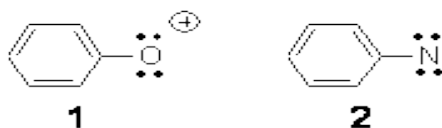


PHENYLOXENIUM CATION

A significant portion of Chapter 4 of my book is devoted to phenylnitrene **2** and phenylcarbene. Phenyloxenium cation **1** is isoelectronic with phenylnitrene and so one might expect similar behavior of the two. Winter has reported a nice computational study of the singlet and triplet phenyloxenium cation and finds some very striking differences between phenyloxenium cation and phenylnitrene.¹



Phenylnitrene has a triplet ground state, with the 1A_1 state about 18 kcal mol⁻¹ higher in energy, and the 1A_2 state higher still.

CASPT2/pVTZ//CASSCF(8,8)/pVTZ computations of **1** find the singlet 1A_1 to be the ground state. The lowest triplet is 22.1 kcal mol⁻¹ higher in energy, and the lowest 1A_1 state lies 30.8 kcal mol⁻¹ above the ground state singlet. (The structures of the lowest singlet and triplet of **1** are shown in Figure 1.) Reanalysis of the ultraviolet photoelectron spectrum of the phenoxy radical² switches the assignments of the observed transitions and is in excellent agreement with these computed values. G3 and CCSD(T)/cc-pVTZ predicts a similar value for the singlet-triplet gap. B3LYP, MPW1PW91, and some other DFT methods predict the

singlet to be lower in energy than the triplet, but with a gap half of the correct value of 22 kcal mol⁻¹.

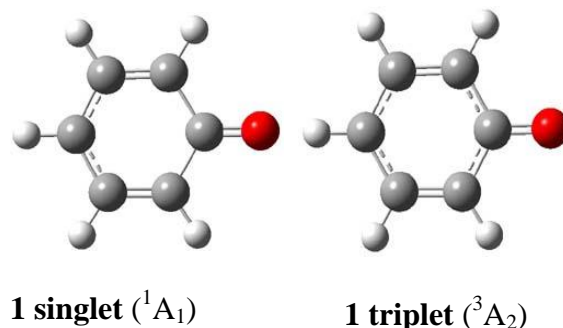


Figure 1. CASSCF(8,8) optimized geometries of the lowest singlet and triplet states of **1**. The origin of the difference between **1** and **2** lies in the description of the singlet state. The singlet state of **1** places the two lone pairs on oxygen into the sp-like orbital and into the in plane p orbital. However, in **2**, the singlet is described by two determinants, one with the nitrogen lone pairs in the sp and in plane p orbital and the second determinant has them in the sp orbital and in the perpendicular p orbital. For **1**, this single determinant allows for the positive charge to delocalize into the phenyl ring and off the very electronegative oxygen; this is manifest in a short C-O bond (1.211 Å). The greater electronegativity of oxygen then nitrogen brings the perpendicular p orbital lower in energy and better able to mix with the phenyl π-orbitals. In other words, the greater electronegativity of O over N results in a large symmetry break of the degenerate p orbitals.

Source: <http://comporgchem.com/blog/?p=1540>