Characterizing 2, 6 didehydropyridine with Quantum Mechanics

Michael Kitimet & Carol Parish

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

This project concentrates on the characterization of the 2, 6 didehydropyridine diradical. This molecule was initially reported as an intermediate in the Chichibabin reaction of 3-substituted pyridines about 4 decades ago (*doi: 10.1002/poc.3120)*. It was also reported that 2, 6 pyridine was responsible for resin formation observed when 2-halopyridines were treated with lithium piperidide. However, thorough evaluation of 2-bromo-3, 5 dialkoxypyridines reacting with potassium amide as well as with lithium piperidide by Adam, Grimisom and Hoffmann, exclusively according to an addition-elimination (AE) mechanism, showed that the molecule wasn't formed as an intermediate (doi:10.1016/S0040-4039(01)87486-4). Additionally, previous work suggests that the 2, 6 didehydropyridine diradical is the least stable of all possible didehydropyridines due to a destabilizing 3-center and 4-electron interaction between the bonding combination of the two nonbonding σ-orbitals and the nitrogen lone pair(doi:10.1016/S0040-4039(01)87486-4). Such study of diradicals is invaluable in facilitating the design of novel DNA-cleaving anticancer drugs as well as understanding intermediates important in combustion and tobacco smoke. Moreover, proper characterization of the structures and excitation energies may allow better control of the chemistry of these intermediates. The molecular orbitals of the 2, 6 pyridine diradical were analyzed and irreducible representations determined under C2V symmetry. The geometry of the molecule was found by optimizing the molecule in both the singlet and triplet states using single point and geometry optimization calculations in MCSCF, CISD and AQCC. These geometries were then used to determine the change in energy for both adiabatic and vertical excitations. Calculations were performed using the Gaussian and Columbus software packages.