# Phenyloxenium Ions: More Like Phenylnitrenium Ions than Isoelectronic Phenylnitrenes?

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Ⓢ *Supporting Information*

ABSTRACT: The geometries and energies of the electronic states of phenyloxenium ion **1** (Ph−O$^+$) were computed at the multireference CASPT2/pVTZ level of theory. Despite being isoelectronic to phenylnitrene **4**, the phenyloxenium ion **1** has remarkably different energetic orderings of its electronic states. The closed-shell singlet configuration ($^1A_1$) is the ground state of the phenyloxenium ion **1**, with a computed adiabatic energy gap of 22.1 kcal/mol to the lowest-energy triplet state ($^3A_2$). Open-shell singlet configurations ($^1A_2$, $^1B_1$, $^1B_2$, 2^1A_1) are significantly higher in energy (>30 kcal/mol) than the closed-shell singlet configuration. These values suggest a revision to the current assignments of the ultraviolet photoelectron spectros-

copy bands for the phenoxy radical to generate the phenyloxenium ion **1**. For para-substituted phenyloxenium ions, the adiabatic singlet−triplet energy gap (ΔE_{ST}) is found to have a positive linear free energy relationship with the Hammett-like σ^+_R/σ^+ substituent parameters; for meta substituents, the relationship is nonlinear and negatively correlated. CASPT2 analyses of the excited states of *p*-aminophenyloxenium ion **5** and *p*-cyanophenyloxenium ion **10** indicate that the relative orderings of the electronic states remain largely unperturbed for these para substitutions. In contrast, meta-donor-substituted phenyloxenium ions have low-energy open-shell states (open-shell singlet, triplet) due to stabilization of a π,π^* diradical state by the donor substituent. However, all of the other phenyloxenium ions and larger aryloxenium ions (naphthyl, anthryl) included in this study have closed-shell singlet ground states. Consequently, ground-state reactions of phenyloxenium ions are anticipated to be more closely related to closed-shell singlet arylnitrenium ions (Ar−NH$^+$) than their isoelectronic arylnitrene (Ar−N) counterparts.
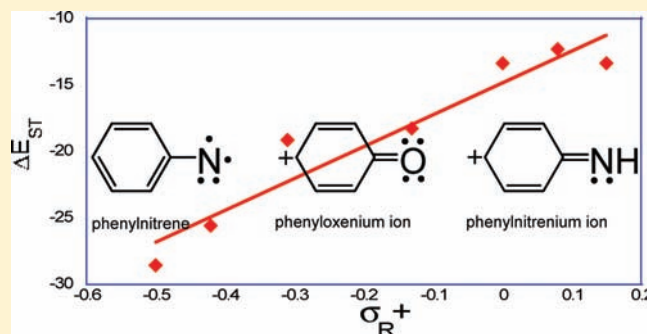
■ INTRODUCTION

Oxenium ions are hypovalent species of formula R−O$^+$. These reactive intermediates are isoelectronic with nitrenes, with a formally monovalent oxygen containing two nonbonding electron pairs. Like nitrenes, the electron-deficient nature of these intermediates makes them powerful electrophiles, further amplified by the formal positive charge on the electronegative oxygen. These species are increasingly being proposed as intermediates in useful *umpolung* synthetic transformations, such as the oxidative Hosomi−Sakurai reaction,[1,2] the oxidative Wagner−Meerwin transposition,[3] electrochemical oxidations of phenols and pheno-lates,[4,5] alkane oxidations,[6] and a wide variety of other phenolic oxidations and tautomerization reactions.[7−11] These reactions convert phenols and alkanes, many of which are derived from petrochemical feedstocks, into value-added products such as cyclohexadienones, substituted phenols, and oxidized alkanes, as well as petrochemicals like poly(1,4-phenylene ether), a high-value industrial thermoplastic.[12−14] They are also formed from exposing phenols, anisoles, and nitrobenzenes to ionizing radiation,[15−17] are reactive intermediates in iron-mediated enzymatic oxidations of phenols into quinone compounds,[18] and persist in interstellar clouds and planet atmospheres.[19,20] Like nitrenes and carbenes, oxenium ions are short-lived in solution but can form stable

complexes with transition metals, acting as novel ligands.[21] Given the importance of these species to such a diverse range of chemists, it is surprising how little basic science is known of this class of reactive intermediates.

This paper attempts to answer two fundamental questions to further the understanding of these reactive intermediates: (1) What is the nature and quantitative energetic orderings of the chemically relevant electronic states of the phenyloxenium ion **1** (Ph−O$^+$)? (2) How do simple substituents perturb these electronic state orderings?

The parent oxenium ion, the hydroxy cation (OH$^+$), is a ground-state triplet ion ($^3\Sigma^-$) with a large adiabatic energy gap of 54 kcal/mol to the lowest-energy singlet state ($^1\Delta$).[22] This favoring of the triplet state in this ion results from a degeneracy in the p orbitals, leading to adoption of a lowest-energy spin-unpaired state following a molecular orbital (MO) extension of Hund's rule. The lowest-energy singlet state can also be nomin-ally described as open-shell.

The ground state of aryloxenium ions, in contrast, is far less certain due to a breaking of the degeneracy of the frontier oxygen
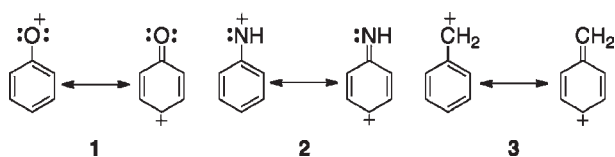
Figure 1. Important canonical forms of the closed-shell singlet phenyloxenium ion **1** ($^1A_1$), phenylnitrenium ion **2** ($^1A'$), and benzyl cation **3** ($^1A_1$).

p orbitals from mixing of the ring π orbitals with the out-of-plane p orbital on the oxenium center. Indeed, in contrast to the parent hydroxy cation, experimental work thus far on aryloxenium ions has tended to implicate two-electron (closed-shell singlet) chemistry for aryloxenium ions rather than diradical chemistry.[1,23−28] It should be noted, however, that since most thermal and photochemical methods generate the nascent oxenium ion in the singlet state irrespective of whether this is the ground state, the observation of singlet reactivity is not conclusive evidence for the ion being a ground-state singlet. For instance, under certain conditions, triplet ground-state nitrenes decay via singlet channels because the reactions of the singlet nitrene occur faster than intersystem crossing;[29,30] for carbenes, dynamic equilibria between a low-energy singlet and a triplet ground-state configuration can lead to predominantly singlet products under Curtin−Hammett conditions.[31,32] Consequently, computation is a crucial partner with experiment in establishing the nature and quantitative orderings of the electronic states of these ions, particularly when experimental methods to obtain values for the singlet−triplet gap (such as ultraviolet photoelectron spectroscopy) are by no means straightforward.

Previous experimental studies of aryloxenium ions have been performed by either photochemical or thermal generation methods. In the 1970s and early 1980s, the laboratories of Abramovitch and Okamoto used thermolytic methods to generate aryloxenium ions.[23−25,33,34] Product studies were subsequently used to indirectly characterize their reactivity. More recently, the laboratory of Novak has studied the reactivities of aryloxenium ions using both thermal and photochemical generation methods.[26] Only recently have oxenium ions been directly detected by solution-phase laser flash photolysis. In a noteworthy study in 2007, the groups of Novak and Platz reported the first direct detection of a discrete aryloxenium ion in solution (biphenylyloxenium ion) using laser flash photolysis; this transient species has a lifetime of 170 ns in water.[35]

Some computational studies of aryloxenium ions have also been reported. In 1989, a study by Houk and Abramovitch (HF/STO-3G) was performed on the phenyloxenium ion **1** (Figure 1) and meta-substituted derivatives.[36] A more recent computational study by Glover and Novak (employing the pBP/DN*//HF/6-31G* level of theory) found that the closed-shell configuration ($^1A_1$) of phenyloxenium ion **1** (Ph−O^+) has more quinoidal character than the phenylnitrenium ion **2** (Ph−NH^+).[37] Additionally, this study computed the singlet−triplet gaps (ΔE_{ST}) of several phenyloxenium ions at this level of theory and rationalized the difference in lifetimes between the *p*-methylphenyloxenium ion and the *p*-biphenylyloxenium ion using thermodynamic arguments from computed isodesmic hydration reactions. A recent study on the effect of meta substitution on the ΔE_{ST} of phenyloxenium ions found that substituting the meta positions of phenyloxenium ions with π donors (e.g., NMe_2) stabilizes an *m*-xylylene-like π,π^* triplet state in preference to the singlet state.[38]

However, the properties and electronic states of oxenium ions still remain poorly understood. In particular, the relevance of open-shell singlet states and triplet states to the chemistry of aryloxenium ions, to our knowledge, has not been rigorously addressed. Given that phenyloxenium ion **1** is isoelectronic to phenylnitrene **4**, and given the importance of open-shell electronic states to the reactivity of arylnitrenes,[39] it is critical to similarly characterize the electronic states of aryloxenium ions if their reactivity is to be fully understood.

The results from this computational study indicate that, in contrast to the parent hydroxy cation, phenyloxenium ions generally have lowest-energy states that are closed-shell singlet states. The singlet−triplet gap (ΔE_{ST}) can be manipulated by the para substituent. Meta-donor-substituted phenyloxenium ions have low-energy open-shell diradical states; however, for the parent phenyloxenium ion and para-substituted derivatives, open-shell states are significantly higher in energy. Consequently, reactions of phenyloxenium ions are expected to be more similar to those of phenylnitrenium ions than their isoelectronic phenylnitrene counterparts.

■ COMPUTATIONAL METHODS

All the molecular geometries of the electronic states of the phenyloxenium ion were optimized at the CASSCF(8,8) level of theory under C_{2v} symmetry constraints.[40] The stationary points were found to have zero imaginary frequencies, and all energies contain a correction for the zero-point energy (unscaled). For the phenyloxenium ion **1**, the active-space electrons included the six benzene π electrons and two oxygen nonbonding electrons. The active-space orbitals included the six benzene π orbitals ($4b_1$ and $2a_2$ orbitals), the oxygen out-of-plane p orbital (b_1), and the oxygen in-plane p orbital (b_2). CASPT2 single-point energy corrections (using the same active space) were computed at the CASSCF geometries, using a level shift to eliminate intruder states and reduce a systematic bias in the method favoring high spin states.[41] The basis set employed was the flexible ANO-L basis set of Widmark et al., of polarized valence triple-ζ (pVTZ) quality.[42] All the CASPT2/CASSCF calculations were performed using the Molcas 6.2 software suite.[43] All the single-reference computations (G3, CBS, and DFT) were done with Gaussian03/09.[44] Principally, the hybrid B3LYP functional was used, which consists of the Becke three-parameter exchange[45,46] functional with the correlation functional of Lee, Yang, and Parr.[47] This and related DFT functionals have been shown to give quite reasonable agreement with experiment for related reactive intermediates such as carbenes and nitrenium ions.[48−50]

■ RESULTS AND DISCUSSION

Electronic State Orderings of the Phenyloxenium Ion. As shown in Table 1, the singlet−triplet gap (ΔE_{ST}) of the phenyloxenium ion **1** is computed to be 22.1 kcal/mol ($^1A_1−^3A_2$). Thus, there can be little doubt that the ground state of phenyloxenium ion **1** is the singlet state. Also noteworthy is that prior DFT estimates of the ΔE_{ST} computed the singlet state to be the ground state.[26,27,37] Open-shell singlet states (e.g., $^1A_2$) are significantly higher in energy than the closed-shell singlet state ($^1A_1$), with the lowest open-shell singlet state ($^1A_2$) being 30.8 kcal/mol higher in energy than the closed-shell singlet state (see Table 1).

Revision to Band Assignments from Photoelectron Spectroscopy of the Phenoxy Radical. The ultraviolet photoelectron (UPE) spectrum of the phenoxy radical was the first UPE spectrum of a complex organic radical assigned in detail.[51] In

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Table 1. Adiabatic and Vertical Energies (kcal/mol) of Phenyloxenium Ion 1 Electronic States (CASPT2(8,8)/pVTZ// CASSCF(8,8)/pVTZ, C_{2v} symmetry)[a]

irreducible representation (C_{2v})	principal determinant(s) (C_i, weight)	relative energy adiabatic (vertical)	exptl[b,51]
1^1A_1	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^2)$ (0.927, 85.9%)	0 (0)	0
1^1A_2	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^1)(3b_1^1)$ (0.948, 89.9%)	30.8 (34.8)	30.9
1^1B_1	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^2)(3b_1^1)$ (0.944, 89.1%)	48.3 (66.6)	
1^1B_2	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^1)(3b_1^2)$ (0.945, 89.3%)	48.0 (58.1)	
$2\,^1A_1$	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^1)(3b_1^1)$ (0.502, 25.2%);	89.0 (102.1)	
	$(1b_1^0)(2b_1^2)(1a_2^2)(1b_2^2)(3b_1^2)$ (0.613, 37.5%)		
1^3A_2	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^1)(3b_1^1)$ (0.941, 88.7%)	22.1 (26.1)	19.8
1^3B_1	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^2)(3b_1^2)$ (0.938, 87.9%)	47.0 (65.7)	
1^3B_2	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^1)(3b_1^1)$ (0.946, 89.4%)	29.9 (38.7)	27.7

[a] Refer to Figure 2 for schematic state configurations. [b] Revised assignments. See discussion in text.
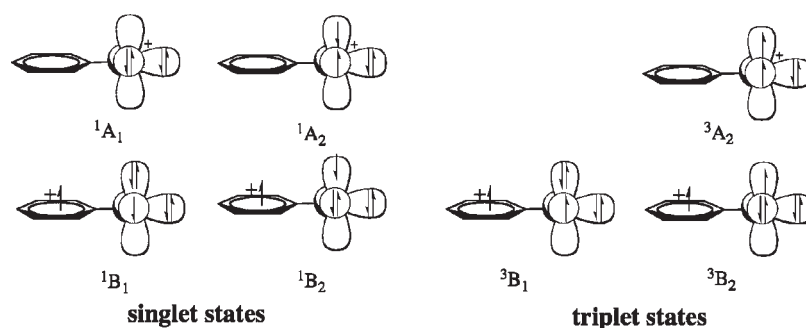
Figure 2. Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of phenyloxenium ion 1.

light of the present study, these computational data suggest that the assignments of the singlet–triplet pairs corresponding to ionization of an n and π electron of the phenoxy radical may have been switched. According to the original assignments, the lowest-energy triplet state is the $^3B_2$ (π,π^*) state, with the $^3A_2$ (n,π^*) state 7.8 kcal/mol higher in energy (see Figure 2 for schematic representations of these states). This assignment was based on the reasonable assumption that, since the π-bonding a_2 orbital is the highest-energy doubly occupied orbital for the phenoxy radical (using MNDO), the $^3B_2$ state derived from ejection of one of these a_2 electrons from the phenoxy radical would yield a triplet oxenium ion lower in energy than the $^3A_2$ state derived from ejection of an n (b_2) electron, which is a lower-energy orbital in the phenoxy radical.

These CASPT2 computations favor reassignment of these bands. As shown in Table 1, the CASPT2 method computes the $^3A_2$ state to be lower in energy than the $^3B_2$ state by 7.9 kcal/mol. If the currently accepted assignments are correct, the CASPT2 calculations are in error by 15.7 kcal/mol for the relative energy between these two states. Alternatively, if the pairs of band assignments were switched, the CASPT2 calculations are in error by 0.1 kcal/mol for the relative energy between the two triplet states.

Typically, one obtains accurate results for CASPT2 with an appropriate active space and a flexible basis set (errors <5 kcal/mol for relative energies are typical). An error of ca. 15 kcal/mol for CASPT2 would be remarkable. We note that our benchmarks of the same computational method (CASPT2(8,8)/pVTZ// CASSCF(8,8)/pVTZ) for the isoelectronic phenylnitrene 4 give energy differences of 17.2 kcal/mol ($^3A_2$ to $^1A_2$) and 31.4 kcal/mol ($^3A_2$ to $^1A_1$). These are close to the experimental values of 18 and 30 kcal/mol derived from photoelectron spectroscopy.[30,52,53] Finally, every theoretical level we used here

(see Table 4 below)—including CCSD(T)/cc-pVTZ—indicates the lowest-energy triplet state is $^3A_2$, not $^3B_2$. We note that switching the assignments of these two pairs of bands gives good quantitative agreement with theory with the computed relative energies (<2.5 kcal/mol relative error).

Comparison of the Electronic States of Phenyloxenium Ion to Phenylnitrenium Ion and Isoelectronic Phenylnitrene. The phenyloxenium ion 1 is isoelectronic to phenylnitrene 4; it is thus interesting to contrast the relative orderings of the electronic states between the phenyloxenium ion 1 ($^1A_1 < {}^3A_2 < {}^1A_2$) and its more highly studied isoelectronic nitrogen counterpart ($^3A_2 < {}^1A_2 < {}^1A_1$).[30,39,54] The ground state of phenylnitrene is the $^3A_2$ state, with a gap of ca. 18 kcal/mol to an open-shell $^1A_2$ singlet state and a gap of 33 kcal/mol to the $^1A_1$ state. The energetic orderings of these states are shuffled in the phenyloxenium ion 1, with the $^1A_1$ state being the ground state with an adiabatic energy gap of ca. 20 kcal/mol to the $^3A_2$ state and a gap of 30 kcal/mol to the open-shell $^1A_2$ state. The gaps and orderings of these electronic states in the phenylnitrene 4 have been established by both experimental and computational studies. Moreover, while the $^1A_1$ state of the phenyloxenium ion 1 can be well described by a single closed-shell determinant (closed-shell reference weight = 86%), the $^1A_1$ state of the phenylnitrene 4 must be described as a linear combination of two closed-shell determinants (Figure 3). This suggests that the degeneracy of the orthogonal p orbitals on the electron-deficient heteroatom is much more strongly broken in phenyloxenium ion than in phenylnitrene.
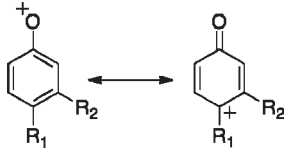
Why is there such a remarkable change in state orderings for isoelectronic species? Both resonance/valence bond and MO arguments suggest themselves. First, a closed-shell singlet state for the phenyloxenium ion 1 allows the positive charge on the

oxenium ion to delocalize off the oxygen and onto the more electropositive ring carbons. In fact, these and prior calculations[37] show that the equilibrium geometry of the $^1A_1$ irreducible representation of the phenyloxenium ion **1** can be reasonably described as a cyclohexadienonyl cation **1** (right resonance structure in Figure 1), in spite of the significant loss of the benzene aromatization energy that is probably inherent to this geometry. This "carbocation-like" structure is also supported experimentally, since nucleophiles add predominantly to the ring carbons rather than to the oxygen. In contrast, in open-shell configurations (open-shell singlet or triplet), the positive charge is formally restricted to the oxygen, which disfavors these configurations. From an MO perspective, the switch from a nitrogen in a nitrene to a more electronegative (and positively charged) oxygen atom in an oxenium ion acts to contract and lower the energy of the p orbitals on the reactive heteroatom. This brings the out-of-plane p orbital on the oxygen closer in energy to the ring π orbitals, allowing the orbitals to mix more strongly. This mixing acts to raise the energy of the MO containing the out-of-plane p orbital on the phenyloxenium ion **1** much more than the same MO on the phenylnitrene **4**. Therefore, the degeneracy of the orthogonal p orbitals is more strongly broken in the phenyloxenium ion **1** than in the phenylnitrene **4**, and the energetic penalty of placing an electron into this π^* orbital—required for open-shell singlet and triplet configurations—is larger for the phenyloxenium ion **1** than the phenylnitrene **4**. Thus, while the ground state of the phenylnitrene **4** is a triplet state ($^3A_2$), the ground state of the phenyloxenium ion **4** is the closed-shell singlet state ($^1A_1$).

Taken in whole, these data appear to be consistent with the solution-phase experiments that have been performed to date. For example, the experimental studies of Abramovitch and Novak on the phenyloxenium ion **1** and its simple derivatives suggest the intermediacy of a closed-shell intermediate that reacts via standard two-electron electrophile chemistry (e.g., rapid nucleophilic additions).[15−20,23−25,33,37,55] To the best of our knowledge, chemical reactions that would implicate an open-shell singlet or triplet electronic state (such as hydrogen atom transfer reactions) have not been reported for the phenyloxenium ion **1** or simple analogues.

Effect of Para Substituents on the ΔE_{ST} of Phenyloxenium ion. This MO analysis suggests that, all things being equal, any substituents on the phenyl ring that act to raise the energy of the out-of-plane p orbital on oxygen (e.g., π-donors) will more strongly favor the closed-shell singlet state relative to open-shell configurations. Conversely, substituents that act to lower the energy of this orbital (π-withdrawers) will lead to lowered-energy open-shell (e.g., triplet) states. This is indeed the case. For these larger systems, we used DFT to compute the ΔE_{ST} of a number of para-substituted phenyloxenium ions. We note that, while the quantitative accuracy of these DFT calculations is likely to underestimate the singlet stability (described *vide infra*), the trends predicted by this method are likely to be qualitatively valid. From these calculations, a linear free energy relationship (LFER) of the ΔE_{ST} with the Hammett-like σ^+[56,57] and σ_R^+[58] substituent parameters is observed (squared correlation coefficients values, R^2, of 0.89 and 0.91, respectively). Additionally, the C−O bond length, which we take as a rough diagnostic of the contribution of the two resonance forms depicted in Table 2, also shows a reasonable, albeit small in magnitude, correlation with these two parameters. (The plots of the σ_R^+ vs the C−O bond length and vs the ΔE_{ST} can be found in Figure 4; plots of the C−O bond length and ΔE_{ST} vs σ^+ can be found in the

Table 2. Changes in the ΔE_{ST} (kcal/mol) and Singlet C−O Bond Length as a Function of the Para Group's σ^+/σ_R Parameter, Computed by DFT (B3LYP/cc-pVTZ)

| compound number	R_1	R_2	ΔE_{ST} (kcal/mol)	C−O (Å)	σ^{+} [25,26]	σ_R^+
5	NH$_2$	H	−28.6	1.210	−1.3	−0.5
6	OH	H	−24.1	1.209	−0.92	–
7	OMe	H	−25.6	1.210	−0.78	−0.42
8	CH$_3$	H	−18.3	1.211	−0.31	−0.13
9	F	H	−19.1	1.209	−0.07	−0.31
1	H	H	−13.4	1.211	0	0
10	CN	H	−12.3	1.212	0.66	0.08
11	NO$_2$	H	−13.4	1.211	0.79	0.15
12	H	NH$_2$	4.9	1.220	−1.3	−0.5
13	H	OH	−7.2	1.215	−0.92	--
14	H	OMe	−4.8	1.216	−0.78	−0.42
15	H	CH$_3$	−13.0	1.213	−0.31	−0.13
16	H	F	−12.4	1.211	−0.07	−0.31
1	H	H	−13.4	1.211	0	0
17	H	CN	−12.3	1.211	0.66	0.08
18	H	NO$_2$	−12.0	1.209	0.79	0.15
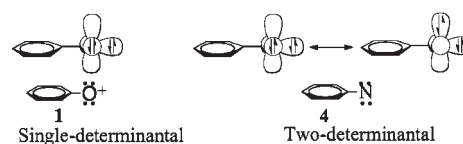
Figure 3. Comparison of the $^1A_1$ states of the phenyloxenium ion **1** and phenylnitrene **4**.

Supporting Information.) This geometrical correlation is interpreted to indicate that phenyloxenium ions with π donors in the para position have equilibrium geometries that are more quinoidal than those substituted with electron-withdrawing groups. These LFERs and geometrical changes as a function of the para substituent are remarkably similar to those observed for phenyl-nitrenium ions.[59]

Effect of Meta and Para Substituents on the Electronic State Orderings of 1. We also considered the possibility that the open-shell singlet state could become chemically relevant by simple substitutions. We chose the *p*-aminophenyloxenium ion **5** and the *p*-cyanophenyloxenium ion **10**. Both remain in the C_{2v} point group and are expected to be fairly representative of both a π-donor-substituted and a π-withdrawer-substituted phenyloxenium ion. For these species, the active space was increased to include the additional π orbitals and electrons. As seen in Table 3, however, the perturbation in the relative energies of the electronic states is small, and the ordering of the electronic states remains unchanged by the para substitutions.

For meta-substituted phenyloxenium ions, one expects to see little perturbation on the electronic states since this position
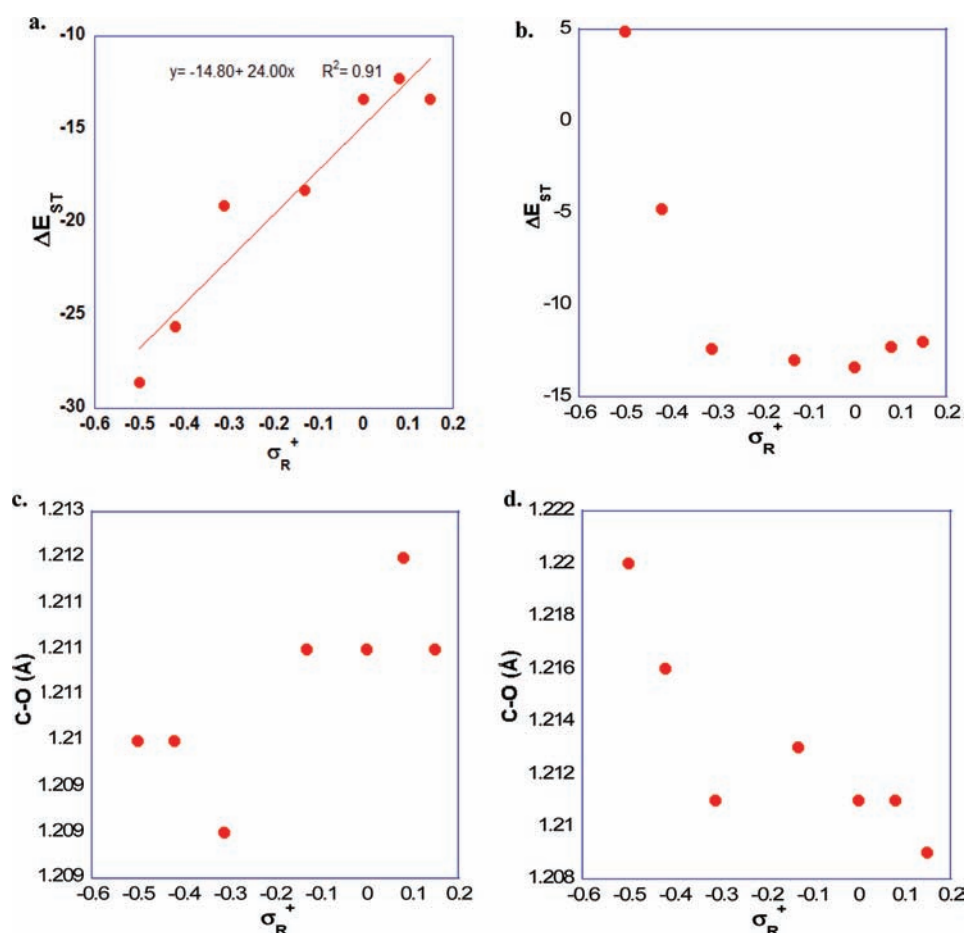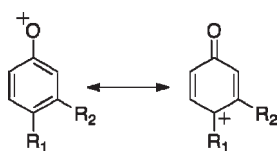
Figure 4. ΔE_{ST} vs σ_R^+ for (a) para and (b) meta substituents, and singlet C–O bond length vs σ_R^+ for (c) para and (d) meta substituents. A negative value for ΔE_{ST} indicates a singlet ground state.

Table 3. Effect of Para (C_{2v}) and Meta (C_s) Substituents on Electronic State Energies (Adiabatic, kcal/mol) and Orderings (CASPT2/pVTZ)

compound number	R_1	R_2	active space	$^1A_1$	$^1A_2$	$^3A_2$
1	H	H	(8,8)	0	30.8	22.1
5	NH_2	H	(10,9)	0	28.8	23.6
10	CN	H	(12,12)	0	23.7	19.4

compound number	R_1	R_2	active space	$^1A'$	$2\,^1A''$	$^3A''$	$^1A''$	$^3A'$
12	H	NH_2	(10,9)	0	6.6^a	12.6	15.4	1.0
17	H	CN	(12,12)	0	53.6^a	17.6	28.2	29.5

^{a} Vertical energies.

cannot communicate with the oxenium center through resonance. As expected, the singlet–triplet gap for withdrawing and weakly donating substituents (Figure 4b) remains largely unperturbed. However, for donating substituents, there is a sharp inflection point at $\sigma_R^+ = -0.3$, where better donors cause a sharp

increase in the singlet–triplet gap in favor of the triplet. This can be explained by a stabilization of a π,π^* triplet state by the meta donor substituent, as can be seen in Table 3. While the parent phenyloxenium ion has a lowest-energy triplet state that can be described as n,π^*, the *m*-aminophenyloxenium ion has a lowest-energy triplet state that is described as π,π^* (this is the $^3A'$ state under C_s symmetry). The inflection point in the graph marks the switch from the n,π^* state ($^1A''$) being the lowest-energy configuration to the π,π^* state ($^1A'$) being the lowest-energy configuration. The meta substituent σ_R^+ value is also correlated with bond length, wherein better meta π donors increase the C–O bond length. For the *m*-aminophenyloxenium ion, the ground state is computed to be the triplet state at the DFT level of theory by ca. 5 kcal/mol, but it is computed to have essentially degenerate singlet and triplet energies at the CASPT2/pVTZ level of theory. Consequently, the ground state of the *m*-aminophenyloxenium ion cannot be predicted with certainty. Reactivity may be possible from both the singlet and triplet states. Also of note is that a further consequence of the narrowing of the frontier orbital energies for the *m*-aminophenyloxenium ion is that the open-shell singlet state is low in energy. While for the parent phenyloxenium ion the adiabatic energy gap from the closed-shell singlet ground state ($^1A_1$) to the open-shell singlet state ($^1A_2$) is 30.8 kcal/mol, for the *m*-aminophenyloxenium ion, the vertical gap from the closed-shell singlet state ($^1A'$) to the open-shell singlet state ($2\,^1A'$) is 6.6 kcal/mol.
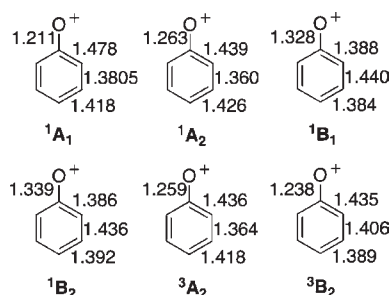
Figure 5. Heavy atom−heavy atom bond lengths (Å) for irreducible representations of **1** (C_{2v}, CASSCF(8,8)/pVTZ).

Table 4. Computed Adiabatic Singlet−Triplet Energy Gaps [$\Delta E_{ST} = E(^1A_1) - E(^3A_2)$] of the Phenyloxenium Ion 1 by Different Methods[a]

computational method	ΔE_{ST} (kcal/mol)
CASPT2/pVTZ//CASSCF/pVTZ	−22.1
G3	−20.6
CBS-Q	−20.5
CCSD(T)/cc-pVTZ	−20.0
experimental value	−19.8
CBS-QB3	−18.2
BVWN/cc-pVTZ	−18.2
B3LYP/cc-pVTZ	−13.5
BLYP/cc-pVTZ	−12.3
MPW1PW91/cc-pVTZ	−10.5
BH&HLYP/cc-pVTZ	−10.0
TPSSTPSS/cc-pVTZ	−9.5

[a] A negative value for ΔE_{ST} indicates a singlet ground state. Geometries were optimized at the same level unless otherwise indicated.

Molecular Geometries. The molecular geometries, computed at the CASSCF(8,8)/pVTZ level, are depicted in Figure 5. The heavy atom−heavy atom bond lengths (Å) are shown for the lowest-energy configuration of each irreducible representation. As shown in Figure 5, the C−O bond length is shortest in the closed-shell singlet irreducible representation ($^1A_1$). Additionally, there is significant bond length alternation in the ring carbons in this electronic state, as well as in the other A_1 and A_2 configurations, suggesting significant quinoidal character. Conversely, the B configurations—$^1B_2$, $^3B_2$, $^1B_1$—which involve promotion of a ring π electron rather than an oxygen n electron, show less bond length alternation. However, these states are significantly higher in energy than the A states.

Larger Aryloxenium Ions. Aryloxenium larger ions than phenyloxenium ions tend to show an increased preference for the singlet state relative to the triplet. At the DFT level, the ΔE_{ST} values of 1- and 2-naphthyl oxenium ions **20** and **19** and the 9-anthryloxenium ion **21** are −23.2, −15.2, and −33.5 kcal/mol, respectively. These ions have larger singlet−triplet splittings in favor of the singlet relative to phenyloxenium ion **1** (−13.5 kcal/mol at this level of theory). To ensure that the lowest-energy singlet state remained closed-shell, stability calculations were performed on the singlet states, and the "wave functions" were found to be stable to an RHF→UHF perturbation. Inspection of the Kohn−Sham SOMOs indicates that, like the phenyloxenium ion, the lowest-energy triplet state is n,π^* for these larger aryloxenium ions, with the exception of the 2-naphthyloxenium

ion, which can be described as a π,π^* triplet state ($^3A'$, see Supporting Information for plots of the Kohn−Sham SOMOs).

Performance of Density Functional Theory. We also examined the ΔE_{ST} by density functional theory (DFT) and other computational methods (see Table 4). While CASPT2 is a rigorous methodology, it is only computationally tractable for small systems, and it would be useful to have a DFT functional that could give reasonable results. DFT, which is relatively inexpensive and easily implemented, has been shown to give quite reasonable values for the ΔE_{ST} of carbenes, nitrenium ions, and related species.[38,60,61] Given that the phenyloxenium ion **1** does not appear to present a pathological case for theory (e.g., an open-shell singlet state), the somewhat disappointing performance of DFT compared to CASPT2 or the compound extrapolation methods (G3, CBS) is somewhat surprising—but not without precedent.

Typically, DFT systematically underestimates the singlet stability of carbenes and related hypovalent species by about 5 kcal/mol because nondynamical correlation is generally more important for singlet states than triplet states.[62] However, in this case, all the DFT functionals we tested except BVWN underestimate the singlet stability by a somewhat larger 5−10 kcal/mol compared to the experimental value or values computed by G3, CBS-Q, or CASPT2. Some of the blame for this relatively poor performance appears to be assignable to poor singlet-state geometries at the DFT level of theory. For example, B3LYP/cc-pVTZ single-point energy differences of the singlet and triplet states at the CASSCF geometries changed from −13.5 to −15.5 kcal/mol—an improvement of 2.0 kcal/mol. A likely origin of the poor singlet geometries is the tendency of DFT functionals to overestimate aromatization. Thus, one obtains geometries that have too much Ph−O$^+$ character (left resonance structure **1** in Figure 1) relative to cyclohexadienonyl cation character (right resonance structure **1** in Figure 1) using B3LYP, as shown by the longer C−O bond lengths using DFT compared to the CASSCF geometries (1.227 Å rather than 1.211 Å). Since CBS-QB3 employs a B3LYP optimization step, and since we estimate the error introduced by using a B3LYP geometry to be ca. 2 kcal/mol, it is not unexpected that the CBS-QB3 value of the ΔE_{ST} is lower than those obtained with G3, CQS-Q, and CCSD(T) by ca. 2 kcal/mol. Multireference computations are needed for species with significant nondynamical correlation; however, for species that do not have significant nondynamical correlation (such as the phenyloxenium ion), single reference methods that capture dynamical correlation better than CASPT2/CASSCF may give better quantitative accuracy. Indeed, it is notable from Table 4 that the most rigorous single-reference computational methodologies predict a ΔE_{ST} value for the phenyloxenium ion **1** close to the experimental value derived from photoelectron spectroscopy of −19.8 kcal/mol.

■ CONCLUSIONS

The singlet−triplet gap of the phenyloxenium ion **1** is ca. 20 kcal/mol, which represents the adiabatic energy difference between the $^1A_1$ state and the $^3A_2$ state. While the parent oxenium ion, hydroxy cation OH$^+$, has a triplet ground state with a very large energy gap to the lowest-energy singlet state, substituting the hydrogen with a phenyl ring strongly breaks the degeneracy between the frontier p orbitals and leads to a closed-shell singlet state ($^1A_1$) being the lowest-energy configuration. Open-shell singlet states do not appear to be chemically relevant

for the parent phenyloxenium ion and para-substituted aryloxenium ions studied here, having energies 20 kcal/mol or higher than their closed-shell counterparts. This stands in contrast to the isoelectronic arylnitrenes, which often have open-shell singlet states lower in energy than the closed-shell singlet states, and more in line with arylnitrenium ions, which are generally closed-shell singlet ground-state species. These aryloxenium ions have two low-energy types of triplet states, n,π^* or π,π^*. The n,π^* triplet is computed to be lower in energy for the parent phenyloxenium ion **1** at the CASPT2 level of theory, but the π,π^* triplet becomes lower in energy for the 2-naphthyloxenium ion and meta-donor-substituted phenyloxenium ions. Meta-donor-substituted aryloxenium ions have low-energy open-shell states due to stabilization of a π,π^* configuration by the meta donor substituent. The ΔE_{ST} of para-substituted phenyloxenium ions correlates with the σ_R^+/σ^+ Hammett substituent parameter, with strong para donors increasing the gap in favor of the singlet and electron-withdrawing substituents decreasing the gap. Experimental studies to generate and characterize these species are needed to fully characterize their properties and reactivity.

■ ASSOCIATED CONTENT

S **Supporting Information.** Complete refs 43b and 44; plots of σ^+ and σ_R^+ values versus ΔE_{ST} and C–O bond length for meta- and para-substituted systems; absolute energies and Cartesian coordinates; and Kohn–Sham SOMO plots for the triplet states of **1**, **19**–**21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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