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On the Electronic Structure of the Hydrogen-Bond: Formamide and its Dimers

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The CNDO/2 method is applied to hydrogen-bonded systems treated as a single entity. The stabilization energies obtained are reasonable. The electron-displacements along the H-bond show σ-gain and π-loss by the proton-donor atom and σ-loss with π-gain by the proton acceptor. A slight overall transfer of charges is observed from one unit to the next.

In the last twenty years the structure of the hydrogen bond and the reasons for its stability have been the subject of a large number of papers which have been surveyed recently [1]. On account of computational difficulties most theoretical calculations on hydrogen-bonded compounds have been performed in the past on highly truncated systems. It seems nowadays that the best way to elucidate the structure of the hydrogen bond is to treat hydrogen-bonded complexes as a single large molecular system. We present here the results of a preliminary attempt in this direction, using the CNDO/2 procedure [2, 3] which has recently proven particularly useful for computations of large heteromolecules [4–7] including all valence electrons. Recently, an all-valence-electrons calculation has been reported on some hydrogen-bonded entities [8] by Hoffmann's extended Hückel procedure [9]. This last method, however, which ignores the effect of the σ-electron charges displacements on the π-electron system cannot give a complete image of the electronic distortions accompanying the hydrogen-bond formation. The results of a self-consistent procedure must be more representative in this connection.

The systems considered here are the hydrogen-bonded dimers of formamide in different configurations, namely the cyclic dimer, (I), which occurs in formamide crystals [10] and the two singly hydrogen-bonded dimers, appearing in the secondary structure of two parallel (II) and antiparallel (III) polypeptide chains respectively [11]. The intermolecular distances and angles of the formamide crystal [10] have been used as input geometries for the cyclic dimer. For the sake of consistency, the same distances have been used for the formamide units in dimers II and III where, however, the length of the hydrogen-bond of glycylglycine [12] has been utilized. A calculation of the isolated formamide molecule has been performed with the corresponding geometry for comparison. Another computation of formamide itself has also been made using the geometry derived from microwave measurements [13]. Moreover, a calculation of N-methyl-formamide in its *cis* and *trans*-configurations has been found useful.

The calculated charges in formamide itself are reported both for the crystal geometry (Fig. 1a) and for the microwave geometry (Fig. 1b)[1]. Although the

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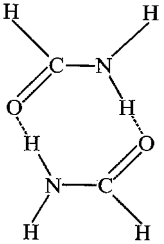
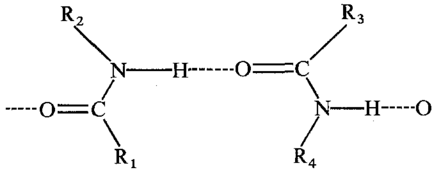
[1] The data are reported for the microwave geometry where the two NH bonds are constrained to be coplanar with the rest of the molecule *(vide infra)*.

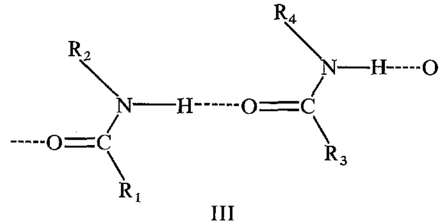
qualitative aspect of the charge distribution is the same, non-negligible differences exist which are reflected in particular in the calculated values of the dipole moment: 4.16 Debye units for the crystal geometry against 3.37 for the microwave geometry, both values bracketing the experimental value of 3.7 [13] (curiously enough the "standard" fictitious intermediate geometry used by Pople and Gordon [4] gives practically the experimental dipole moment: 3.8 Debye). The angle of the moment with the N→C direction is obtained as 40° in both calculations in excellent agreement with experiment (39°). Another interesting effect of varying the input geometry concerns the relative order of the two highest filled energy levels: in the first case the *homo* is a π-orbital closely followed by a σ-orbital, whereas a reversal occurs by lengthening the bonds. This shows again [14] that, particularly when close σ and π levels appear, one should be careful in drawing conclusions.



I



II



III

The calculations on the monomer show two other interesting features:

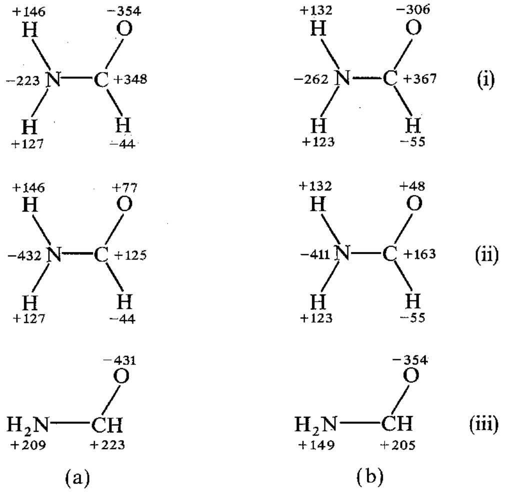


Fig. 1 a and b. Net electronic charges in formamide ($10^{-3}e$). a) geometry of the dimer; b) microwave geometry (H constrained to be in the plane); (i) total net charges; (ii) σ net charges; (iii) π net charges

i) The hybridization ratios of the different atoms are very similar to those previously obtained in other similar environments [5] and the presence of a nearly pure oxygene lone-pair perpendicular to the C=O bond appears in formamide as well as in the other carbonyl compounds already studied [5].

ii) The overall results are not strongly affected by taking into account the fact that the two NH bonds are not in the plane of the N–C–O atoms but slightly above it, although a general mixing of all atomic orbitals occurs in the nonplanar computation.

In order to assess the kind of reliability to be expected from energy calculation by CNDO/2 a computation of the *cis* and *trans* forms of N-methyl formamide has been made: we have obtained the *trans* compound to be more stable than the *cis* form by 1.25 kcal/mole, a value which is not unreasonnable with respect to the experimentally evaluated value of approximately 2 kcal/mole [15]. The calculated dipole moment of the *trans* form is 0.3 Debye units higher than that of the *cis* form.

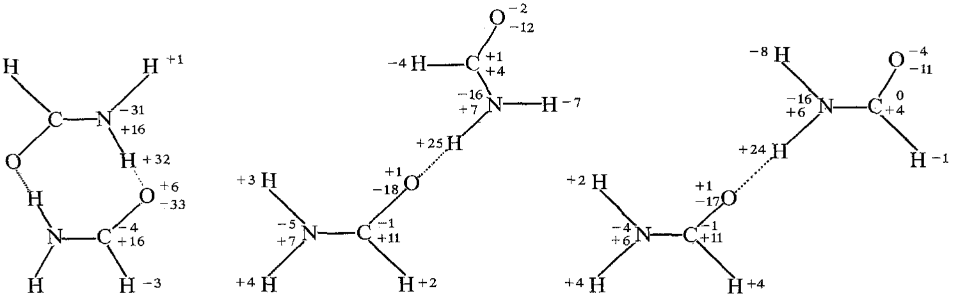


Fig. 2. Variation of the σ-(upper number) and π-(lower number) population with respect to the isolated molecule ($10^{-3}\,e$)

Considering now the hydrogen-bonded dimers of formamide, the most interesting results concern the stabilization energies and the perturbation of the electron distribution brought about by hydrogen bonding. The stabilization energy of the cyclic dimer with respect to two isolated monomer units (with the same geometries) is 11.7 kcal/mole, thus 5.8 kcal per hydrogen bond. The corresponding stabilization energies are 4.9 and 4.6 kcal/mole for the singly-bonded dimers II and III respectively. All these values are in very good agreement with the mean experimental value of hydrogen bond energies in this type of systems.

The modifications of the electronic structure of the monomer brought about by hydrogen-bonding are given in Fig. 2 for the three kinds of dimer. It is seen that in all cases the nitrogen involved in the hydrogen-bond (the proton-donor) shows a net *gain* of electron as well as does the oxygen (proton-acceptor) while the hydrogen increases its positive charge. But whereas the electron-gain by the nitrogen results from a piling-up of σ-charges associated with a loss of π-ones, on the contrary the oxygen net gain is the result of a small σ-loss and of a larger π-gain. Moreover, it may be observed that in the unsymmetrical dimers a small transfer of electrons occurs from the "proton-accepting" unit to the "proton-donating" unit (in spite of the increase of the positive charge on the hydrogen atom of the bridge). From the point of view of π-electron displacements these results confirm the empirical procedure proposed earlier [16] in which the local attraction for π electrons was empirically decreased for the proton-donor and increased for the proton-acceptor. The same reasoning however does not seem to apply uniformly to σ-electrons. In fact, as far as the present results give a reliable image of charge displacements it appears that the net electron transfer from one unit to the other is essentially σ.

Another interesting comparison is that of the calculated dipole moments of the dimers II and III compared to that of the monomer unit (Table). In both cases the moment of the dimer is about 0.4 D larger than the value obtained by simple vector addition of the unit moments.

Table. *Dipole moments (Debye units)*

	monomer[a]	dimer II	dimer III
(a)	4.16	7.92	8.68
(b)	—	7.49	8.23

(a) calculated total dipole moment, (b) value obtained by vector addition of the two unit moments (see text).

[a] With the distances as in the dimer.

Addendum

After completion of this paper a short note appeared on a CNDO/2 computation of the formic acid dimer and the hydrogen bis-(trifluoroacetate)ion [17]. The authors conclude that the method gives unreasonnably large values of delocalization energies (which they do not indicate) that they attribute to exaggerated σ-charge displacements. The total charge variations which they give seem indeed unreasonable and may possibly be due to the parametrization used which *is not* the CNDO/2 parametrization. At any rate, we do not observe anything of this kind.

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