# Molecular Orbital Calculations on the Structure of "Polywater"

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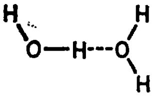
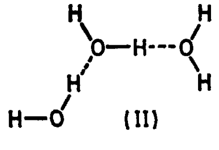
*Summary* Molecular orbital calculations indicate that the structure of polywater may be a hydrogen-bonded polymer formed by $sp^2$ hybridized water molecules.

THE new polymeric form of water with anomalous properties discovered by Deryagin and his co-workers[1] has attracted wide attention in recent months. There have been several speculations regarding the structure of this "polywater." The suggestions include: (i) square tetramers[2] with linear unsymmetrical hydrogen bonds with an OOO angle of 90°; (ii) planar branched polymeric chains[3] with short symmetrical hydrogen bonds with an OOO angle of 120°, and (iii) planar hexagonal layers[3] consisting of symmetrical hydrogen bonds. We report the preliminary results of our CNDO/2 molecular orbital calculations[4] on the different structures of polywater. The CNDO/2 method has been quite successful in predicting properties of hydrogen bonds in a variety of systems.[5–8]

In order to investigate model (i), we calculated the energy of the water monomer with a valence angle of 90°. The energy of the monomer was minimum when the O–H distance, $r_{\mathrm{OH}}$, was 1·04 Å; the dipole moment, $\mu$, of the molecule was 2·23 D compared to 2·10 D of an $sp^3$ hybridized molecule. We then calculated the energy of the linear water dimer as a function of the O $\cdots$ O distance, $R$, and found the $R_{\mathrm{min}}$ to be 2·6 Å; the $\mu$ of the dimer was 3·60 D. The hydrogen bond dissociation energy, $D_e$, was 7·3 kcal/mole. The $R_{\mathrm{min}}$, $D_e$, and $\mu$ of the linear dimer formed by $sp^3$ hybridized water molecules are 2·5 Å, 8·0 kcal/mole, and 4·30 D respectively. The square tetramer (with an OOO angle of 90°) was, however, not very stable, the average $D_e$ being rather small. This is what one would expect since the tetramer would be highly strained due to the large deformation of the valence angle. On similar grounds, we feel that the tetrahedral cluster model[9] with an OOO angle of 60° is also unlikely.


(I)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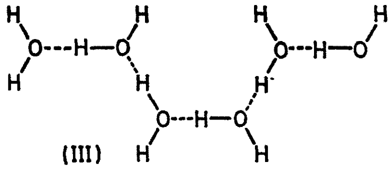
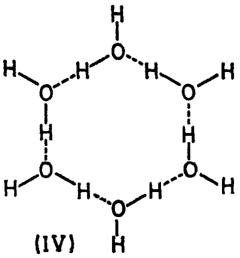

(III)


(IV)

Since models (ii) and (iii) consist of water molecules with $sp^2$ hybridization, we next examined the linear hydrogen bond formed between two such molecules. In its minimum energy configuration, an $sp^2$ hybridized water molecule has an O–H distance of 1·03 Å and a $\mu$ of 1·98 D. The $sp^2$ water dimer (I) forms an unsymmetrical hydrogen bond ($R_{\min} = 2{\cdot}5$ Å) with a $D_e$ of 9·3 kcal/mole; this value of $D_e$ is higher than that of the dimer formed by $sp^3$ hybridized water molecules. We have also examined the trimer (II) and the various possible structures of the open chain hexamer [(III) is the most stable structure] formed by $sp^2$ water molecules. In all these polymers the average $D_e$ is quite large (Table). The CNDO/2 charges on the various atoms in the hydrogen-bonded species (Table) show that the electron density at the acceptor oxygen atom ($O_A$) increases, while that on the donor oxygen ($O_D$) as well as the bonded proton decreases on hydrogen bond formation.

*Hydrogen bonds formed by water molecules with* sp² *hybridization*

| Molecule | $R_{\min}$ (Å) | $D_e$ (kcal/mole) | Charges $O_A$ | Charges $O_D$ | Charges H | Dipole moment (D) |
|---|---|---|---|---|---|---|
| Monomer .. .. .. .. | — | — | −0·292 | −0·292 | +0·146 | 1·98 |
| Dimer (I) .. .. .. .. | 2·5$^{a}$ | 9·3 | −0·353 | −0·288 | +0·192$^{d}$ | 3·98 |
| Trimer (II) .. .. .. .. | 2·5$^{a}$ | 10·4 | −0·363 | −0·293$^{c}$ | +0·202$^{d}$ | |
| | | | −0·350$^{b}$ | | +0·215$^{d}$ | 5·14 |
| Open hexamer (III) .. .. .. | 2·5$^{a}$ | 10·2 | −0·362 | −0·295$^{c}$ | +0·229$^{d}$ | |
| | | | −0·371$^{b}$ | | +0·222$^{d}$ | |
| | | | −0·364$^{b}$ | | +0·219$^{d}$ | 12·0 |
| | | | −0·358$^{b}$ | | +0·203$^{d}$ | |
| | | | −0·341$^{b}$ | | +0·219$^{d}$ | |
| Dimer (I) .. .. .. .. | 2·35$^{e}$ | 5·2 | −0·429 | −0·262 | +0·229 | 4·95 |
| Open hexamer (III) .. .. .. | 2·35$^{e}$ | 22·1 | −0·494 | −0·281$^{c}$ | +0·331$^{d}$ | |
| | | | −0·457$^{b}$ | | +0·326$^{d}$ | |
| | | | −0·455$^{b}$ | | +0·320$^{d}$ | 20·0 |
| | | | −0·447$^{b}$ | | +0·315$^{d}$ | |
| | | | −0·422$^{b}$ | | +0·269$^{d}$ | |
| Cyclic hexamer (IV) .. .. | 2·35$^{e}$ | 33·5 | −0·462$^{f}$ | — | +0·335$^{d}$ | 0·0 |

[a] Unsymmetrical hydrogen bond in the minimum energy configuration, where the O–H bond is stretched by 0·01 Å.

[b] Charges on the oxygen atom functioning both as an electron donor and acceptor.

[c] Charges on the oxygen atom where it functions only as a donor.

[d] Charges on the hydrogen bonded protons; the charge on the protons not forming hydrogen bonds is essentially the same as in the free monomer.

[e] Symmetrical hydrogen bond (of minimum energy) where the proton is at the centre of the O · · · O bond.

[f] All the oxygen atoms have the same charge.

The SCF calculations of Ellison and Shull[10] on $H_2O$ indicate a significant decrease in the ionization potential (and an increase in electron affinity) as the HOH angle is increased to 120°. There is also an increase in the polarity of the O–H bond.[11] These observations are consistent with the greater strength of the hydrogen bond formed by $sp^2$ hybridized water molecules. The cyclic hexamer (IV) formed through unsymmetrical hydrogen bonds was found to be unstable; similar instability of cyclic structures of methanol has been reported.[7]

While the unsymmetrical hydrogen bonds formed by $sp^2$ hybridized water molecules predict higher stabilities for the linear polymers of water (than those formed by $sp^3$ hybridized water molecules[12]), still stronger hydrogen bonds are required to account for the reported vibrational spectra and other properties of polywater.[3] For this purpose, we have calculated the energies of symmetrically hydrogen bonded open chain as well as cyclic hexamers formed by $sp^2$ hybridized water molecules (Table). The $R_{\min}$ in these structures was 2·35 Å and the average $D_e$ was between 20 and 30 kcal/mole. This $R_{\min}$ is consistent with the low O–H stretching frequency (1600 cm$^{-1}$) and high O · · · O stretching frequency (630 cm$^{-1}$) in polywater. The changes in the electron densities of the hydrogen as well as the donor and acceptor oxygens in these polymers seem to be much more marked compared to those in the unsymmetrical hydrogen bonds (Table).

One of the resonance structures suggested for the polymeric layer structures involves hydrogen bonds formed between hydronium ion and the hydroxyl ion. Preliminary calculations of the extended Hückel type[13] on the hydrogen bond formed between these two ions showed the bond to be rather weak ($D_e = 1{\cdot}4$ kcal/mole; $R_{\min} = 2{\cdot}8$ Å).

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