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Relationes

Application of CNDO/II to Some Hydrogen-Bonded Systems

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Short results are given of the application of the CNDO/II method to hydrogen bonding. Formic acid (monomer and dimer), trifluoroacetic acid and the hydrogen bis(trifluoroacetate)ion were treated.

Though this work is of a preliminary character, we belive that the results may already be of interest.

We applied CNDO/II [1] to hydrogen-bonded complexes treating the complex as a unit molecule (for an extensive review see [2]). Our calculations were done on the formic acid dimer and on the hydrogen bis-(trifluoroacetate) ion. The geometry of the first one is the same as in [3] and the data for the second were taken from [4]. In the calculations all valence electrons were included and in some also a $2p\pi$ orbital on the hydroxyl hydrogens. For the semiempirical values of the core and one-center integrals we used values prescribed by Sichel and Whitehead [5], and for the resonance integrals the values were calculated by the pro-

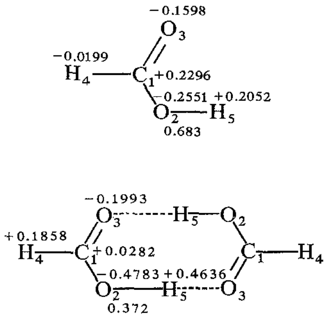

Fig. 1. Net charges and bond orders in monomeric and dimeric HCOOH

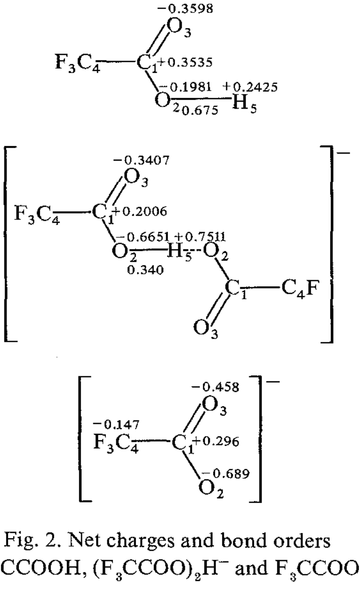

Fig. 2. Net charges and bond orders in F_3CCOOH, $(F_3CCOO)_2H^-$ and F_3CCOO^-

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cedure of Pople and Segal [1]. The two-center Coulomb integrals were evaluated using theoretical values for Slater orbitals [6] or the Mataga-Nishimoto formula [7]. There are small differences between the values calculated by both approximations for charges and bond orders, and slightly greater for the energy levels. All data given in this paper were calculated with theoretical values for Slater orbitals. In Figs. 1 and 2 the charges and some bond orders are given. On the whole they are not in disagreement with chemical intuition. The situation is less satisfactory when the energy levels in monomers and dimers are compared. For instance in the formic acid monomer the two highest occupied orbitals are π and σ (very close) and the first and second unoccupied π^* and σ^*. The $n-\pi^*$ transition energy is 7.2 eV and $\pi-\pi^*$ 10.4 eV. In the dimer there are small changes in occupied levels but the first unoccupied level is of σ^* character in opposition to the monomer. The same features are observed in the hydrogen bis-(trifluoroacetate) ion and its monomeric parts CF_3COOH and CF_3COO^-. The values for the delocalisation energies are unreasonably large and thus meaningless.

When the $2p\pi$ orbital of hydrogen is taken into account there are only minor changes in all quantities mentioned and the influence of this orbital is negligible.

The conclusions from our calculations are: The method works quite well with the monomers, but in the case of hydrogen bond formation the delocalisation energy seems to be too large. The discrepancies seem to be caused by the delocalisation of σ bonds in the hydrogen bond formation which is overestimated. The work is being continued in order to reduce these effects.

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References

1. Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, 129—136 (1965).
2. Bratož, S.: Advances in quantum chemistry, edited by Per-Olov Löwdin, vol. 3, p. 209. New York: Academic Press 1967.
3. Barnes, E. E., and W. T. Simpson: J. chem. Physics **39**, 670 (1963).
4. Golič, L., and J. C. Speakman: J. chem. Soc. (London) **1965**, 2530.
5. Sichel, J. M., and M. A. Whitehead: Theoret. chim. Acta (Berl.) **7**, 32 (1967).
6. Roothaan, C. C. J.: Special Technical Report 1955.
7. Mataga, N., and K. Nishimoto: Z. Physik. Chem. N. F. **13**, 140 (1957).

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