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Extended Hückel Calculations on the Bonding in Oxyhaemoglobin

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Extended Hückel calculations are performed for two theoretical models of oxygenated iron porphyrin. In both cases the Pauling geometry is predicted to have the lowest energy and hence to simulate the bonding in oxyhaemoglobin.

The bonding of molecular oxygen to the iron in haemoglobin, and myoglobin, has been the subject of much study for several years. Although X-ray analyses have been performed on oxyhaemoglobin [1], the resolution is not sufficiently accurate to determine the position of the oxygen molecule relative to the haem (iron porphyrin). Indirect methods have been employed [2] but conclusions are contradictory; in addition, several workers have performed calculations on the iron oxygen system [3–5] but again results are conflicting. Two particular geometries have been favoured, the Pauling [3] and Griffith [4] models (systems *A*, $a = 60°$ and *B*, $b = 0°$ respectively in Fig. 1). In this note, the results of Extended Hückel (EH) calculations on a number of geometrical arrangements (Fig. 1) are reported. Two theoretical models were employed in order to minimise inherent errors in the choice of basis set.

Both models used the Wolfsberg-Helmholz approximation [6] and Slater atomic orbitals, assumed a ground state singlet configuration of the iron (II)

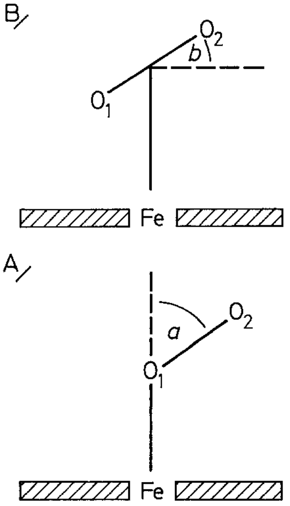

Fig. 1. Geometries of oxygenated iron porphyrin

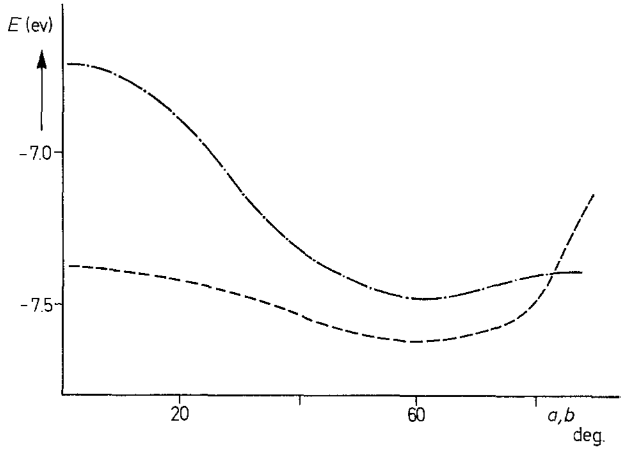

Fig. 2. Calculated relative energies from Model I, as a function of angle. (- - - System *A*; —·—·— System *B*)

porphyrin (oxyhaemoglobin is diamagnetic [7]), and calculations for each geometry were repeated assuming, in turn, an effective charge on the iron of 0.5^+ and 1.0^+. In model I, all valence orbitals of the iron (3*d*, 4*s*, 4*p*), oxygen, porphyrin nitrogen atoms, and a fifth ligand nitrogen, were included in the basis set. All ligands were assumed to be neutral. A variety of iron-oxygen and oxygen-oxygen bond lengths were considered and those leading to the system of the lowest energy were found to be $r_{Fe-O} = 2.1$ Å and $r_{O-O} = 1.48$ Å. Fig. 2 illustrates the resultant trends of relative total energies as a function of angle for the geometrical systems *A* and *B*. Both of these have minima at 60° with system *A*, $a = 60°$ (corresponding to the Pauling model) having lowest energy of all geometries. The Griffith model ($B, b = 0°$) is the least stable.

Model II adopted the basis orbitals used by Ohno *et al.*, [8] for the iron porphyrin, but all valence orbitals for the oxygen. The carbon atoms were assumed to be neutral and the porphyrin nitrogens to bear a charge of 0.5^-. As from Model I, system *A*, $a = 60°$ was calculated to have the lowest energy, and consequently is predicted to simulate the bonding in oxyhaemoglobin.

In a subsequent paper we will show that the use of iterative EHT on a third model system allows an independent prediction of the bonding in oxyhaemoglobin, from other considerations. The Pauling model is confirmed to be the best representation of oxyhaemoglobin.

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