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THE EFFECT OF FLUORINE ON SMALL ORGANIC SYSTEMS – AN *AB INITIO* APPROACH

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In cyclopropane systems, gem-difluorosubstitution has a substantial impact on the electron distribution (and hence on structure). Successive fluorination of the trimethylene methane diradical will lead to an increasing singlet-triplet splitting. For both the di- and the tetrafluorinated forms, there are low-lying, planar, triplet forms that have no counterpart in the hydrocarbon analogue. The distributed species has three different singlet state conformers at energies around 30-40 kcal/mole above the closed ring (difluoromethylene cyclopropane). From comparison with experimental value of activation energy, any of these forms could be a reaction intermediate. In contrast, the tetrafluorinated diradical has no low-lying singlet form that is likely as a candidate for intermediate in the rapid, sigmatropic rearrangement reaction of tetrafluoromethylene cyclopropane. Furthermore, the calculations show a dramatic change in the charges of the carbon skeleton of the diradical as a result of fluorination. Whereas the hydrocarbon central carbon bears a highly positive charge, fluorination will lead to a normal, slightly negative charge of the central carbon atom. The calculation on the closed shell systems are performed within the Hartree-Fock approximation. Geometries are optimized by using the gradient technique. The open shell triplets are calculated within the framework of Unrestricted Hartree-Fock. The singlet states are calculated by a Restricted Hartree-Fock procedure. A 3 x 3 CI correction was incorporated. The calculations were performed with a 4-31G basis set, and no geometry optimization was performed on the open shell systems.