The Valence Electron Density Distribution of Hydrogen Bonded Systems in the Iterative Extended Hückel Approach

II. The Dimer of Formamide*

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The present paper is part of a series of investigations directed towards the study of hydrogen-bonding in terms of valence electron densities. The first paper in this series [1] dealt with the dimers of both formic and acetic acid. The hydrogen bonds in these cases were of O–H···O type and comparatively strong. It would also be of interest to treat a somewhat weaker class of hydrogen bond, namely the N–H···O type. For this purpose we selected the dimer of formamide, the geometry of which has been determined experimentally by Ladell and Post.[2] Although their interpretation of the structure in terms of dimers is questionable, this system is nevertheless of interest in so much as it has recently been the subject of non-empirical SCF-calculations.[3] An interesting comparison between results obtained with the two methods can thus be made.

Calculations. The method used, the iterative extended Hückel approach, has already been extensively described.[4–6] We will give here only the constants used in the charge iterative process. They are in decreasing order of charge:

0.000	12.750	— 26.450	for	H	1*s* orbital
−1.244	21.698	— 86.317	»	C	2*s* »
−1.639	24.915	— 84.373	»	C	2*p* »
−1.616	29.302	—131.703	»	N	2*s* »
−1.038	24.552	—110.591	»	N	2*p* »
−1.493	33.365	—178.646	»	O	2*s* »
−3.487	57.925	—107.694	»	O	2*p* »

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The orbital exponents used were obtained from Slater's rules except in the case of hydrogen, where we preferred to use the value 1.2 for the 1*s* orbital exponent. The value 1.75 was used for the Wolfsberg-Helmholz constant. The geometry used for the dimer was the one obtained by Ladell and Post,[2] and is shown in Fig. 1.

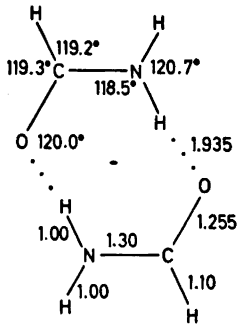

Fig. 1. The geometry of formamide. Bond distances in Å (lower part) and angles in degrees (upper part). The same geometry was used for the monomer and the constituents of the dimer.

Results and discussion. The gross atomic charges for the monomer and dimer are given in Fig. 2. The corresponding valence electron distributions are shown in Figs. 3 and 4 in the form of density level diagrams. The levels are given in units of eÅ^{-3} and the coordinate axes in Å. It should be pointed out that only the valence shell electrons are included, leading to broad minima at the nuclei for all atoms except hydrogen.

Since the effect of hydrogen bonding is difficult to distinguish by comparing total charge distributions, we have subtracted the densities of the two monomers from that of the dimer, thereby

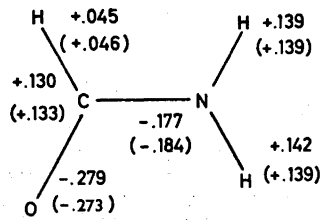

Fig. 2. Gross atomic charges for the monomer and the dimer. Figures in parenthesis refer to the monomer.

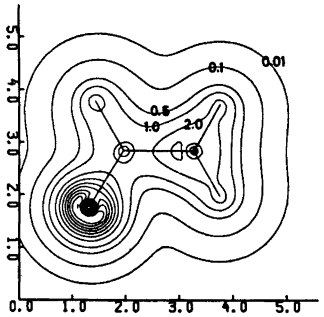

Fig. 3. Charge density of the monomer in the plane of the molecule. Density levels are drawn at 0.01, 0.1, 0.5 (0.5), 7.5 eÅ^{-3}.

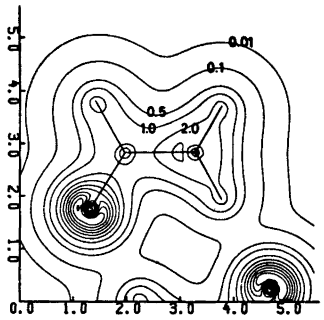

Fig. 4. Charge density of the dimer. The levels are the same as in Fig. 3.

obtaining the difference density diagrams shown in Figs. 5 and 6. These plots show the shifts in electron density for the case of idealized hydrogen-bond formation in which neither the internal molecular geometry nor the inner electron cores are affected by the hydrogen bonding. It is noticeable that there is only a small increase of charge density at the centre of the hydrogen bond, but in addition a strong decrease at the acceptor atom, indicating a fundamental difference between a hydrogen bond and a normal, covalent bond. The accumulation of charge in the N–H bond should also be noted. Its magnitude is probably too large, since the hydrogen-bonded system has been formed from rigid molecules. A "real" hydrogen bonding situation would cause a lengthening of the N–H distance and a resulting decrease of density in the bond.

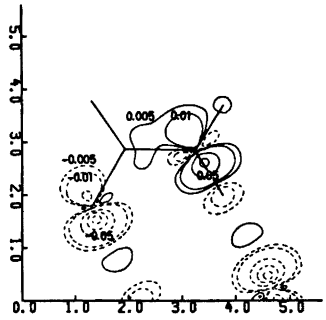

Fig. 5. Difference density in the plane of the molecule. The levels are drawn at ±0.001, ±0.01, ±0.1, ±0.2, ±0.4 and ±0.6 eÅ^{-3}.

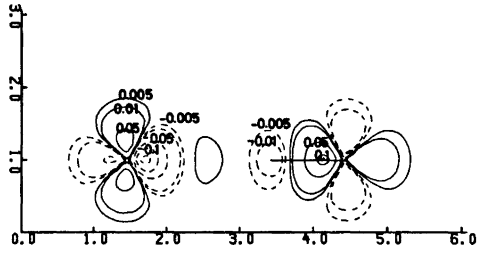

Fig. 6. Difference density in a plane containing the hydrogen bond, perpendicular to the molecular plane. The levels are drawn as in Fig. 5.

A most interesting additional observation is the close similarity between our diagrams and those obtained from the much more time-consuming *ab-initio* calculations.[3] This is especially encouraging since it is planned to study large hydrogen-bonded systems of biological importance, where rigorous *ab-initio* methods would require computer time far beyond that which is available.

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