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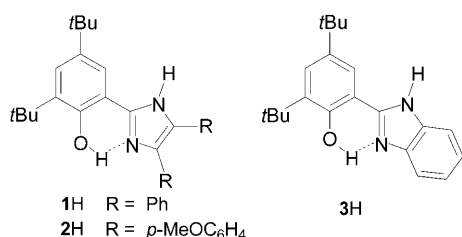
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Phenoxy Radicals Hydrogen-Bonded to Imidazolium: Analogues of Tyrosyl D[•] of Photosystem II: High-Field EPR and DFT Studies**

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Tyrosyl radicals play a crucial role in many biological systems.^[1] The remarkably stable tyrosyl radical, Tyr_D[•] in photosystem II (PSII)^[2] is suggested to be hydrogen-bonded to an imidazolium proton from a nearby histidine residue^[3] (His 190 in higher plants; His 189 in cyanobacteria). Oxidation of Tyr_D to Tyr_D[•] probably proceeds via proton-coupled electron transfer (PCET) with migration of the phenoxy proton to the imidazole group of the adjacent histidine.^[4] Production of chemical analogues of Tyr_D[•] is of much current theoretical and experimental interest. Three recent studies have reported the oxidation of an α -alkylaminophenol derivative by a quasireversible PCET process, to form a phenoxy radical hydrogen-bonded to an alkylammonium center.^[5]

We have reported the synthesis and characterization of (1–3)H,^[6] each of which has an intramolecular hydrogen bond



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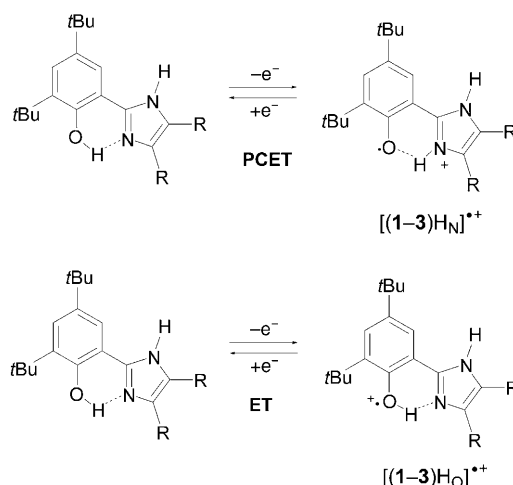
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involving the phenolic proton and an imidazole nitrogen atom. (1–3)H undergo a reversible, one-electron oxidation to form the corresponding radical cation, [(1–3)H]^{•+}. The oxidation of (1–3)H (see Scheme 1) could occur either by



Scheme 1. Possible mechanisms for the oxidation of (1–3)H to [(1–3)H]^{•+}.

PCET to produce an R–O[•]–H–N⁺ arrangement (designated [(1–3)H_N]^{•+}) or by electron transfer (ET) to produce an R–O[•]–H⁺–N arrangement (designated as [(1–3)H_O]^{•+}). Herein, we report the results of high-field EPR studies and DFT calculations that provide a definitive interpretation of the geometric and electronic structure of these [(1–3)H]^{•+} radical cations.

The X-band EPR spectra of [(1–3)H]^{•+} in CH₂Cl₂ at 77 K each consist of a single isotropic signal, centered at $g \approx 2.004$ with a linewidth of about 10 G and no discernible hyperfine splitting.^[6] The absence of hyperfine splitting and the unresolved g -tensor anisotropy preclude any geometric and electronic structural information being obtained from the X-band EPR spectra alone. The lack of resolved proton hyperfine splittings may be taken as evidence for the presence of the [(1–3)H_N]^{•+} forms of the radicals. However, a more positive experimental proof for this conjecture is required and is provided by high-field EPR. W-band (94.0 GHz) high-field EPR spectra, recorded for electrochemically generated [(1–3)H]^{•+} in CH₂Cl₂ solution (1 mM) at 80 K (Figure 1 and Supporting Information) show three well-resolved g values; each spectrum was simulated successfully with $g_x = 2.0063$ – 2.0067 , $g_y = 2.0043$, and $g_z = 2.0022/3$ (Table 1).

Density functional calculations were performed to interpret the W-band EPR spectra of [(1–3)H]^{•+} and to investigate whether these data discriminate between the possible structures [(1–3)H_N]^{•+} and [(1–3)H_O]^{•+} (Scheme 1). As a calibration, the DFT calculations were performed initially for (1–3)H. In each case, the calculated structural parameters were in good agreement with the corresponding data obtained by X-ray crystallography;^[6] the value of each bond length was reproduced to an accuracy of not worse than ± 0.03 Å (see Supporting Information). For the corresponding [(1–3)H]^{•+}(g) radical cations, DFT calculations were performed for the two forms [(1–3)H_N]^{•+} and [(1–3)H_O]^{•+}, and in each

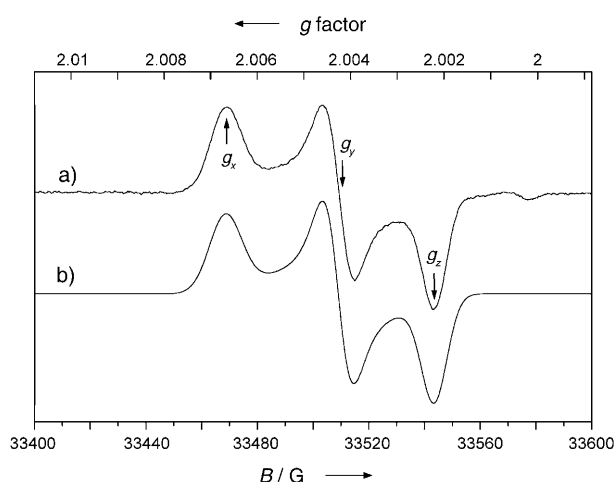


Figure 1. W-band EPR spectra of $[3\text{H}]^+$. a) Spectrum recorded for electrochemically generated $[3\text{H}]^+$ (1 mM) in CH_2Cl_2 at 80 K. b) Spectrum simulated by using the parameters listed in Table 1.

Table 1: Comparison of the experimental W-band g values obtained for $[(1-3)\text{H}]^+$ and those calculated by DFT for $[(1-3)\text{H}_\text{O}]^+$ and $[(1-3)\text{H}_\text{N}]^+$.

Radical		g_x	g_y	g_z	g_{iso}
$[1\text{H}]^+$	exptl	2.0065	2.0043	2.0022	2.0043
$[1\text{H}_\text{N}]^+$	calcd	2.0066	2.0043	2.0023	2.0044
$[1\text{H}_\text{O}]^+$	calcd	2.0034	2.0030	2.0023	2.0029
$[2\text{H}]^+$	exptl	2.0063	2.0043	2.0023	2.0043
$[2\text{H}_\text{N}]^+$	calcd	2.0064	2.0042	2.0023	2.0043
$[2\text{H}_\text{O}]^+$	calcd	2.0036	2.0031	2.0024	2.0030
$[3\text{H}]^+$	exptl	2.0067	2.0043	2.0022	2.0044
$[3\text{H}_\text{N}]^+$	calcd	2.0068	2.0043	2.0023	2.0044
$[3\text{H}_\text{O}]^+$	calcd	2.0044	2.0038	2.0022	2.0035

case convergence to a distinct energy minimum occurred. The difference in energy of the two forms of $[(1-3)\text{H}]^+(g)$, $\Delta E = [E([(1-3)\text{H}_\text{N}]^+) - E([(1-3)\text{H}_\text{O}]^+)]$, is calculated as -4.8 , $+7.7$, and $-26.4 \text{ kJ mol}^{-1}$ for **1H**, **2H**, and **3H**, respectively. These results suggest that $[(1-3)\text{H}_\text{N}]^+$ (the proton-transferred species) is favored for $[1\text{H}]^+(g)$ and $[3\text{H}]^+(g)$, but not for $[2\text{H}]^+(g)$.

The bond lengths calculated for the geometry-optimized structures of $[(1-3)\text{H}_\text{N}]^+$ and $[(1-3)\text{H}_\text{O}]^+$ are listed in Table S12. Each optimized structure involves an intramolecular hydrogen bond: for $[(1-3)\text{H}_\text{O}]^+$, the $\text{H}\cdots\text{N}$ distances are calculated as 1.600 (**1H**), 1.623 (**2H**), and 1.435 Å (**3H**); for $[(1-3)\text{H}_\text{N}]^+$, the $\text{O}\cdots\text{H}$ distances are calculated as 1.832 (**1H**), 1.781 (**2H**), and 1.867 Å (**3H**; see Supporting Information).

The g -tensor parameters calculated by DFT for $[(1-3)\text{H}_\text{N}]^+$ and $[(1-3)\text{H}_\text{O}]^+$ are compared with those observed experimentally in Table 1. In each case, the g values calculated for $[(1-3)\text{H}_\text{N}]^+$ correspond very closely (within 100 ppm) to those observed experimentally; however, this is not true for the g values calculated for $[(1-3)\text{H}_\text{O}]^+$: in particular, each g_x is calculated to be significantly lower (2000–3000 ppm) than the experimental value. Moreover, the W-band EPR spectrum of each $[(1-3)\text{H}]^+$ is consistent with the presence of only a single species. Therefore, we conclude

that all of the radical cations $[(1-3)\text{H}]^+$ in CH_2Cl_2 solution at 80 K are present as $[(1-3)\text{H}_\text{N}]^+$. Consequently, the slight energetic preference ($+7.7 \text{ kJ mol}^{-1}$) for $[2\text{H}_\text{O}]^+(g)$ given by the DFT calculations is considered to be in error.

The nature of the singly occupied molecular orbital (SOMO) and the corresponding unpaired spin-density distribution were analyzed for both $[(1-3)\text{H}_\text{N}]^+$ and $[(1-3)\text{H}_\text{O}]^+$ (Figure 2 and Supporting Information). Each $[(1-3)\text{H}_\text{O}]^+$

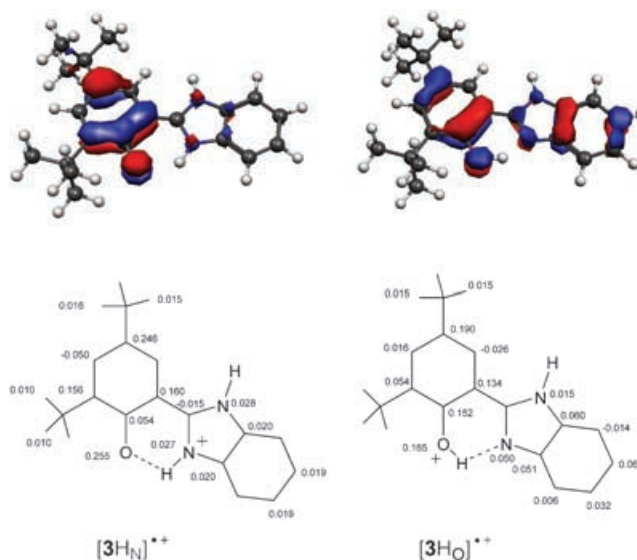


Figure 2. SOMO orbitals (top) and the spin populations (bottom) for $[3\text{H}_\text{N}]^+$ and $[3\text{H}_\text{O}]^+$.

involves a SOMO that extends over the phenol and imidazole rings with phenol/imidazole distributions of the unpaired spin population of approximately 70:30, 40:60, and 25:75 for $[3\text{H}_\text{O}]^+$, $[1\text{H}_\text{O}]^+$, and $[2\text{H}_\text{O}]^+$, respectively. In contrast, the SOMO of each $[(1-3)\text{H}_\text{N}]^+$ is localized primarily on the phenol ring, and the phenol/imidazole distribution of the unpaired spin population is approximately 90:10, 80:20, and 65:35 for $[3\text{H}_\text{N}]^+$, $[1\text{H}_\text{N}]^+$, and $[2\text{H}_\text{N}]^+$, respectively. Thus, these calculations indicate that the electronic structure of $[3\text{H}_\text{N}]^+$ is essentially that of a phenoxyl radical hydrogen-bonded to an imidazolium cation.

For the phenol ring of each $[(1-3)\text{H}_\text{N}]^+$, the typical^[5b,7] pattern of an alternating spin-density distribution is obtained with a significant amount of positive spin population located at the O, C_{ortho} , and C_{para} atoms (Figure 2 and Supporting Information). Also, there is a positive spin population at the phenolic carbon atom that is indicative of a redistribution of the spin density from that of an isolated phenoxyl radical and is attributed to hydrogen-bond formation.^[7] The length of the C–O bond is calculated (Table S12) to be significantly longer in $[(1-3)\text{H}_\text{O}]^+$ (1.332 (**1H**), 1.343 (**2H**), and 1.307 Å (**3H**)) than in $[(1-3)\text{H}_\text{N}]^+$ (1.265 (**1H**), 1.270 (**2H**), and 1.261 Å (**3H**)). The latter values are in excellent agreement with: 1) the length of the C–O bond of **1** \cdot (1.264(5) Å) in the Cu^{II} -phenoxyl radical complex $[\text{Cu}(\text{I}^{\cdot})(\text{I})](\text{BF}_4)_{6a,b}$ and 2) those calculated (1.26–1.27 Å) for the C–O bond of a phenoxyl radical hydrogen-bonded to an imidazolium group.^[7]

The above analysis of the g tensors has illustrated that this approach represents a powerful tool for determining the nature of a phenoxyl radical. Theoretical^[7,8] and experimental studies^[4,5b,9] have indicated that hydrogen bonding to a phenoxyl (or tyrosyl) radical results in a considerable lowering of the g_x value but leaves g_y and g_z essentially unaffected. The g_x values observed for each [(1–3) H_N]^{•+} (2.0065–2.0067, Table 1) are very similar to those observed for hydrogen-bonded tyrosyl radicals; for example, for γ -irradiated crystals of tyrosine·HCl, $g_x = 2.0067$;^[10] Tyr_D[•] of PSII, $g_x = 2.00643$ (radical generated at cryogenic temperature)^[4] and $g_x = 2.00756$ (radical generated at physiological temperature);^[11] Tyr[•] of HSV1 RNR: $g_x = 2.0076$ ^[12] and hydrogen-bonded phenoxyl radical compounds (g_x ranging from 2.0061 to 2.0066).^[5b] These g_x values are significantly lower than those observed for non-hydrogen-bonded tyrosyl radicals; for example, Tyr[•] of *E. coli* RNR, $g_x = 2.0087$,^[9] or of *S. typhimurium* RNR,^[13] $g_x = 2.0089$.

Theoretical studies of the g tensors of aromatic free radicals^[14] indicate that variations in the g_x value of a phenoxyl radical may be understood as arising from a combination of two effects: 1) changes in the unpaired spin population at the oxygen atom, the constituent atom with the largest spin–orbit coupling constant; and 2) changes in the relative energies of two oxygen-based orbitals, the out-of-plane p_z orbital, which makes a significant contribution to the SOMO of a phenoxyl radical, and the in-plane p_y lone pair orbital, the contribution of which to the g shift arises as a result of spin–orbit coupling with the electron in the SOMO. This latter effect produces a magnetic moment along the C–O axis that increases the value of g_x . Formation of an in-plane hydrogen bond stabilizes the p_y lone pair, increases the energy difference between this orbital and the SOMO, and results in less effective spin–orbit coupling and a decrease in the g_x value (vide infra). In this respect, the species [(1–3) H_O]^{•+} represent extreme cases in which the p_y lone pair is directly involved in the O–H bond and therefore, is not involved in efficient spin–orbit coupling with the SOMO, which explains the very low g_x values calculated for these species. For the [(1–3) H_N]^{•+} radical cations, the DFT calculations indicate that the strength of the hydrogen bond increases across this series, that is, the O···HN distance decreases (1.867, 1.832, and 1.781 Å, respectively; see Supporting Information) and leads to a decreased g_x value. For these [(1–3) H_N]^{•+} systems, in addition to the effect of hydrogen bonding on the g_x value, the extent of the delocalization of the unpaired electron onto the imidazole ring must be considered. Across this series, the unpaired spin population at the oxygen atom ($\rho(O) = 0.255$, 0.230, and 0.189, respectively; see Figure 2 and Supporting Information) decreases as a result of the increased delocalization of the unpaired spin density onto the imidazole ring (vide infra), and this also will lead to a decrease in the g_x value. Thus, these two effects operate in the same sense, consistent with the relative magnitudes of the g_x values of [3 H_N]^{•+} (2.0067), [1 H_N]^{•+} (2.0065), and [2 H_N]^{•+} (2.0063).

In conclusion, we have demonstrated that the one-electron oxidation of (1–3)H occurs by a PCET mechanism and produces the corresponding [(1–3) H_N]^{•+}; that is, a phenoxyl radical hydrogen-bonded to an imidazolium

cation. The resolution of the principal g values by W-band EPR spectroscopy and the interpretation of these data by DFT calculations were essential in determining the nature of the [(1–3)H]^{•+} radical cations. Furthermore, the DFT calculations provided valuable insight into the electronic structure of these species. The g_x value of the [(1–3) H_N]^{•+} radical cations is lower than that of a simple phenoxyl radical owing to delocalization of the unpaired spin and orbital-stabilization effects, both of which are directly related to the formation of an O···HN hydrogen bond. These [(1–3) H_N]^{•+} radical cations, notably [3 H_N]^{•+}, represent valuable chemical analogues of Tyr_D[•] in PSII, and further spectroscopic and theoretical studies of these species are currently being undertaken in our laboratories.

Experimental Section

Each radical cation was generated electrochemically by controlled potential coulometry with a platinum-grid working electrode, an Ag/AgNO₃ reference electrode, and a platinum brush in a counter electrode compartment. Each experiment was performed under dinitrogen at –25 °C with the compound (1 mM) in degassed CH₂Cl₂ containing [*n*Bu₄N](BF₄) (0.2 M) as background electrolyte. The solution was transferred under exclusion of dioxygen into a W-band quartz tube (inner diameter 0.7 mm, length 3 cm) with a microsyringe. Each tube was inserted into a cryovial which was immediately frozen and stored in liquid nitrogen.

All calculations were performed with the ORCA program.^[15] Geometry optimizations were performed in redundant internal coordinates by using the pure density functional^[16] BP^[17] method with the TZVP^[18] basis set on all atoms. For both the geometry optimization of the radical species and the g -tensor calculation, the CH₂Cl₂ solvent ($\epsilon = 9.08$) was simulated by the COSMO dielectric continuum approach.^[19] The B3LYP^[20] hybrid DFT method, together with the EPR-II^[21] basis set, was employed for the calculation of the magnetic properties at the optimized geometries of the radical species. Molecular g tensors were calculated by the coupled-perturbed Kohn–Sham method^[22] and the multicenter, spin–orbit mean-field^[23] (SOMF) spin–orbit coupling operator in the resolution-of-the-identity approximation.^[24]

W-band (94 GHz) spectra were recorded on a Bruker Elexsys E680 spectrometer at 80 K with a microwave power of 0.32 μ W, 5 G field modulation amplitude at 10 kHz modulation frequency, and a lock-in time constant of 82 ms. The magnetic field was calibrated against a LiLiF g standard^[25] at microwave frequencies measured by the integrated frequency counter; all spectra were normalized to 94.0 GHz. The simulated spectra and the associated parameters were obtained with Bruker Simfonia software.

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