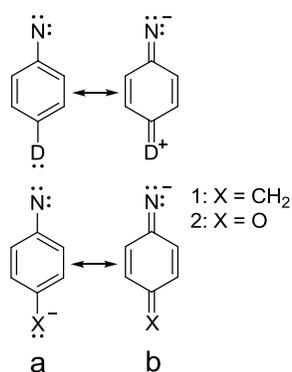


# SUBSTITUENT DEPENDENT SPIN-STATES IN NITRENES: A GROUND-STATE SINGLET AROMATIC NITRENE

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## INTRODUCTION

Phenylnitrene is a highly reactive molecule with a triplet ground state and an open-shell singlet 15 kcal/mol higher in energy (1). Calculations predict the lowest energy closed-shell singlet is 30-40 kcal/mol higher than the triplet (2). It has been previously proposed that strong pi-donating substituents ortho-



**Figure 1.** Nitrene (a) and quinoidal (b) resonance structures of closed-shell singlet aromatic nitrenes with neutral (D) and anionic (X)  $\pi$ -donating groups.

and para- to the nitrene on the aromatic ring can be used to stabilize the closed-shell singlet. However, this strategy suffers from diminishing returns due to increased zwitterionic character (3). In this work we use anionic pi-donating groups to avoid formation of the zwitterion (Figure 1). We use ion-molecule reactivity studies to show that aromatic nitrenes with anionic pi-donating groups can have closed-shell singlet ground states.

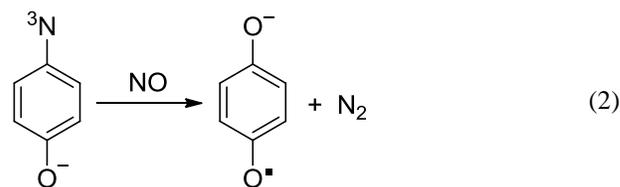
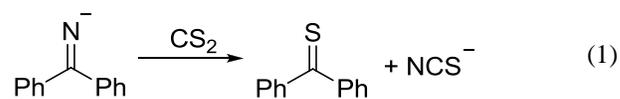
## EXPERIMENTAL

Reactivity studies used to determine the electronic structure of the ions are carried out in a high-pressure (0.4 Torr) flowing-afterglow ion source equipped with a triple-quadrupole mass spectrometer (4). Reagent ions, HO<sup>-</sup> or F<sup>-</sup>, are generated by electron ionization and carried down a 1 m long flowtube by a helium carrier gas (0.4 Torr, 190 STP cm<sup>3</sup>/s) where they are allowed to react with sample vapor introduced at one of six reagent inlets. At the downstream end of the flowtube, ions are sampled into the mass spectrometer through a 1 mm nosecone orifice where they are analyzed based on their mass-to-charge ratio (m/z). All ions in this work are generated by electron ionization or deprotonation of the corresponding aromatic azides. Experimental results are compared with calculated predictions performed at BLYP/6-311++G(3df,2p) level of theory.

## RESULTS

Calculations of the energies of pNC<sub>6</sub>H<sub>4</sub>X ions predict that the singlet-triplet gap,  $\Delta E_{ST}$ , becomes smaller as the pi-donating strength of X increases (Figure 1). For X = O<sup>-</sup>

(2), the calculated  $\Delta E_{ST} = -1.5$  kcal/mol indicating that it has a triplet ground state but the singlet is close in energy. For stronger pi-donors such as -NH<sup>-</sup> and -CH<sub>2</sub><sup>-</sup> (1), calculations predict the singlets to be the ground states by 1.4 and 5.2 kcal/mol, respectively. Reactivity studies agree with the predictions and we found that **1** reacts with CS<sub>2</sub> by formation of NCS<sup>-</sup>. This product has been observed previously in the reaction of azide anion (N<sub>3</sub><sup>-</sup>) and CS<sub>2</sub> (5), and is also formed in the reaction of deprotonated benzophenone imine with CS<sub>2</sub> (Equation 1).



Thus, the formation of NCS<sup>-</sup> indicates the presence of a closed-shell singlet N-based anion. The NCS<sup>-</sup> product is also formed in the reaction with ion **2** along with a CS<sub>2</sub> adduct.

Ion **2** is also found to react with nitric oxide by nitrogen-oxygen exchange (Equation 2). This reaction is characteristic of open-shell nitrene anions and has been observed previously with doublet phenylnitrene anion (6). We interpret the reactivity shown in equation 2 to indicate the presence of the triplet state. When nitric oxide reacts with **1**, only addition products are obtained, consistent with what is observed with other closed-shell anions.

These reactivity results are in agreement with the calculated predictions. The nitrene with the strongest pi-donor, **1** ( $\Delta E_{ST} = 5.2$  kcal/mol), displays only closed shell reactivity. When a slightly weaker donor is used, **2** ( $\Delta E_{ST} = -1.5$  kcal/mol), both closed and open-shell reactivity is observed. We interpret the latter result as indicating a triplet ground state for **2** but that the low-lying closed-shell singlet is accessible though inter-system crossing, especially within the CS<sub>2</sub> adduct.

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