

06.2-4 THE ELECTRON DENSITY DISTRIBUTION IN THE HYDROGEN BOND: QUANTUMCHEMICAL CALCULATIONS; COMPARISON WITH DIFFRACTION RESULTS ON OXALIC ACID. By M. Krijn and D. Feil, Chemical Physics Laboratory, Twente University of Technology, Enschede, The Netherlands

Quantumchemical calculations of the electron density distribution in hydrogen bonded dimers abound but their relevance is severely restricted by two important factors: the basis sets used are too small and the assumed gasphase geometry differs considerably from the geometry found in short hydrogen bonds in condensed matter. The present calculations are based on the Hartree-Fock-LCAO method, using the local density approximation to account for exchange effects. (Baerends & Ros, Int. J. Quant. Chem. S12, 169 (1978)). The basis set effect is shown by carrying out calculations on the water dimer, using two different sets of Slater-type orbitals as basis functions and the frozen core approximation for the oxygen atoms. The basis sets are:

I) O: s,s,p,p,d H: s,s,s,p,p,d

II) O: s,s,s,p,p,p,f H: s,s,s,p,p,d

The smaller one is slightly more extensive than the much used 6-31G\*\* set of Gaussian orbitals.

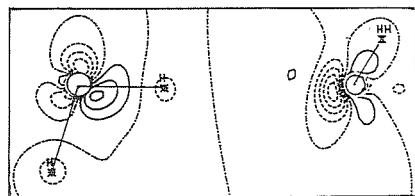


Figure 1. The difference in electron density between dimer and monomers. O-O distance 2.98 Å as in gasphase. Basisset I.

$$\Delta\rho_h = \rho(\text{H}_2\text{O})_2 - \rho_A(\text{H}_2\text{O}) - \rho_B(\text{H}_2\text{O})$$

Figures 1 and 2 show the effect of hydrogen bonding on the density of the molecules.

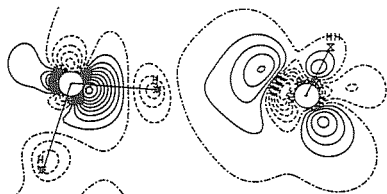


Figure 2.  $\Delta\rho_h$  O-O distance 2.49 Å as in oxalic acid dihydrate. Basisset II.

The difference between the two figures is shown to be due to the extension of the basis set and to the shortening of the O-O distance. The distribution in the hydrogen bond region is similar to the corresponding distribution in oxalic acid·2H<sub>2</sub>O, as shown in Figure 3.

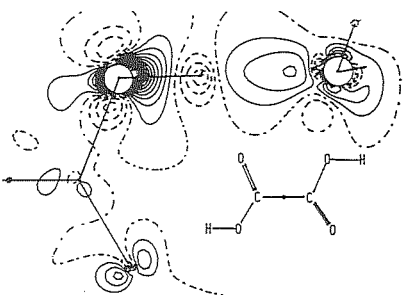


Figure 3.  $\rho(\text{oxalic acid}\cdot 2\text{H}_2\text{O}) - \rho(\text{oxalic acid}) - \rho(\text{H}_2\text{O})$ ; basisset II.

The various effects are of such a magnitude that comparison with the results of accurate X-ray diffraction experiments becomes meaningful. The most important features of the hydrogen bond are confirmed by the diffraction results on oxalic acid·2H<sub>2</sub>O and oxalic acid·urea.

06.2-5 EXPERIMENTAL ELECTRON DEFORMATION DENSITY OF 7,7,8,8-TETRACYANOQUINODIMETHANE (TCNQ) AT 110K. By Ashfaqurraman Syed and Edwin D. Stevens, Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, U.S.A.

Since the discovery of high electrical conductivity in the organic charge transfer complex TTF-TCNQ, interest in the physics and chemistry of the organic solid state has undergone an explosive growth. Although TCNQ itself is not highly conducting, its ability to form the radical anions TCNQ<sup>-</sup> and (TCNQ)<sub>2</sub><sup>-</sup> as well as forming partially charged species make it a frequent component of charge transfer salts. We have begun low temperature studies of the electron density distributions in some of these salts to obtain a direct measure of the charge transfer.

The electron distribution of TCNQ has been determined from high resolution x-ray measurements at 110K. Cell dimensions (110K): a=8.865(2), b=6.883(1), c=16.387(1) Å,  $\beta=98.21(3)^\circ$ , C2/c, Z=4. Experimental X-ray deformation maps have been calculated using atomic parameters from a refinement of data with  $\sin\theta/\lambda > 0.65 \text{ \AA}^{-1}$ . As expected, density accumulation is observed in all covalent bonds, and in the lone pair regions of the nitrogen atoms. The triple bond is clearly distinguished by a large density peak extending perpendicular to the bond axis. The quinoid character of the aromatic ring is also clearly evident in the deformation density. Model dynamic and static deformation densities based on a least-squares fit to the x-ray data using multipole deformation functions will be presented.

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06.2-6 ELECTRON DENSITY MAPPING IN HEMOGLOBIN MODEL SYSTEMS: COMPARISON OF CHARGE DENSITIES IN SEVERAL IRON PORPHYRINS AND PHTHALOCYANINES By P. Coppens, C. Lecomte, K. Tanaka and Liang Li, Department of Chemistry, SUNY/Buffalo, Buffalo, NY 14214, USA.

Accurate crystallographic methods are being applied to the mapping of the three-dimensional electron distribution in iron porphyrins and phthalocyanines with different spin states, metal oxidation number and coordination geometry. Studies on Fe(III) methoxytetraphenylporphyrin (=TTP)(Lecomte, Chadwick, Coppens and Stevens, Inorg. Chem (1983) 22, 2982) and Fe(II) phthalocyanine (=Pc)(Coppens, Li and Zhu, J. Am. Chem. Soc. (1983) 105, 6173) have been completed, while studies on Fe(II) bis-tetrahydrofuran tetraphenylporphyrin, FeTPP and Fe(III) bis 2-imidazole octaethylporphyrin are in progress. In all but the Fe(III) high spin complexes a marked asphericity of the iron valence density is observed, which can be quantitatively expressed in terms of the occupancies of the Fe d-orbitals (Holladay, Leung and Coppens, Acta Cryst. (1983) A39, 377), thus leading to an assignment of the ground state electronic configuration. In particular in the case of the intermediate spin complexes Fe-Pc and FeTPP the assignment resolves an existing controversy caused by conflicting results from theoretical calculations. The electric field gradient calculated from the X-ray data is within its large error limits in agreement with values from Mössbauer spectroscopy and serves to interpret the Mössbauer results. The electron density in the porphyrin macrocycle is remarkably similar in the different complexes, except at the nitrogen pyrrole atoms where the effect of the iron configuration is discernable.

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