EXTENDED HÜCKEL CALCULATIONS ON BIS-IMIDAZOLE LOW-SPIN FERRIPORPHYRINS

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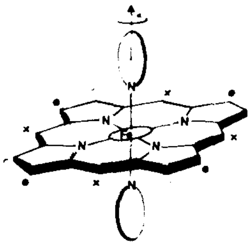
The biological function of metal porphyrins rests largely upon their ability to exchange ligands coordinated in axial position to the metal ion. The kinetic of the ligand exchange has been studied extensively in the past(1-3). It turned out that other physical properties,such as the hyperfine coupling constant for the different nuclei in the porphyrin skeleton strongly depend on the temperature.It was postulated that this temperature dependence is caused by rotations of the axially bound ligands between different energetical stable positions (4).This hypothesis was supported,for example, by the unusual temperature variation of the chemical shift found for the four pyrrole nitrogen atoms in the porphyrin ring plane (5).



In order to get a more quantitative impression on the influences of the charge distribution in the porphyrin ring caused by the dynamics of axially bound ligands, several EH-calculations on the bis-imidazole ferriporphyrin complex have been performed at varying Fe-N distances and rotation angles of the ligand molecules, as it is indicated in the figure.In a previous NMR study (6) it was suggested that the main influence involved in spin delocalization results from an interaction between the metal-e_g and the filled porphyrin $3e_g$ orbital. Our investigation on the bis-imidazole complex supports this idea. There is indeed one filled molecular orbital(MO) which belongs to the e_g representation in the D_{4h} point group. It is the energetical highest occupied e_g-MO. This orbital, which was calculated for the complete bis-imidazole complex, is characterized by a zero charge density (nodes) at the methene carbon atoms (X) and high charge density at the pyrrole ring carbons (O,●) in the porphyrin skeleton. The calculated charge distribution is in qualitative agreement with experimental results deduced from NMR chemical shift measurements (4-6). Tremendous changes of the charge density at the position of the pyrrole carbon (O,●) and nitrogen atoms occur in this particular MO for any alterations of the coordinates of the ligands perpendicular to the porphyrin ring plane. The changes of the charge distribution in all other occupied MO's was found to be moderate or even zero compared to this energetical highest e_g-MO.

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