Diradical Isomers of Pyrazine

Thais Scott, Carol Parish*

Department of Chemistry, Gottwald Center for the Sciences,

University of Richmond, Richmond VA 23713

Abstract

Diradical pyrazine isomers, 2,3-didehydropyrazine (2,3), 2,6-didehydropyrazine (2,6), and 2,5-didehydropyrazine (2,5), were characterized using MCSCF, MR-CISD with and without an *a posteriori* Davidson correction, and MR- AQCC methods with cc-pVDZ and cc-pVTZ basis sets. These methods were used on the lowest lying singlet and triplet states with the COLUMBUS software. Initial molecular orbitals were generated using the ROHF/cc-pVDZ method and assigned irreducible representation labels under C_{2v} symmetry for 2,6 and 2,3 and under C_{2h} for the 2,5 isomer. CAS(8,8) active space orbitals included each molecule's specific σ and σ^* orbitals and π and π^* orbitals. MCSCF was used to optimize the orbitals and generate the reference wavefuntion for further geometry optimization using the MR-CISD and MR-AQCC methods. Adiabatic and vertical gaps between the lowest lying singlet and triplet states, optimized geometries, orbital energies, unpaired electron densities, and spin polarization effects were also compared. The 2,3 singlet state is stabilized by weak interactions between dehydrocarbons in the singlet. The triplet state in 2,3 is stabilized by weak interactions between the nitrogen lone pair and the dehydrocarbons. For 2,6 the singlet is destabilized by spin polarization and a high energy σ-orbital doubling as the anti-bonding orbital for the 3-center 4-electron interaction. In 2,5 the ground state singlet is stabilized by through-bond coupling, spin polarization, and stabilizing interactions between the nitrogen lone pairs and dehydrocarbons. Preliminary MCSCF calculations with a CAS(12,10) active space indicate that the nitrogen atoms may be necessary in the active space and further investigation is needed.