and then the residue was triturated with ether to give the product as yellowish-orange solid which can be used without further purification (5.60 g, 10.87 mmol, 99%). IR (KBr; cm^{-1}): 3276, 3060, 2953, 2925, 2261, 1703, 1643, 1609, 1449, 1060, 985, 858. ^{1}H NMR (CD$_3$CN): δ 2.06 (s, 12H, 4 CH$_3$), 2.27 (s, 6H, 2 CH$_3$), 3.33 (m, 4 H, 2 CH$_2$), 4.22 (m, 1H, CH), 4.25 (s, 3H, CH$_3$), 6.88 (s, 4H, mesityl CH), 8.11 (d, *J* = 6.8 Hz, 2H, pyridinium CH), 8.56 (d, *J* = 6.8 Hz, 2H, pyridinium CH). ^{13}C NMR (CD$_3$CN): δ = 18.1, 20.2, 35.5, 47.7, 48.6, 127.7, 128.4, 132.6, 138.3, 138.9, 144.6, 164.8, 207.7.

Synthesis of *N*-Methyl-2,6-dimesityl-4,4′-pyrylogen Bistetrafluoroborate, 1^{2+}. A solution of tetrafluoroboric acid (11.6 g of 48% solution in H$_2$O, 63.41 mmol) in 10 mL acetic anhydride was gently added under a nitrogen atmosphere to a mixture of *N*-3-(1-methylpyridium-4-yl)-1,5-dimesitylpentane-1,5-dione tetrafluoroborate (2.0 g, 3.88 mmol) and triphenylmethanol (8.3 g, 31.92 mmol) in 40 mL of an acetic anhydride/acetic acid mixture and then heated in oil bath at 95 °C for 2 days. The reaction mixture was cooled to room temperature, and then diethyl ether was added to precipitate the product. The solid was recrystallized from acetonitrile/acetic acid to give the pure product as yellowish-brown solid (1.30 g, 2.23 mmol, 57%). IR (KBr; cm^{-1}): 3068, 2975, 1626, 1609, 1515, 1449, 1190, 1065, 849, 768. ^{1}H NMR (TFA-CDCl$_3$, 1:2): δ 2.34 (s, 12H, 4 CH$_3$), 2.44 (s, 6H, 2 CH$_3$), 4.58 (s, 3H, CH$_3$), 7.17 (s, 4H, mesityl CH), 8.54 (s, 2H, pyrylium CH), 8.63 (d, *J* = 6.4 Hz, 2H, pyridinium CH), 9.01 (d, *J* = 6.4 Hz, 2H, pyridinium CH). ^{13}C NMR (TFA-CDCl$_3$, 1:2): δ 19.6, 20.7, 48.8, 123.3, 125.5, 127.7, 130.2, 138.2, 145.7, 146.6, 148.5, 160.2, 179.9. Mass spectrometry (ESI): M$^{\bullet+}$ = 409.33 (calculated 409.24)

Electrochemical Reduction of Pyrylogen (Cyclic Voltammetry). An acetonitrile solution 2×10^{-3} M in pyrylogen, 0.1 M in Bu$_4$N$^+$ClO$_4^-$, and 2×10^{-3} M in ferrocene as an internal standard was placed in a five-neck electrochemical flask containing a glassy carbon electrode, silver wire reference electrode, and a platinum wire electrode. The cyclic voltammogram was obtained for both the deoxygenated and oxygen-saturated solutions. Deoxygenation of the solution was achieved by bubbling argon for 20 min while the oxygen saturated solution was obtained by bubbling oxygen in the solution for 20 min prior to the electrochemical experiment. In each case, 100 mV and 500 mV were used as scan rates.

Chemical Reduction of Mesityl Pyrylogen (Reduction with Zn Metal): Synthesis of *N*-Methyl-2,6-dimesityl-4,4′-pyrylogen Tetrafluoroborate Radical Cation, 1$^+$. A 3 mL acetonitrile solution containing 8×10^{-5} M of the pyrylogen dication was placed into a side arm attached to a quartz cuvette. This solution was then subjected to three freeze−pump−thaw cycles and then tilted in order to pour the solution into the cuvette containing 200 mg (3.06 mmol) of zinc dust. The UV−vis spectrum was recorded at different time intervals. The solution turned faint violet upon mixing with zinc and the color continued to intensify to reach its maximum after about 2 min then faded until it became colorless after 8 min. The violet color is due to the formation of the pyrylogen radical cation having an absorption maximum around 572 nm and the fading due to its conversion to the neutral species with an absorption maximum at 382 nm. At the end of the reaction (8 min and longer), the concentration of the neutral pyrylogen reaches a steady state and the solution remained colorless.

HYDROLYSIS

Hydrolysis of the mesityl pyrylogen was carried out in dilute acetonitrile and was found to give a 1:4 mixture of two geometrical isomers. The identity of the products were confirmed by NMR and mass spectrometry. ^{1}H NMR (CD_3CN, major isomer): δ 2.21 (s, 6H, 2 CH_3), 2.24 (s, 6H, 2 CH_3), 2.29 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.31 (s, 3H, CH_3), 4.84 (s, 2H, CH_2), 6.92 (s, 2H, aromatic CH), 6.95 (s, 2H, aromatic CH), 7.04 (s, 1H, =CH), 8.11 (d, J = 6.8 Hz, 2H, aromatic CH), 8.66 (d, J = 6.8 Hz, 2H, aromatic CH). ^{1}H NMR (CD_3CN, minor isomer visible signals): δ 2.16 (s, 3H, CH_3), 2.19 (s, 6H, 2 CH_3), 2.27 (s, 6H, 2 CH_3), 4.10 (d, J = 0.8 Hz, 2H, CH_2), 4.28 (s, 3H, CH_3), 7.84 (d, J = 6.8 Hz, 2H, aromatic CH), 8.51 (d, J = 6.8 Hz, 2H, aromatic CH). Mass spectrometry (EI): $M^{\bullet +}$ 426.33 (calculated 426.24)

KINETICS OF THE HYDROLYSIS REACTION

The hydrolysis of mesityl pyrylogen, **1**$^{2+}$, phenyl pyrylogen, **2**$^{2+}$, and the **TPP**$^+$ was conducted in various phosphate buffer solutions at different pH values (pH = 2.5, 3, 4.5, and 6.5). Identical concentrations of each compound in acetonitrile were prepared, and identical volumes of each solution was added to the buffers. The hydrolysis reaction was followed by recording UV−vis spectra at different time intervals. The change in absorbance was monitored at 432, 442, and 404 nm for **1**$^{2+}$, **2**$^{2+}$, and **TPP**$^+$, respectively. These wavelengths were chosen because they represent the long wavelength maximum for each compound and are devoid of interfering absorbance from the hydrolysis products. The pseudo-first-order rate constant for hydrolysis of **1**$^{2+}$ at pH 2.5 under these carefully controlled conditions was 0.042 ± 0.001 min^{-1}. The phenyl pyrylogen, **2**$^{2+}$, reacted too fast to allow determination of a rate constant over the preferred 3-half-lives using the conventional UV−vis method, however, it is clear that it disappeared approximately 20 time more rapidly than the mesityl-substituted pyrylogen, **1**$^{2+}$.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Computational details; UV−vis, fluorescence, UV−vis for reduction, and cyclic voltammogram for **1**$^{2+}$; UV−vis spectra for hydrolysis reactions of **1**$^{2+}$ and **2**$^{2+}$; proton and carbon NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: (T.T.E.) tamertawhid@yahoo.com; (E.L.C.) clennane@uwyo.edu.

ACKNOWLEDGMENT

We thank the USA National Science Foundation (ELC) and the Bibliotheca Alexandrina-Center for Special Studies and Programs (BA/CSSP) under Grant No. BA2007/2008 (TTE) for their generous support of this research.

REFERENCES

(1) Clennan, E. L.; Liao, C.; Ayokosok, E. *J. Am. Chem. Soc.* **2008**, *130*, 7552.

(2) Warrier, A. K. S.; Clennan, E. L. *ARKIVOC* **2009**, *8*, 95.

(3) Clennan, E. L.; Warrier, A. K. S. *Org. Lett.* **2009**, *11*, 685.

(4) Clennan, E. L.; Warrier, A. K. S. *J. Sulfur Chem.* **2009**, *30*, 212.

(5) Warrier, A. K. S.; Clennan, E. L. *J. Phys. Org. Chem.* **2011**, *24*, 22.

(6) El-Idreesy, T. T.; Clennan, E. L. *Tetrahedron Lett.* **2010**, *51*, 1249.

(7) El-Idreesy, T. T.; Clennan, E. L. *Photochem. Photobiol. Sci.* **2010**, *9*, 796.

(8) Berson, J. A. *J. Am. Chem. Soc.* **1952**, *74*, 358.

(9) Williams, A. *J. Am. Chem. Soc.* **1971**, *93*, 2733.

(10) Young, D. N.; Serguievski, P.; Detty, M. R. *J. Org. Chem.* **1998**, *63*, 5716.

(11) Miranda, M. A.; García, H. *Chem. Rev.* **1994**, *94*, 1063.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; M. A. Al-Laham, Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03 (Revision C.02)*; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Balaban, A. T.; Fischer, G. W.; Dinculescu, A.; Koblik, A. V.; Dorofeendo, G. N.; Mezheritskii, V. V.; Schroth, W. Pyrylium Salts: Synthesis, Reaction, and Physical Properties. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1982; Suppl. 2.

(14) Casida, M. E., In *Recent Advances in Density Functional Methods*; World Scientific: Singapore, 1995; Vol. 1.

(15) Dreuw, A.; Head-Gordon, M. *Chem. Rev.* **2005**, *105*, 4009.

(16) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51.

(17) The *E* isomer of **5**$^+$ and its phenyl analogue exist in two rotomers that differ primarily by rotation around the vinyl−CH_2 bond. The rotomer with a C−H bond eclipsed with the double bond is the most stable by approximately 0.96 kcal/mol. The *Z* isomer of **5**$^+$ is 1.9 kcal/mol more stable than the most stable *E* isomer at the B3LYP/6-31G(d) computational level. On the other hand in the phenyl analogue of **5**$^+$ the *Z*-isomer is actually 2.2 kcal/mol more stable than the most stable *E*-isomer. The phenyl analogue, **5**$^+$**-Ph**, behaves very similar to **5**$^+$. The *E* isomer of **5**$^+$**-Ph** exists in two rotomers that differ primarily by rotation around the vinyl−CH_2 bond. The rotomer with a C−H bond nearly eclipsed with the double bond is the most stable by 0.29 kcal/mol.

(18) Gaviña, P.; Lavernia, N. L.; Mestres, R.; Miranda, M. A. *Tetrahedron* **1996**, 4911.