

The Valence Electron Density Distribution of Hydrogen Bonded System in the Iterative Extended Hückel Approach: I. The Dimers of Formic and Acetic Acid *

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The valence electron densities of the hydrogen bonds in the dimers of formic and acetic acid have been calculated in the IEH approach and the results presented in the form of contour diagrams. The formation of a dimer causes a charge redistribution, consisting essentially of a displacement of charge from the oxygen and hydrogen atoms of the bridge and formation of a slight maximum between these two atoms. This is best seen from difference density diagrams, which also show that there is a flow of charge from the hydrogen bond region, and an increase in the region of the covalent O-H bond.

Hydrogen bonds have been intensely studied from various points of view, but fairly little attention has been paid to their electron density distribution. In this paper, we shall report some results from calculations of the valence electron density distribution in dimers of formic and acetic acid, in which the monomers are held together by pairs of hydrogen bonds. The results are presented in the form of contour diagrams which in a simple, un-sophisticated way give valuable information as to the nature of the most important, non-classical bond.

METHODS AND CALCULATIONS

The valence electron densities were obtained from eigenvectors, calculated by the charge iterative extended Hückel approach. This method, as well as the technique of obtaining the density level diagrams, have been discussed in previous papers,^{1,2} and will not be subject to further comments. The orbital exponents used were those obtained by Slater's rules. The value 1.75 was

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chosen for the Wolfsberg-Helmholz constant. The constants in the second order charge iterative process were in decreasing order of charge:

0.000	12.750	- 26.450	for hydrogen	1s orbital
- 1.244	21.698	- 86.317	carbon	2s
- 1.639	24.915	- 84.373	"	2p
- 1.493	33.365	- 178.646	oxygen	2s
- 3.487	57.925	- 107.694		2p

The geometry of the dimer of acetic acid was obtained from standard tables of interatomic distances³ and is shown in Fig. 1.

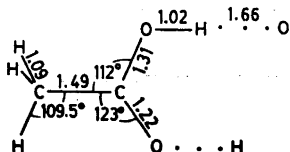


Fig. 1. The geometry of dimeric acetic acid.

The geometry of dimeric formic acid was assumed the same as that of dimeric acetic acid, the methyl group being replaced by a hydrogen atom at a distance of 1.09 Å from the carbon atom of the carboxyl group.

The difference density was obtained simply by subtracting the density of the two monomers (with the same geometry and the same position as in the dimer) from the density of the dimer.

RESULTS AND DISCUSSION

The total atomic populations are given in Table 1. The corresponding charge density distributions are shown in Figs. 2a-2c and 3a-3c for formic acid,

Table 1. Total atomic populations for the carboxyl groups of formic and acetic acid.

	Formic acid		Acetic acid	
	Monomer	Dimer	Monomer	Dimer
C	3.856	3.852	3.859	3.855
=O	6.248	6.230	6.277	6.260
-O-	6.167	6.194	6.185	6.213
H	0.803	0.798	0.805	0.801

and in 4a-4c and 5a-5c for acetic acid. The density levels are given in $e\text{Å}^{-3}$, and the units of the coordinate axes in Å.

A population analysis in terms of orbital populations indicates shifts in charge density when dimers are formed, although the total charge on each atom remains nearly the same.

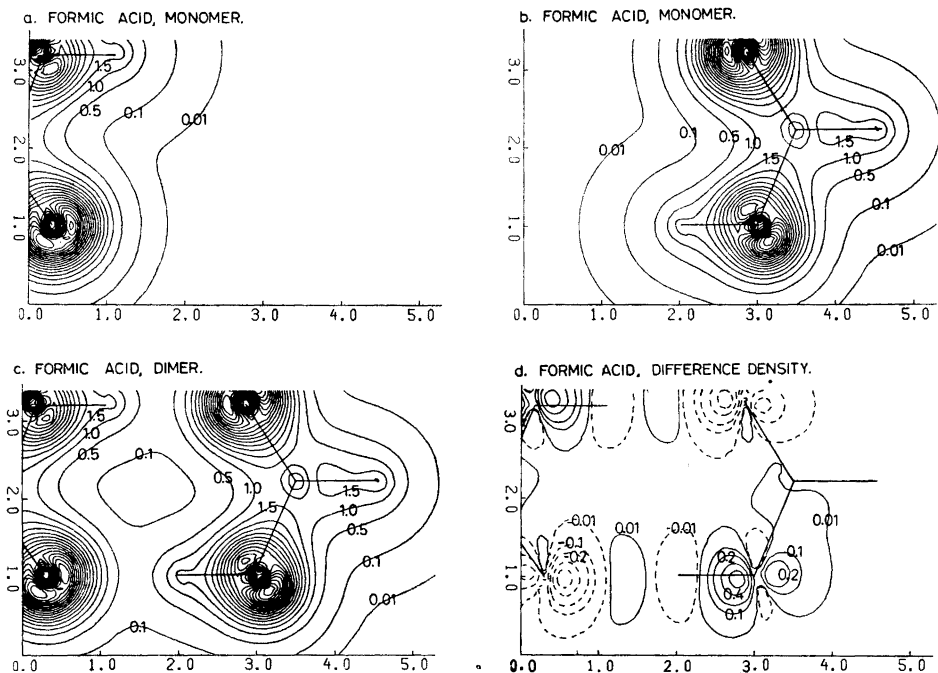


Fig. 2. Contour diagrams showing the valence electron density of formic acid in the molecular plane: a) and b) the monomer; c) the dimer; d) the difference density. The densities are given in $e\text{\AA}^{-3}$.

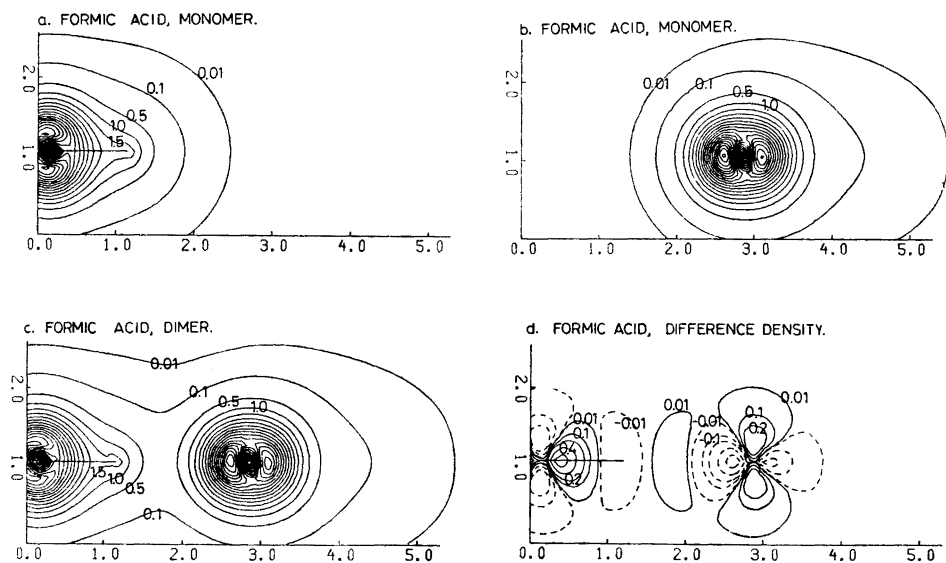


Fig. 3. Contour diagrams showing the valence electron density of formic acid in the plane of the hydrogen bond and perpendicular to the molecular plane: a) and b) the monomer; c) the dimer; d) the difference density. The densities are given in $e\text{\AA}^{-3}$.

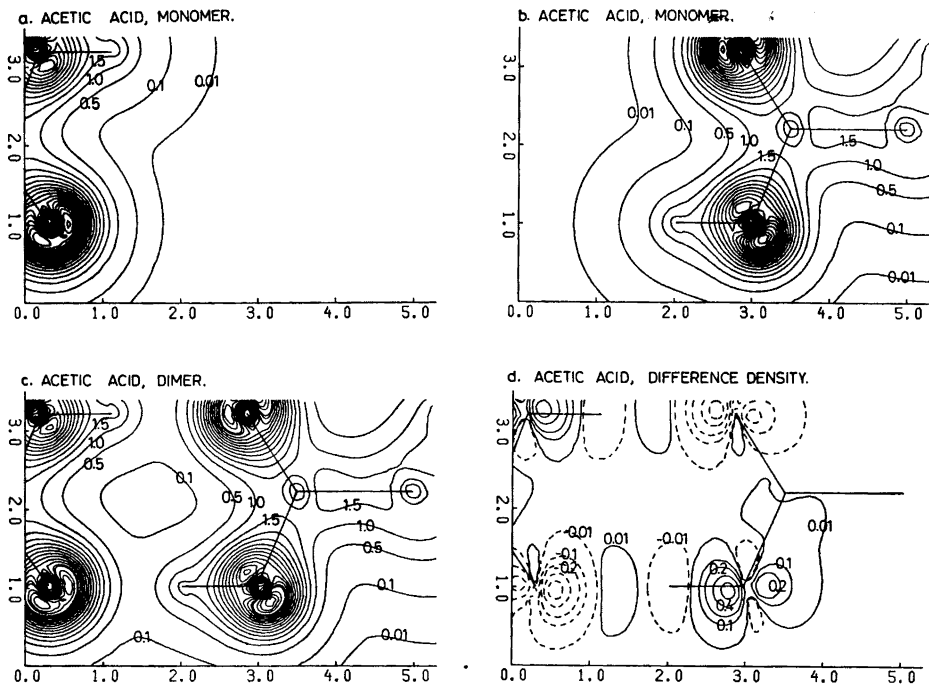


Fig. 4. Contour diagrams showing the valence electron density of acetic acid in the molecular plane: a) and b) the monomer; c) the dimer; d) the difference density. The densities are given in $e\text{\AA}^{-3}$.

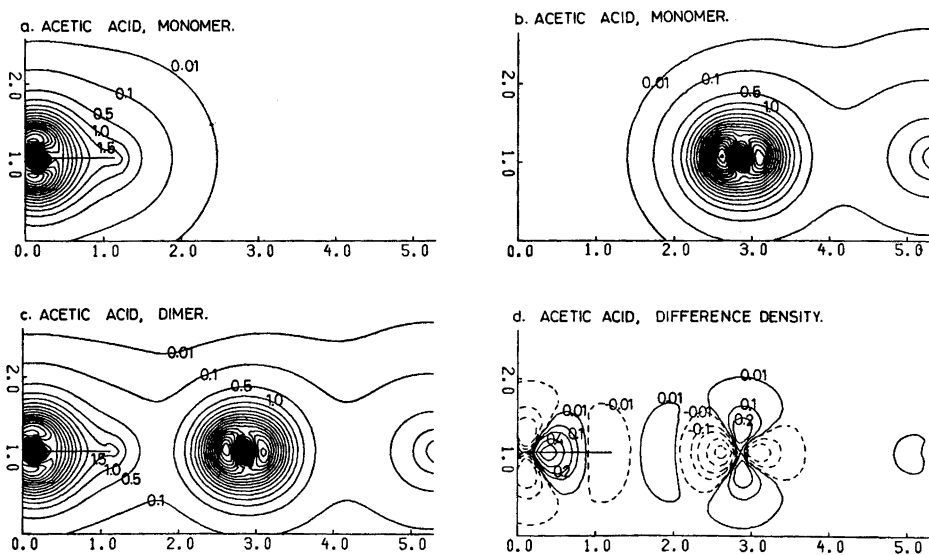


Fig. 5. Contour diagrams showing the valence electron density of acetic acid in the plane of the hydrogen bond and perpendicular to the molecular plane: a) and b) the monomer; c) the dimer; d) the difference density. The densities are given in $e\text{\AA}^{-3}$.

This is illustrated in Figs. 2d, 3d, 4d, and 5d, where the difference densities $\rho_{\text{diff}} = \rho_{\text{dimer}} - (\rho_{\text{mon}}^{\text{A}} + \rho_{\text{mon}}^{\text{B}})$ are plotted. It is noticeable that the charge density decreases in the region of the hydrogen bond interaction, whereas ordinary covalent bonding causes an increase relative to the isolated atoms. The relatively low maximum in the bond region has also to be observed. No significant difference between the hydrogen bonds of the dimers of the two acids can be observed.

Similar results have been found from *ab initio* calculations on small hydrogen-bonded systems. A recent *ab initio* treatment of the hydrogen-bonded dimer of formamide by Dreyfus *et al.*⁴ gave results which are in surprisingly good agreement with ours.

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