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Relationship of Conformational Effects in Phenyloxenium and Phenylnitrenium Cations to Intramolecular Reactivities. Ab Initio Electronic Structures

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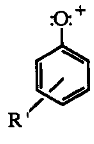
Ab initio STO-3G optimizations of the lowest singlet and triplet states of the phenyloxenium and phenylnitrenium cations have been carried out. Although only small basis sets could be used, rough estimates of the singlet–triplet gaps for phenyloxenium and phenylnitrenium were made. Calculations were also performed on the *m*-hydroxyphenyloxenium ion in order to help understand the failure of intramolecular reactions of those compounds in which a side chain is attached to the meta position of phenyloxenium by an ether oxygen. The preferred conformation of the side chain is planar, and a significant barrier must be overcome in order to achieve the conformation necessary for cyclization.

Introduction

Aryloxenium cations **1** and arylnitrenium cations **2** are of considerable importance in organic chemistry and biochemistry. Compounds **1** and **2** are substituted versions of the hydroxyl cation, HO^+ (**3**), and the amino cation, H_2N^+ (**4**). These are both even-electron, open-shell species, like carbenes, and as a consequence they may have singlet and triplet states of comparable energy. The parent oxenium and nitrenium cations both have triplet ground states, as does the parent methylene. However, aryl-substituted compounds may have either singlet or triplet ground states, since aryl groups are expected to stabilize singlet states more than triplet states, as known for carbenes.[2]



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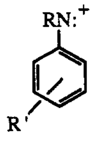

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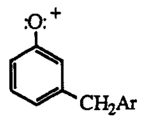

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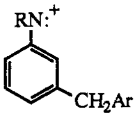

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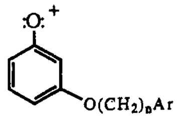
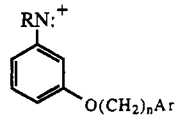


7 (n=0,1)



8 (n=0,1)

Aryloxenium ions have been invoked as intermediates in phenol oxidations and in biomimetic oxidative coupling reactions.[3] Arylnitrenium ions have been postulated to be the metabolically activated forms of some carcinogens.[4,5] Many methods have been developed for the generation of aryloxenium[6,7] and arylnitrenium[8] ions.

Our theoretical studies of some of these species were prompted by some unexpected reactivity patterns uncovered during studies of intramolecular reactions of aryloxenium and arylnitrenium cations.[9–11] Intramolecular trapping occurred readily for reactions of compounds such as **5** and **6**, but no cyclization occurred at all when an oxygen was included in the side chain, as in **7**. Nevertheless, intermolecular reactions of **7** occurred readily with benzene and anisole, so that only intramolecular reaction is prevented by the side chain.[9b] A very small amount of cyclization occurred when *n* was increased to two in **7**. Arylnitrenium ions **8** generated from the corresponding azides in the presence of strong acids such as trifluoromethanesulfonic acid behave in a similar fashion.[10,11] It was suggested[9b] that the oxygen atom in the side chain imposed a rotational or inversion barrier that had to be surmounted in order for the aryloxy or aralkyloxy group to achieve the conformation in which intramolecular nucleophilic attack on the cation is geometrically likely. Figure 1 shows a sketch of the approximate geometries required for this type of intramolecular reaction. We now report theoretical studies of some aryloxenium and arylnitrenium ions designed to explore the geometries and electronic structures of these species and to learn why compounds such as **7** and **8** do not cyclize. Because of the sizes of these systems and the low level of theory employed, the calculations are of qualitative significance at best.

Results and Discussion

The singlet and triplet states of phenyloxenium and phenylnitrenium were optimized with the STO-3G basis

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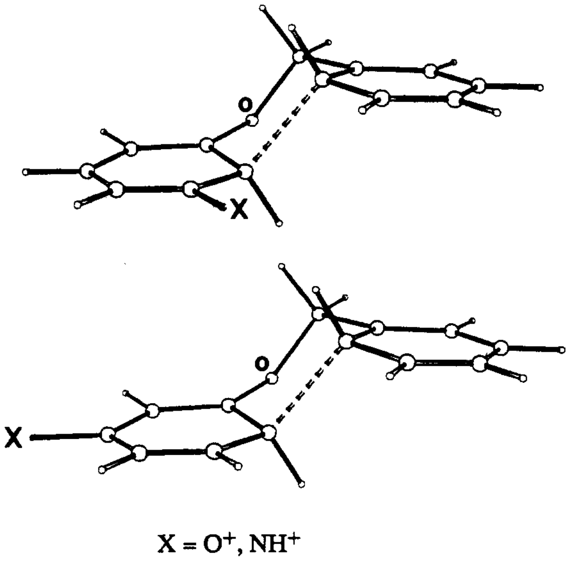
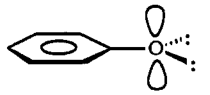


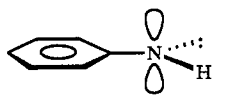
Figure 1. Approximate geometries of the transition states for the intramolecular cyclization of *m*-benzyloxy-substituted PhO^+ and $PhNH^+$ cations, either ortho or para to O^+ or NH^+.

set and the GAUSSIAN 80 series of programs.[12] RHF theory was used for the singlet state and UHF theory for the triplet state, and all species were assumed to be planar. This is a very low level of theory at which to calculate open-shell species, but we chose it because the molecules were too large for practical calculations with large basis sets and MCSCF theory. The gross electronic and structural features in which we were interested should be revealed even at this level of ab initio molecular orbital theory.

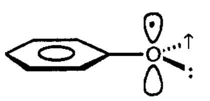
The lowest lying states of **1** and **2** are singlets, which can be represented in localized valence-bond terms by the structures **1s** and **2s** shown below. Both have a vacant p orbital that overlaps with the π orbitals of the benzene ring. In structures **1s** and **2s**, the positive charge residues on the heteroatom. The charge is delocalized onto the aromatic ring by electron donation, analogous to the situation for the benzyl cation. The triplet states **1t** and **2t** have one of the lone-pair electrons promoted to the π-type p orbital. Here resonance involving the benzene ring is analogous to that in the benzyl radical, and the positive charge remains on the heteroatom in all resonance structures. This first-order description suggests that the singlet states of **1** and **2** will be stabilized considerably with respect to the triplet states by interactions with the benzene ring, since the resonance stabilization of the benzyl cation is larger than that of the benzyl radical, and the singlet-state resonance is more effective since it removes positive charge from the electronegative heteroatom.[13,14]



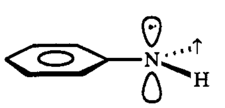
1s



2s



1t



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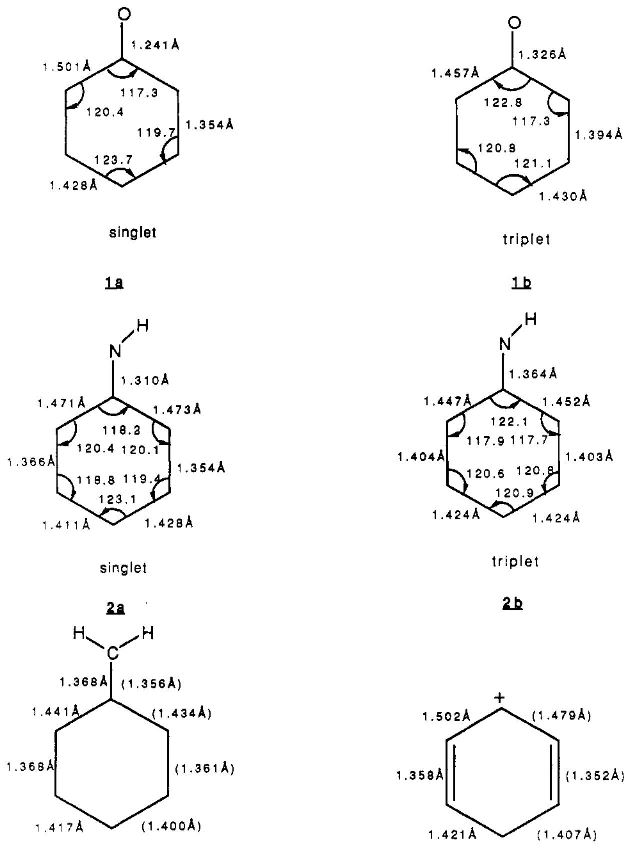

Figure 2. STO-3G optimized geometries of PhO^+, $PhNH^+$, $PhCH_2^+$, and $C_6H_7^+$ cations. 3-21G optimized geometries are shown in parentheses.

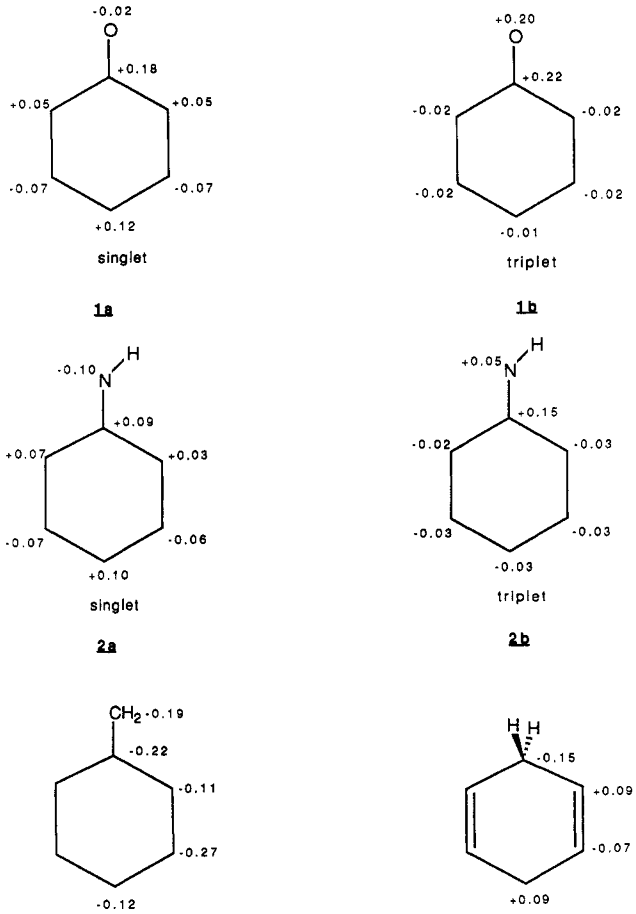

Figure 3. Calculated total Mulliken charges of PhO^+, $PhNH^+$, $PhCH_2^+$, and $C_6H_7^+$ cations.

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Table I. Calculated Relative Energies (kcal/mol)[a]

basis set	E(singlet) − E(triplet) HO^+	H_2N^+
HF/STO-3G	91.8	58.3
HF/3-21G	85.1	58.1
HF/6-31G*	86.9	51.0
HF/6-31G**//6-31G*	86.4	51.4
MP4SDTQ/6-31G**//HF/6-31G*	71.5	35.2
HF/3-21G//STO-3G	85.1	58.9
MP2/3-21G//HF/STO-3G	74.5	47.9
exptl	54.4[b]	22.8[c]

[a] Reference 16. [b] Reference 17. [c] Reference 18.

The optimized structures are shown in Figure 2 along with those of the benzyl and cyclohexadienyl cations.[13,15] Figure 3 shows the calculated charge distributions for each of the species in Figure 2. The singlet-state geometries of PhO^+ (**1a**) and $PhNH^+$ (**2a**) are very similar to those of the benzyl[13] and cyclohexadienyl[15] cations, with considerable double-bond character to the exocyclic bond, and much of the positive charge in the ortho and para positions of the ring. Both **1a** and **2a** have slightly stretched C=X (X=O, NH) double bonds, and the ring bond lengths are like those of the cyclohexadienyl cation, with largest positive charge at the para position.[13,15]

The triplet states, **1b** and **2b**, are much more like phenol and aniline, with only slightly shortened C–O or C–N single bonds and with the positive charge located mainly at the heteroatom. The π systems of these molecules are isoelectronic with phenoxy and anilinyl radicals.

The relative energies of singlet and triplet states can only be predicted accurately by using much larger basis sets and extensive correlation energy corrections. It is not possible to carry out calculations at this level on such large molecules, and so we have tried to estimate the errors involved in our calculations by comparison with the calculations carried out by Pople and co-workers or by us at various levels for the parent oxenium and nitrenium ions, HO^+ and H_2N^+.[16] The ground states of both of these species are triplets according to several theoretical calculations and experimental data.[17,18]

Table I compares the singlet–triplet gaps calculated at a variety of levels and the experimental values for these species. At all of these meager levels, the singlet–triplet gap is much too large, because the UHF calculations carried out on the triplet states are superior to the RHF calculations on the singlet. Even at the highest level of calculation (MP4) the triplet is more stable than the singlet by ~72 kcal/mol[16] for HO^+ and ~35 kcal/mol[5,16] for H_2N^+, whereas those values are 54 kcal/mol and 23 kcal/mol, respectively, experimentally. At the same computational level, the singlet–triplet gap of CH_2 is 16 kcal/mol,[16] while the experimental value is 9 kcal/mol.[19]

Table II. Calculated Relative Energies (kcal/mol)

	E(singlet) − E(triplet) PhO^+	$PhNH^+$
HF/STO-3G	39.4	23.7
HF/3-21G//STO-3G	11.8	9.1
MP2/3-21G//STO-3G	−32.8	−40.2

The calculated SCF energies at the STO-3G level and single point MP2 calculations at the 3-21G level for phenyloxenium and phenylnitrenium ions are shown in Table II. There are enormous lowerings of the energies of the singlet states relative to the triplets with the larger basis set and inclusion of correlation energies. Nevertheless, it is clearly not possible to predict the singlet–triplet gap on the basis of these results. On the other hand, the pronounced lowering of the singlet state with respect to the triplet is shown clearly in these calculations. If we make the rash assumption that the corrections to be made to the calculated singlet–triplet gap are the same for both the parent and phenyl-substituted species, then the 3-21G and MP2/3-21G calculations predict that the singlet state of PhO^+ is 20 to 50 kcal/mol more stable than the triplet.[20] However, this is only tentative, and much better calculations will be required in order to determine the singlet–triplet gap.

The pattern for $PhNH^+$ is similar, and correcting the STO-3G results give a singlet–triplet gap of 10 kcal/mol, with a predicted singlet ground state. Ford and co-workers[5] have performed MNDO calculations on phenylnitrenium ion, and they predicted that arylnitrenium ions have singlet ground states. For comparison, the ground-state multiplicity of phenylcarbene depends on the calculation methods used.[21,22] whereas the triplet ground state is favored experimentally by only a few kcal/mol.[23] Note that the differential stabilization of the singlet by phenyl is only 7–8 kcal/mol for the carbene,[14] whereas it is about 54 and 32 kcal/mol for the oxenium and nitrenium cations.

The calculated triplet states of phenyloxenium and phenylnitrenium ions with the UHF theory were significantly contaminated by higher spin states. The values of $\langle S^2 \rangle = S(S + 1)$ are 2.4 and 2.6 for PhO^+ and $PhNH^+$, respectively, whereas $\langle S^2 \rangle$ is 2.0 for a pure triplet. Spin contamination makes the calculated triplet energy too high, but the more flexible wave function of the UHF calculation more than compensates for this. This problem is also present in the calculations of phenylcarbene when the UHF theory is employed for the triplet phenylcarbene. The calculated singlet–triplet gap of phenylcarbene is 39 kcal/mol,[14] and 35 kcal/mol[16] for methylene, with the triplet lower in energy with the use of the 3-21G basis set. Similar calculations predict that the singlet–triplet gap of phenylcarbene is 24 kcal/mol and that the molecule has a triplet ground state.[21] The stabilization of the singlet

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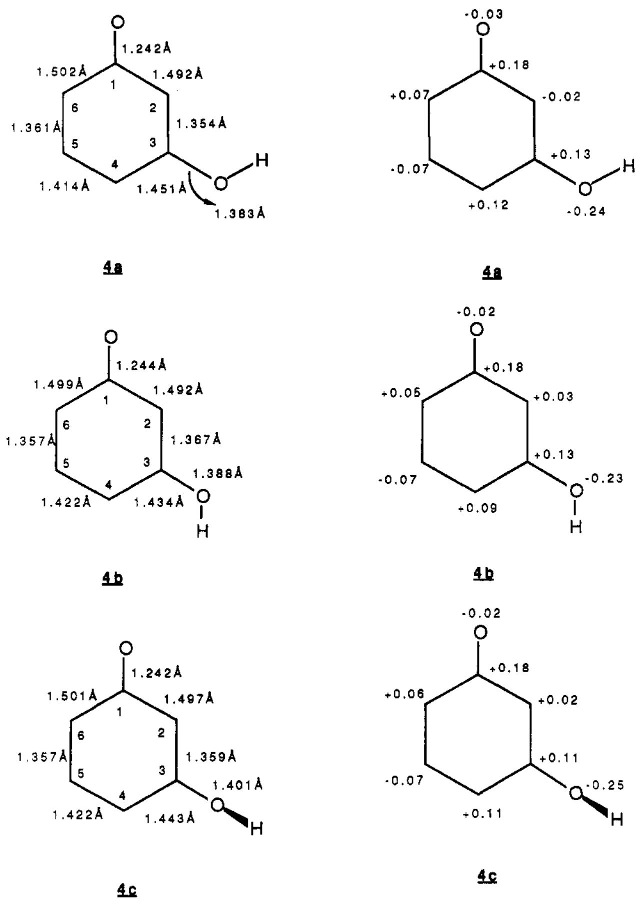
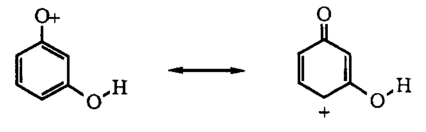


Figure 4. STO-3G optimized geometries and the calculated total Mulliken charges of the *m*-hydroxyphenyloxenium cation.

state with respect to the triplet state by a phenyl group is much greater for the charged oxenium and nitrenium species than for the neutral methylene. The differential stabilization of the singlet is about 9 kcal/mol for methylene, 33 kcal/mol for nitrenium, and 54 kcal/mol for oxenium. This is in qualitative order of the stabilization of the system by charge delocalization. Resonance donation in a carbene occurs with charge separation, while resonance donation in oxenium and nitrenium is quite favorable and removes positive charge from the electronegative oxygen and nitrogen, without additional charge separation.

In order to probe the cyclization chemistry of substituted molecules, the geometries of singlet *m*-hydroxyphenyloxenium were optimized at the STO-3G level. Although we are not certain of the ground states of these species, they are likely singlet, and in any case the methods of generation will give singlets. Two energy minima were found for the *m*-hydroxyphenyloxenium cation. These are shown in Figure 4. The species with OH syn to C_2–C_3 (**4a**) is more stable than the planar structure with the anti geometry (**4b**) by 2.6 kcal/mol. This is most likely an electrostatic effect, since the more stable structure has the negative end of the OH dipole pointing in the direction of the greater positive charge at the C-4 position. Considering the dominant resonance structure **9**, this conformation also resembles that which is preferred for enol ethers and alcohols.[24]



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The structure with H–O–C–C = 90° (**4c**) is an energy maximum, with an energy calculated to be 5 kcal/mol above that of the minimum (**4a**). The calculated barrier to rotation is identical with that calculated for phenol[25] and close to the experimental barrier of 3.4 kcal/mol of phenol.[26] Thus, the rotational barriers of OH groups and presumably OR groups that are meta to the phenyloxenium oxygen are predicted to be identical with those of the neutral species. For aryl ethers, barriers to rotation are about 6 kcal/mol.[27] The linear C–O–C is calculated to be 30 kcal/mol above that of **4a**, so that we do not consider further this high-energy species as a potential intermediate in these reactions.

The relatively rigid planar conformation preferred for *m*-aryl ethers must prevent the intramolecular cyclization of **7** and **8**. In the predominant conformation, **4a**, cyclization is disfavored since there is little positive charge at the C-2 position. The electrophilicity of C-2 should be substantially less than that of C-4.[6a] Conformation **4b** is 2.6 kcal/mol higher in energy than that of **4a**, so that intramolecular reactions of **4b** will also be disfavored. The perpendicular conformations that are most favorable for cyclization (Figure 1) are about 6 kcal/mol higher in energy. Intermolecular reactions are expected to dominate for such compounds. The same would be true for the *m*-aryloxy or aralkyloxy aryloxenium ions with even higher rotation barriers, and intramolecular cyclizations are unlikely to occur. By contrast, the preferred conformation of an alkyl side chain will have C–C–C–C = 90°, ideal for the intramolecular cyclization.

Conclusion

We have investigated the electronic structures and geometries of phenyloxenium and phenylnitrenium cations. Both are predicted to have singlet ground states. Calculations on the substituted molecules provide an explanation for the reluctance of some alkoxy-substituted compounds to undergo intramolecular cyclizations.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research.

Registry No. **1a**, 41071-17-4; **2a**, 65756-50-5; 3-$HOC_6H_4O^+$, 119696-15-0; $PhCH_2^+$, 6711-19-9; $C_6H_7^+$, 26812-57-7.

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