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Heteroaryl Oxenium Ions Have Diverse and Unusual Low-Energy Electronic States

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Abstract

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Disciplines

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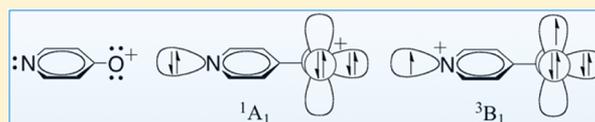
Heteroaryl Oxenium Ions Have Diverse and Unusual Low-Energy Electronic States

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S Supporting Information

ABSTRACT: The electronic state orderings and energies of heteroaryl oxenium ions were computed using high-level CASPT2//CASSCF computations. We find that these ions have a number of diverse, low-energy configurations. Depending on the nature of the heteroaryl substituent, the lowest-energy configuration may be open-shell singlet, closed-shell singlet, or triplet, with further diversity found among the subtypes of these configurations. The 2- and 3-pyridinyl oxenium ions show small perturbations from the phenyl oxenium ion in electronic state orderings and energies, having closed-shell singlet ground states with significant gaps to an n,π^* triplet state. In contrast, the 4-pyridinyl oxenium ion is computed to have a low-energy nitrenium ion-like triplet state. The pyrimidinyl oxenium ion is computed to have a near degeneracy between an open-shell singlet and triplet state, and the pyridinyl oxenium ion is computed to have a near-triple degeneracy between a closed-shell singlet state, an open-shell singlet state, and a triplet state. Therefore, the ground state of these latter heteroaryl oxenium ions cannot be predicted with certainty; in principle, reactivity from any of these states may be possible. These systems are of fundamental interest for probing the spin- and configuration-dependent reactivity of unusual electronic states for this important class of reactive intermediate.



INTRODUCTION

Oxenium ions are hypovalent oxygen-containing reactive intermediates. As isoelectronic analogs of nitrenes, oxenium ions are monovalent cations of formula $R-O^+$, with a positively charged oxygen bearing two nonbonding electron pairs. These species are proposed to be intermediates in a number of important reactions including alkane oxidations,¹ electrochemical oxidations of phenols and phenolates,^{2,3} the oxidative Wagner–Meerwin transposition⁴ the oxidative Hosomi–Sakurai reaction,^{5,6} and a number of other phenolic oxidations and tautomerization reactions.^{7–10} These reactions convert phenols and alkanes into products such as cyclohexadienones, substituted phenols, and oxidized alkanes.^{11–13} They can also be formed by exposing phenols, nitrobenzenes, and anisoles to ionizing radiation,^{14–16} persist in interstellar clouds and planet atmospheres,^{17,18} and are intermediates in iron-mediated enzymatic oxidations of phenols into quinone compounds.¹⁹ Whereas these ions are generally short-lived, they also can form stable complexes with transition metals acting as ligands.²⁰

Recently, the electronic state energies of phenyl oxenium ions and simple derivatives were computed using the CASPT2//CASSCF computational method.²¹ These computational studies suggested that oxenium ions undergo large changes in the electronic state orderings by changing the substituent attached to the formally positive oxygen. For instance, the simplest oxenium ion, OH^+ , has a triplet ground state with a gap of 54 kcal/mol to the lowest energy singlet state.²² Substituting the hydrogen with a phenyl ring leads to the lowest-energy state being the closed-shell singlet ground state.²¹ The singlet ground state of phenyl oxenium ion is supported by both photoelectron spectroscopy and high-level

computational methods. In particular the parent phenyl oxenium ion ($Ph-O^+$) was computed by us to have a singlet–triplet gap (ΔE_{ST}) of -22.1 kcal/mol (CASPT2/pVTZ, a negative value indicates a singlet ground state);²¹ this value compares favorably with the value of -19.8 kcal/mol found from photoelectron spectroscopy experiments.²³ This study also provided evidence that simple ring substituents could lead to significant changes in the ΔE_{ST} .²¹ For example, *m*-aminophenyl oxenium ion was computed to have essentially degenerate singlet and triplet states. Whereas oxenium ions are common reactive intermediates that are important to a diverse groups of chemists, the properties, electronic states, and reactivities of these species are poorly understood. Furthermore, the exuberant change of ca. 70 kcal/mol in the ΔE_{ST} on substituting the hydrogen for a phenyl ring at the oxenium center suggests that the ground-state configurations of these ions are highly sensitive to the substituent.

In this study, we computed the electronic states of heteroaryl oxenium ions using CASPT2//CASSCF computations as well as high-level single-reference methods (CCSD(T), CBS-Q) for ions found to be compatible with a single-reference approach. From these computations, we find that heteroaryl oxenium ions have a number of low-energy electronic states. The lowest energy configuration of these heteroaryl oxenium ions can be the open-shell singlet, closed-shell singlet, or triplet configuration. Therefore, these heteroaryl oxenium ions may prove to

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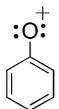
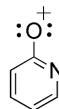
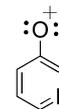
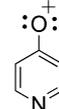
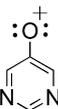
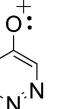
						
Compound Number	1	2	3	4	5	6
ΔE_{ST} (CASPT2/pVTZ)	-22.1	-16.4	-19.2	-3.4	-0.4	-1.3

Figure 1. Computed ΔE_{ST} of the phenyl oxenium ion and heterocyclic oxenium ions.

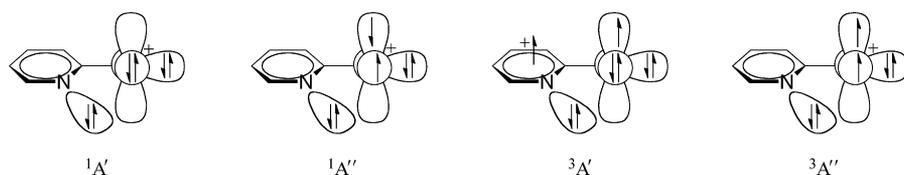


Figure 2. Approximate schematic configurations of the singlet and triplet irreducible representations (C_s) of the 2-pyridinyl oxenium ion 2.

be interesting test cases for studying the spin-selective reactivity of oxenium ions.

COMPUTATIONAL METHODS

The geometries and energies for the different electronic states of the heteroaryl oxenium ions reported in this article were computed using the CASPT2//CASSCF methodology. This methodology has proven to be robust for obtaining accurate energies with appropriate active space selection for excited electronic states.^{24–26} It is worth noting that our calculation of the phenyl oxenium ion (Ph-O⁺) using this same method gives a ΔE_{ST} of -22.1 kcal/mol,²¹ in good agreement with experiment (-19.8 kcal/mol).²³ Additionally, our benchmarks with this method and software for the isoelectronic phenyl nitrene are $+17.2$ and $+31.4$ kcal/mol for the gaps between the 3A_2 - 1A_2 and the 3A_2 - 1A_1 states²¹ (experimental values for these gaps are 18 and 30 kcal/mol, respectively^{27–29}). These benchmarks for related species give us confidence in this computational method for the systems described here for which experimental values have not been reported. Additionally, for those systems that are computed to have lowest energy singlet states that are closed shell and essentially single-reference, we used high-level single reference methods to corroborate the CASPT2 results (CCSD(T) and CBS-Q), for which we found good agreement with the CASPT2 results.

For the CASPT2/CASSCF computations, the active space orbitals included all of the π and π^* orbitals, the in-plane oxygen p orbital, and any lone pair electrons and σ orbitals on nitrogen atoms. Therefore, all of the molecular geometries of the electronic states of 2-, 3-, and 4-pyridinyl oxenium ions were computed at the CASPT2(10,9)/pVTZ//CASSCF(10,9)/pVTZ level. The basis set employed was the flexible ANO-L basis set of Widmark et al., which is of polarized valence triple- ζ (pVTZ) quality.³⁰ All active space orbitals were inspected using the Molden software. The pyrimidinyl and pyridinyl oxenium ions, which have an additional lone pair of electrons and orbital in the active space, were computed at the CASPT2(12,10)//CASSCF(12,10) level of theory.³¹ Except where noted, all of these optimized structures were found to have zero imaginary frequencies, and all of the energies contained a correction for the zero point energy (unscaled). Optimizations were initially carried out using the highest molecular symmetry (C_{2v} or C_s) possible. For those states that had imaginary frequencies under high symmetry, optimizations were performed under reduced symmetry constraints. To keep the state under discussion clear,

we designate the states using the irreducible representations for that configuration at the highest possible molecular symmetry (C_{2v} or C_s), even in cases in which the optimized structure for that electron configuration is nonplanar. (These lower-symmetry geometries are designated with a * in the Tables.) In the few cases where the lone pair of electrons does not contribute significantly (e.g., electron population ~ 2), the orbital containing the lone pair was sometimes replaced with a σ orbital of identical symmetry, also with an occupation of ~ 2 . All CASPT2/CASSCF calculations were performed using the MOLCAS 7.4 software suite.^{32,33} All CCSD(T), B3LYP, and CBS-Q calculations were computed using Gaussian 09.³⁴

RESULTS AND DISCUSSION

The degenerate p orbitals on OH⁺ lead to the triplet being the ground state following a molecular orbital extension of Hund's

Table 1. Energies of the Lowest Irreducible Representations of the 2-Pyridinyl Oxenium Ion 2^a

irreducible representation (C_s)	relative energy adiabatic (vertical), kcal/mol
$1^1A'$	0
$1^1A''$	23.8
$1^3A'$	36.3 [†] (49.0)
$1^3A''$	16.4

^a \dagger indicates that an imaginary frequency was encountered upon optimization under symmetry.

Table 2. Energy of the Irreducible Representations of the 3-Pyridinyl Oxenium Ion 3^a

irreducible representation (C_s)	relative energy (adiabatic) kcal/mol
$1^1A'$	0*
$1^1A''$	22.8
$1^3A'$	41.9
$1^3A''$	19.2

^a* designates a lower-symmetry geometry.

rule. In contrast, substituting the hydrogen for a phenyl ring strongly breaks the degeneracy of the frontier orbitals in the phenyl oxenium ion and leads to the ground state being a singlet (1A_1) with the lowest triplet state (3A_2) 20 kcal/mol higher in energy. Intuitively, one expects substituting carbons for nitrogen in the aryl ring would shift the ΔE_{ST} back toward the triplet because the electron-donating capacity of the ring is

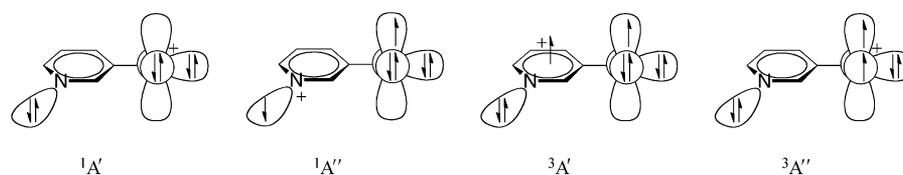


Figure 3. Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of the 3-pyridinyl oxenium ion 3.

Table 3. Energies of the Lowest Irreducible Representations of the 4-Pyridinyl Oxenium Ion 4^a

irreducible representation (C_{2v})	relative energy adiabatic (vertical) kcal/mol
1^1A_1	0
1^1A_2	22.4 [†] (24.8)
1^1B_1	10.6 [†] (9.7)
1^1B_2	33.5
1^3A_1	60.1
1^3A_2	13.4
1^3B_1	3.4
1^3B_2	15.1

^a† indicates that an imaginary frequency was encountered upon optimization under symmetry.

reduced, leading to poorer energy match and poorer mixing of the ring π orbitals with the out-of-plane p orbital on the oxenium center. This is indeed the case. Figure 1 depicts the overall ΔE_{ST} of heteroaryl oxenium ions computed in this study and compares these values to the parent phenyl oxenium ion. It is clear that the addition of nitrogen into the aromatic ring favors the triplet when compared with the phenyl oxenium ion.

2-Pyridinyl Oxenium Ion 2 and 3-Pyridinyl Oxenium Ion 3 Have Only Slightly Perturbed Energetic Orderings from the Phenyl Oxenium Ion 1. For each ion, the lowest energy configuration for each irreducible representation at its highest molecular symmetry was computed. Most of these states can be reasonably well-represented as a single-determinant, and thus the electronic configuration of the major determinant is depicted in Figure 2 to help guide the discussion. As shown in Table 1, the ΔE_{ST} ($1^1A' - 3^1A''$) of the 2-pyridinyl oxenium ion 2 is computed to have a gap of 16.4 kcal/mol between the closed-shell singlet and an n, π^* triplet state. Therefore, there can be little doubt that the ground state of the 2-pyridinyl oxenium ion is the closed-shell singlet state. A very short C–O bond length of 1.205 Å for the ground singlet state implicates a quinoidal structure with significant charge on the carbon para to the oxygen (e.g., a structure resembling an azacyclohexadienonyl cation). These two states are identical to the lowest energy states for the phenyl oxenium ion but with a

Table 4. Energies of the Lowest Irreducible Representations of the Pyrimidinyl Oxenium Ion 5^{a,b,c}

irreducible representation (C_{2v})	relative energy adiabatic (vertical) kcal/mol
1^1A_1	5.8*
1^1A_2	0 [†] (1.4)
1^1B_1	57.4
1^1B_2	77.7
1^3A_1	74.1
1^3A_2	0.4
1^3B_1	57.1 [†] (63.0) ^a
1^3B_2	65.1

^aAn expanded (12,12) active space was needed to achieve convergence. ^b† indicates that an imaginary frequency was encountered upon optimization under symmetry. ^c* designates a lower-symmetry geometry.

reduced energy gap of 6 kcal/mol. (The ΔE_{ST} of phenyl oxenium ion is –22 kcal/mol between 1^1A_1 and 3^1A_2 at the same level of theory.)

Like the 2-pyridinyl oxenium ion 2, as shown in Table 2, the ΔE_{ST} of the 3-pyridinyl oxenium ion 3 is computed to be 19.2 kcal/mol ($1^1A' - 3^1A''$). As with its isomer 2, this value leaves little doubt that the singlet state is the ground state for this ion. The $3^1A''$ state derives from promoting an electron from an oxygen lone pair to the formally oxygen-centered π^* orbital (Figure 3). Because 3-pyridinyl oxenium has the nitrogen in the meta position to the oxenium center, it would be expected that this heteroaryl oxenium ion would vary the least from the phenyl oxenium ion because it lacks a resonance structure that would formally place the positive charge on the nitrogen. Indeed, the ordering of the three lowest electronic states is the same at the phenyl oxenium ion (ground state singlet < triplet < open-shell singlet), and even the energy gaps are only slightly perturbed. As with the 2-pyridinyl oxenium ion 2 the 3-pyridinyl oxenium ion 3 has a short C–O bond distance of 1.195 Å showing a quinoidal structure.

In Contrast with the 2- and 3-Pyridinyl Oxenium Ions, the 4-Pyridinyl Oxenium Ion Has a Significantly Smaller Singlet–Triplet Gap than the Parent Phenyl Oxenium

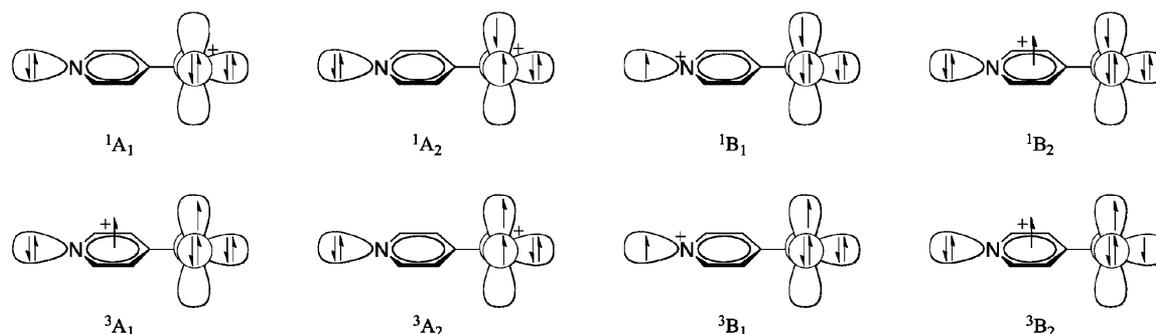


Figure 4. Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of 4-pyridinyl oxenium ion 4.

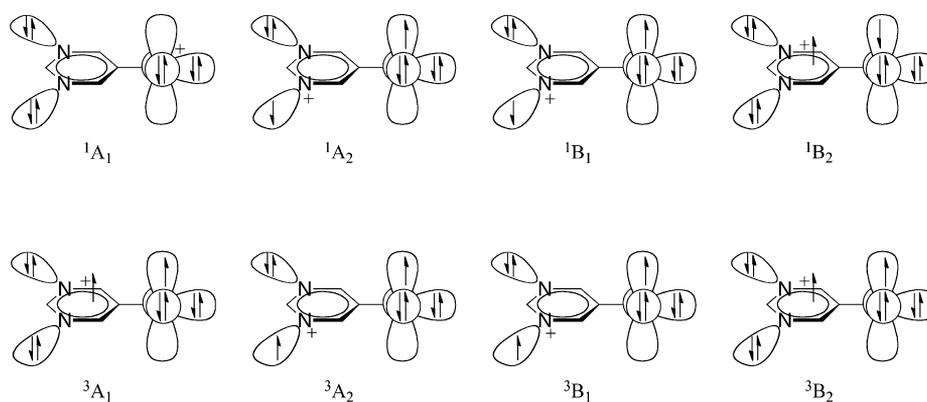


Figure 5. Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of the pyrimidinyl oxenium ion 5.

Table 5. Energies of the Lowest Irreducible Representations of the Pyridinyl Oxenium Ion 6^{ab}

irreducible representation (C_s)	relative energy adiabatic (vertical) kcal/mol
$1^1A'$	0*
$1^1A''$	3.9 [†] (3.9)
$1^3A'$	9.5
$1^3A''$	1.3

^{a†} indicates that an imaginary frequency was encountered upon optimization under symmetry. ^{b*} designates a lower-symmetry geometry.

Ion. As shown in Table 3, the singlet–triplet gap of the 4-pyridinyl oxenium ion 4 is computed to be -3.4 kcal/mol (1^1A_1 – 3^1B_1). Interestingly, the lowest energy triplet state for this ion is not the typical oxygen-centered n,π^* triplet state seen with the phenyl oxenium ion and the 2- and 3-pyridinyl oxenium ion but is better described as an n,π^* triplet nitrenium ion, with the ring nitrogen n electron promoted to the π^* orbital (Figure 4). Both the closed-shell singlet and the lowest energy triplet state have C–O bond lengths that are very short (1.216 and 1.234 Å, respectively), suggesting quinoidal nitrenium ion character for both the singlet and triplet states.

In some cases indicated with a [†] in the Tables, optimization under symmetry gives imaginary frequencies. Unfortunately, without symmetry, optimizing a particular excited-state root when there are numerous similar-energy roots is a challenging problem. Despite numerous attempts with varying input geometries, state averaging, and manual single-step optimization approaches, we were unable to achieve an optimized geometry for these states. Attempting to optimize these excited states without symmetry led to problems with root switching upon optimization, wherein the optimization would reach a conical intersection and convergence problems or root switching would be encountered. For the optimizations of the excited state roots that were unsuccessful, we report the energy for this state at the geometry optimized under symmetry as well as the vertical energy with CASPT2 from the ground-state

optimized geometry (in parentheses). Fortunately, because these are excited states at the CASSCF level, these states are probably less chemically relevant for the 4-pyridinyl oxenium ion.

Absolute Energies Indicate Singlet Destabilization Is the Dominant Factor for Changing the ΔE_{ST} for 2, 3, and 4. A natural question is whether the difference in singlet–triplet gaps for the 2-, 3-, and 4-pyridinyl oxenium ions can be explained by stabilization/destabilization of the triplet state, stabilization/destabilization of the singlet state, or a combination both. Because these ions are isomers of each other the absolute energies can be compared to provide insight into this question. Absolute energies indicate that the singlet state of the 4-pyridinyl oxenium ion 4 is 19 kcal/mol less stable than the singlet state of 3-pyridinyl oxenium ion 3, whereas the triplet state shows only a 3.5 kcal/mol destabilization. Therefore, the reason 4 has a nearly zero singlet–triplet gap compared with 3 is primarily due to ion 4 having a considerably destabilized singlet state. When comparing the 2- and 4-pyridinyl oxenium ions, the singlet state was more stable by a remarkable 67 kcal/mol, but this was offset by the triplet being stabilized by 53 kcal/mol. We attribute this stabilization of 2 due to the ability of the oxenium ion to delocalize the positive charge on a less electronegative para carbon rather than a para nitrogen or a carbon adjacent to nitrogen. However, again it is seen that the singlet state destabilization is the major factor in altering the ΔE_{ST} .

Pyrimidinyl Oxenium Ion May Have a Remarkable Open-Shell Singlet Ground State. As shown in Table 4, the ΔE_{ST} of the pyrimidinyl oxenium ion 5 is essentially zero. Therefore, there is little certainty as to whether the 1^1A_2 or the 3^1A_2 state is the ground state of the pyrimidinyl oxenium ion. Unfortunately, we were not able to obtain the optimized structure of the open-shell 1^1A_2 state. Optimization of this irreducible representation under symmetry leads to an imaginary frequency. In a broken molecular symmetry calculation of this state, CASPT2 places the 1^1A_2 state as the ground state, but it is an excited-state root at the CASSCF level

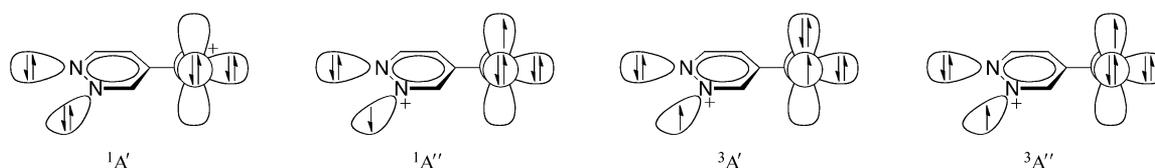


Figure 6. Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of pyridinyl oxenium ion 6.

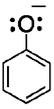
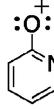
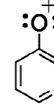
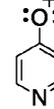
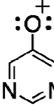
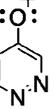
						
Compound Number	1	2	3	4	5	6
ΔE_{ST} (B3LYP/cc-pVTZ)	-13.5	-1.4	-3.8	+0.9	--	--
ΔE_{ST} (CASPT2/pVTZ)	-22.1	-16.4	-19.2	-3.4	-0.4	-1.3
ΔE_{ST} (CBS-Q)	-20.5	-14.1	-15.6	-6.5	--	--
ΔE_{ST} (CCSD(T)/cc-pVTZ// CCSD/cc-pVDZ)	-16.5	-10.6	-15.4	-4.4	--	--

Figure 7. Calculated ΔE_{ST} of the phenyl oxenium ion and heteroaryl oxenium ions.

of theory. Our optimization suffered from intractable root switching problems upon optimization, as described above due to a near-degeneracy with the closed-shell singlet state at the CASSCF level. However, inspection of the energy of the symmetry-optimized structure as well as the vertical energy from the closed-shell singlet state shows that the energy is similar to the 3A_2 state, although the open-shell singlet state is likely to be lower in energy because it is computed to be slightly lower in energy even without a fully optimized geometry.

The significance of having the 1A_2 state lower than the 1A_1 state suggests that this ion may have an open-shell singlet ground state—quite unusual indeed. As seen in Figure 5, both the 1A_2 and 3A_2 states can be conceptually derived by starting with the closed-shell singlet and promoting an electron from the nitrogen lone pair to the oxygen π^* orbital. In most cases, ground-state singlet molecules are closed shell, but if the frontier orbitals approach each other in energy then it is possible for an open-shell singlet to be the ground state. Typically, molecules that have lowest energy singlet states that are open-shell have triplet ground states due to the favorable exchange energy favoring the triplet given equal orbital occupation. However, the open-shell singlet state can become the ground state if the exchange energy is small and higher-order correlation favors the singlet over the triplet. The possibility of an open-shell singlet ground state for this ion makes it particularly intriguing for experimental study because there are few examples of ground-state open-shell singlet states for reactive intermediates^{35–38} and the reactivity of open-shell singlet species is not well understood. The short C–O bond length (1.914 Å) shows its quinoidal character placing the positive charge on the carbon para to the oxygen.

Electronic State Orderings of the Pyridinyl Oxenium Ion 6 Show a Near-Triple Degeneracy in Electronic States. As shown in Table 5, the ΔE_{ST} of the pyridinyl oxenium ion 6 is computed to be -1.3 kcal/mol. Therefore, as with the pyrimidinyl oxenium ion, there can be little certainty as to whether the $^1A'$ or $^3A''$ state is the ground state of the pyridinyl oxenium ion. Indeed, with the open-shell ($^1A''$) state calculated to be only 3.9 kcal/mol higher in energy than the closed-shell ($^1A'$) state, it is uncertain if the closed shell is actually the lowest energy singlet state. It should be noted that the lone pair orbitals of the two adjacent nitrogens overlap, as inspection of the orbitals shows that there is a “bonding” and “antibonding” set of lone pair orbitals. Therefore, whereas Figure 6 shows the promotion of the electron from the meta nitrogen, it is better to ascribe this electron as originating from the “bonding” pair of electrons, which has amplitude on both ring nitrogens. As with the 4-pyridinyl oxenium ion 4, the

closed shell singlet is likely destabilized because it has a quinoidal structure that places the positive charge on the electronegative nitrogen.

High-Level Single-Reference Computations Corroborate CASPT2 Singlet–Triplet Gaps for Ions with a Lowest-Energy Singlet State That Are Single-Reference and Closed-Shell. For ions with lowest-energy singlet states that were found to be essentially single-determinantal by CASSCF, we performed additional CCSD(T), CBS-Q, and B3LYP computations to obtain the singlet–triplet gaps shown in Figure 7. These included calculations using these methods for ions 2, 3, and 4. (Ions 5 and 6 probably have an open-shell singlet ground state, or near-degenerate open-shell singlet states, and so are not amenable to calculation by single-reference methods.) Our previous report on the phenyl oxenium ion showed that whereas B3LYP computed the ΔE_{ST} of phenyl oxenium to be -13.5 kcal/mol, CBS-Q and CCSD(T)/cc-pVDZ compute the singlet–triplet gap of phenyl oxenium ion to be -20.5 and -16.5 kcal/mol, respectively, in good agreement with experiment (-19.8 kcal/mol). As in our previous study, B3LYP performs very poorly here for 2 and 3 compared with the CASPT2, CBS-Q, or CCSD(T) computations, underestimating the singlet energy by >10 kcal/mol. However, the CCSD(T)/cc-pVDZ computations as well as the CBS-Q computations are in good agreement with the CASPT2 results, differing by <5 kcal/mol for both species. This agreement among these best methods increases our confidence in the quantitative validity of these CASPT2 computations reported herein.

CONCLUSIONS

Compared with the phenyl oxenium ion 1 (Table 6), heteroaryl oxenium ions have reduced singlet–triplet gaps in favor of the triplet states. The 2- and 3-pyridinyl oxenium ions have only slightly reduced singlet–triplet gaps, but the 4-pyridinyl, pyridinyl, and pyrimidinyl oxenium ions all have a computed

Table 6. Previously Computed Energies of the Lowest Irreducible Representations of the Phenyl oxenium Ion 1²¹

irreducible representation (C_{2v})	relative adiabatic energy (kcal/mol)
1^1A_1	0
1^1A_2	30.8
1^1B_1	48.3
1^1B_2	48.0
1^3A_2	22.1
1^3B_1	47.0
1^3B_2	29.9

ΔE_{ST} of less than -4 kcal/mol, opening up the possibility of reactivity from the triplet as well as rare open shell singlet states, sometimes seen in isoelectronic phenylnitrenes. We are currently working on developing photochemical precursors to these oxenium ions to study their reactivity; these computational studies will aid us in selecting the most interesting candidates for experimental study. These ions may be of fundamental interest as platforms for studying the relationship between electronic structure and reactivity for this important class of reactive intermediates.

■ ASSOCIATED CONTENT

■ Supporting Information

All Cartesian coordinates, geometries, and absolute energies for all structures and electronic states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

DFT, density functional theory; ΔE_{ST} , singlet–triplet energy gap (negative value indicates singlet ground state); CASPT2, complete active space second-order perturbation theory; CASSCF, complete active space self-consistent field theory; CBS-Q, complete basis set method

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