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Short Communications

The Most Stable CNDO/2 Water Dimer

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The most stable CNDO/2 water dimer is a planar C_{2h} species with a partial O–O bond. STO-3G calculations indicate that the stability of this structure is due to an artifact of the CNDO/2 method.

Key words: Hydrogen bonding – Water dimer

Hydrogen bonding has been studied extensively both by semiempirical and *ab initio* molecular orbital techniques [1, 2]. Especially for larger hydrogen-bonded systems, the semiempirical CNDO/2 method [3] is widely used [1, 4].

In the present communication, the water dimers are reinvestigated using an automatic CNDO/2 geometry optimization program based on the Davidon-Fletcher-Powell algorithm [5, 6]. Fig. 1 shows the structures of the four energy minima obtained. The linear (I), cyclic (II), and bifurcated (III) dimers are known from previous CNDO/2 studies [1, 7–9] without complete geometry optimization; their CNDO/2 binding energies (see Fig. 1) are in reasonable agreement with those from the most accurate *ab initio* calculations [10, 11]. The C_{2h} species (IV) has not been considered previously; it contains a partial O–O bond, but no O–H···O moiety, and is the most stable CNDO/2 dimer, with a binding energy of 14.3 kcal/mole.

The surprising stability of (IV) was checked by *ab initio* STO-3G [12] calculations. Fig. 2 shows the energy of C_{2h} dimers of type (IV) as a function of the O–O distance. Contrary to CNDO/2, STO-3G predicts a strongly repulsive potential for such a C_{2h} approach of two water molecules, without any trace of a minimum. At the optimized CNDO/2 geometry of (IV), STO-3G gives an energy of +129.1 kcal/mole relative to the monomers.

Hence the stability of the C_{2h} structure (IV) must be regarded as an artifact of the

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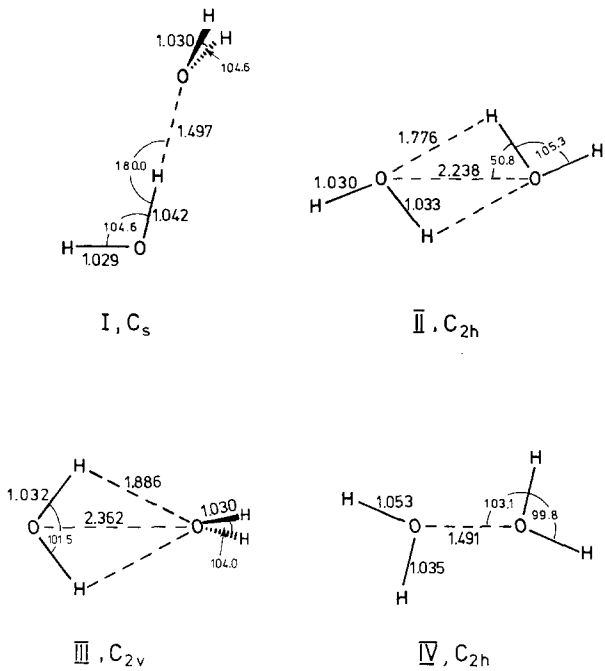

Fig. 1. CNDO/2 optimized geometries for water dimers (distances in Å, angles in degree). Calculated binding energies, in kcal/mole: (I) 8.6, (II) 4.3, (III) 3.8, (IV) 14.3

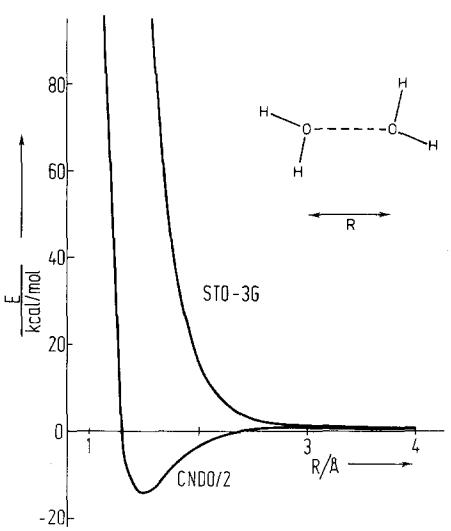

Fig. 2. STO-3G and CNDO/2 energies of C_{2h} dimers of type (IV) as function of the O–O distance (energies relative to the monomers)

CNDO/2 method. CNDO/2 geometry optimizations for larger hydrogen-bonded systems should therefore be carried out with great caution since unrealistic energy minima may be expected to occur.

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