Fundamental Characterization of Diradical Pyrazines

Thais Scott and Carol Parish

Department of Chemistry, Gottwald Center for the Sciences, University of Richmond, Richmond, VA 23173

My project focuses on the fundamental characterization of the diradical isomers associated with the pyrazine molecule. Since oil shale contains a high proportion of cyclic species and radical recombination reactions are significant in the combustion of oil shale, characterizing diradical pyrazines provides valuable information to improving the productivity of oil shale.

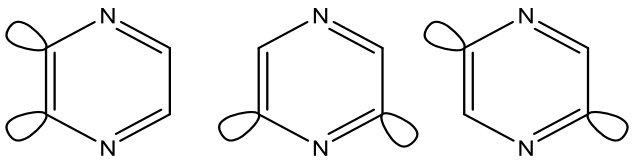

Figure 1. 2,3-didehydropyrazine, 2,6-didehydropyrazine, and 2,5-didehydropyrazine

Molecular orbitals were generated using ROHF/cc-pvDZ and assigned irreducible representation labels under C_{2v} symmetry for 2,3 and 2,6 didehydropyrazine and under C_{2h} symmetry for 2,5-didehydropyrazine. Complete active space orbitals included the σ and σ* orbitals (2,6: $11a_1$ and $7b_2$; 2,3: $10a_1$ and $8b_2$; 2,5: $9b_u$ and $9a_g$) and the π and π* orbitals (2,6: $1b_1$, $2b_1$, $1a_2$, $3b_1$, $2b_2$, $4b_1$; 2,3: $1b_1$, $1a_2$, $2b_1$, $3b_1$, $2a_2$ $4b_1$; 2,5: $1a_u$, $1b_g$, $2b_g$, $2a_u$, $3a_u$, $3b_g$). Geometry optimizations were performed on both the ground and excited triplet states at the MCSCF, MR-CISD, and MR-AQCC levels of theory, using both cc-pvDZ and cc-pvTZ basis sets with the COLUMBUS software. Single point calculations were calculated using the MR-CISD/cc-pVTZ geometry for the ground state, which in each isomer was the lowest lying singlet. From the adiabatic gaps and geometries it was found that 2,5-didehydropyrazine is the most stable followed by 2,6-didehydropyrazine, and then 2,3-didehydropyrazine.This follows the opposite trend of the ortho, meta, and para benzynes which parallel these diradicals.