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All-Valence MO Study of Hydrogen Bonding in Water

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Theoretical hydrogen bond energies and proton barriers for water dimer and trimer calculated by semiempirical all-valence MO methods have been compared. The results of CNDO/2 and INDO calculations are more adequate than those obtained by the MINDO/1 approach.

A barrier for proton motion within the hydrogen bond seems to be of great importance for a number of molecular processes including those occurring in hydrogen bonded biological systems. On the other hand a questionable discovery of the so-called polywater [1–4] stimulated interest in hydrogen bonding studies of the polymeric forms of water [5–8].

In this paper the hydrogen bond in water has been studied within the framework of CNDO/2, INDO and MINDO/1 approximations [9]. The original parametrization was used except of the INDO approach where for the $0.5\,(I+A)$ values those for the CNDO/2 were taken [10]. The model systems of (sp^2 hybridized) water monomer, dimer and trimer were studied with the molecular geometry according to the Shibata and Bartell data [11] ($r_{\mathrm{O-H}} = 0.976$ Å, $\sphericalangle\,\mathrm{HOH} = 107.2°$). The hydrogen bond distance was assumed to be 2.76 Å.

The hydrogen bond energies calculated by the CNDO/2 and INDO methods (Table) are in good agreement with experimental data (4.25–7.7 kcal [12]). The respective energies found by the MINDO/1 approach seem, however, to be too large. Non-additivity in the hydrogen bond energies is observed to be of the same order as that found by Hankins *et al.* [13] in their *ab initio* calculations. The magnitude of deviations from additivity (0.15–0.63 kcal) coroborate the existence of long sp^2 hybridized structures in the polymeric forms of water [7].

The results obtained by the MINDO/1 approach (similarly to the CNDO/2 calculations with semiempirically evaluated coulomb repulsion integrals for HF and HF_2^- systems [14]) do not describe correctly the barrier shape for proton (Fig. 1). No difference is observed in the barrier shape as calculated by the CNDO/2 and INDO methods (Fig. 1). Thus, contrary to the parametrization of the repulsion

Table. *Theoretical hydrogen bond energies for dimer and trimer water*

	CNDO/2	INDO	MINDO/1
Dimer	5.02	6.93	10.43
Trimer	5.17	7.16	11.06

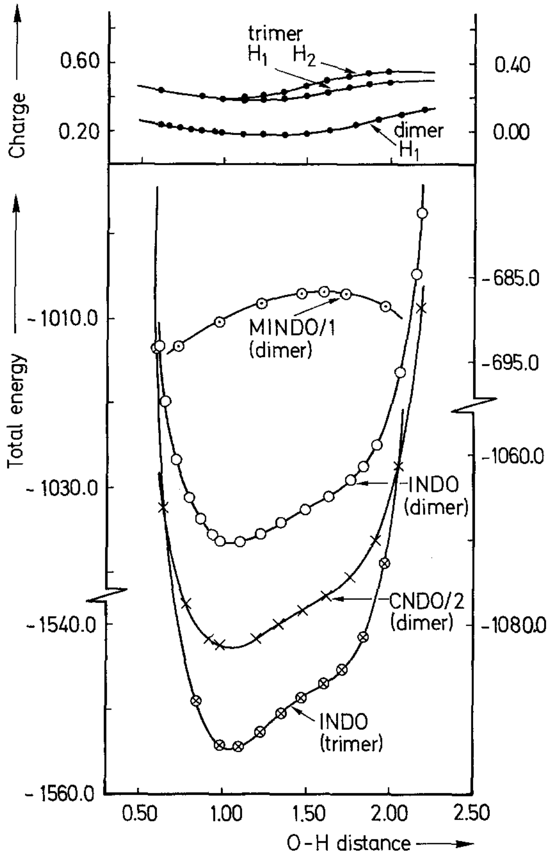

Fig. 1. Total energy (in eV) as a function of the O–H distance (in Å) calculated for water dimer and trimer by CNDO/2, MINDO/1 and INDO methods:

—×—×—×— water dimer, CNDO/2, right-hand lower energy scale,
—⊙—⊙—⊙— water dimer, MINDO/1, right-hand upper energy scale,
—○—○—○— water dimer, INDO, left-hand upper energy scale,
—⊗—⊗—⊗— water trimer, INDO, left-hand lower energy scale.

At the upper part of figure the respective charge distribution for hydrogen bond protons is given calculated by INDO method (left scale is for water dimer, right one for water trimer)

integrals γ_{AB}, the role of the one-center exchange integrals G^1 and F^2 in the approximations used seems to be rather of little importance for hydrogen bonding studies.

The minimum in the total energy as a function of the dimer O ... O distance found by the INDO approach amounts to 2.46 Å. (This calculated by means of the CNDO/2 method is of 2.54 Å [15]). The energy curve for proton shows its minimum at a longer r_{O-H} distance (c.a. 0.02 Å) for trimer than for dimer. The energy curve for trimer seems to be somewhat narrower, non-additivity in the barrier shape requires, however, some further studies.

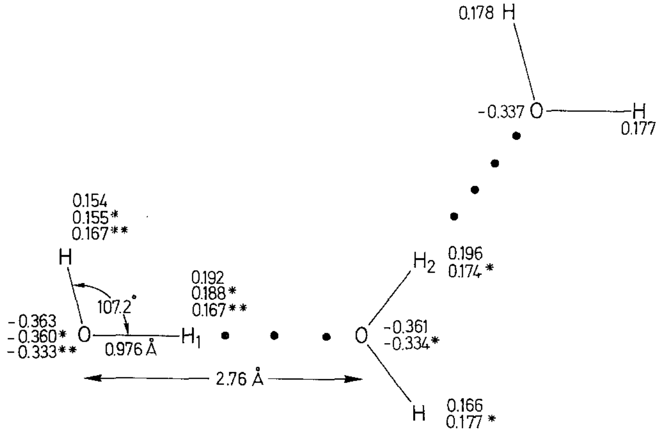

Fig. 2. Charge distribution in water monomer (double starred), water dimer (single starred) and in water trimer (not starred) calculated by the INDO method

Similarly to Hoyland and Kier's CNDO/2 results [16], the larger charge shift is found in the trimer of water than in the dimer (Fig. 2) as well as the greater amount of charge transfer between neighbouring molecules is noted.

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