MO-Theoretical Studies on a Model Complex for Deoxymyoglobin

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Z. Naturforsch. **53 a,** 755–765 (1998); received July 1, 1998

The origin of the displacement of the Fe atom in deoxymyoglobin with respect to the porphyrin plane in the high-spin state is examined by a qualitative molecular orbital (MO) analysis on the extended Hückel level. We find that attachment of a fifth ligand (imidazole in our model complex) to Fe(II)porphyrin favors the out-of-plane shift due to a strengthening of the bonding interaction between Fe and the nitrogen of the imidazole ligand. This results in a high-spin (S = 2) ground state with Fe shifted out-of-plane for the five-coordinate complex instead of an intermediate spin ground state (S = 1) with Fe lying in the plane for four-coordinate Fe(II)porphyrin. The relative energies of the different spin states as a function of the distance between Fe and the porphyrin plane are evaluated using an ROHF (restricted open shell Hartree-Fock) version of an INDO (intermediate neglect of differential overlap) method. We observe a level crossing between high-spin and intermediate spin states whereas the low-spin (S = 0) state remains always higher in energy.

Key words: Metalloporphyrines, Electronic Structure, Structural Preferences,
Molecular Orbital Model.

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