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## Can Water Polymerize? An Inquiry into the Possible Existence of Strong Bonds between Water Molecules

BY condensing water vapour into glass and quartz capillaries at reduced pressures, several groups[1-4] have obtained small amounts of a substance which seems to contain only the constituents of water. It displays physical properties which differ markedly from those of water and so has been called "anomalous water". Suggestions that this substance is in fact an oligomer[5] or polymer[4] have appeared since the publication of the original observations, and several hypothetical structures[3-6] have been put forward. The stability of "anomalous water" is attributed to the existence of a heretofore unobserved type of chemical bond between water molecules of the type O′HO″ (if the bond is asymmetric, the hydrogen atom is more closely bound to O′). The energy of the bond is an order of magnitude greater than that of currently recognized hydrogen bonds. My purpose here is to report on calculations which call into serious question the existence of the proposed strong OHO bond and, consequently, polymeric structures based on it.

A modified version of the Iterated Extended Huckel Theory (IEHT) has been used[7,8] to make electronic structure calculations for an isolated molecule of $H_2O$ complexes of up to eight $H_2O$ molecules in ice-like geometries, and an isolated molecule of $H_2O_2$ (my unpublished results). Using a single set of semi-empirical parameters, the equilibrium configurations of both the $H_2O$ and $H_2O_2$ molecules were calculated fairly accurately (Table 1) and calculations on the complexes yielded reasonable binding energies ($0.1 - 0.2$ eV/interaction or 2–4 kilocalories/mole of interactions) as well as potentials for restricted rotation in accordance with infrared and Raman spectral observations (unpublished).

Table 1. CALCULATED AND OBSERVED CONFORMATIONS OF $H_2O$ AND $H_2O_2$

| | $H_2O$ Calc | Exp. (ref. 9) | | $H_2O_2$ Calc | Exp. (ref. 10) |
|---|---|---|---|---|---|
| OH bond length (Å) | 0·96 | 0·965 | OH bond length (Å) | 0·92 | 0·965 ± 0·01 |
| | | | OO bond length (Å) | 1·44 | 1·49 ± 0·01 |
| HOH bond angle (deg) | 103 | 104·52 | HOO bond angle (deg) | 104 | 100 ± 2 |
| | | | Dihedral angle (deg) | 73 | 80 ± 20 |

Using the same method, three possible structures (I, II and III in Fig. 1) for oligomeric or polymeric water were investigated. Within the confines of a basic structure, a large number of combinations of interoxygen distances, HOH bond angles and relative placements of the bridge hydrogen atom between two adjacent oxygen atoms were used in a search for minimum energy configurations. The energy of a configuration was then compared with that of the same number of isolated water molecules in order to assess the binding (or repulsion) energy. Stable configurations corresponding to conventional hydrogen bonding similar to that found in ice were observed in structures I and II. No stable configuration could, however, be found for structure III; in every case calculated, the energy of the complex exceeded that of the isolated water molecules by at least several electron volts. Furthermore, no metastable configurations of III were found.

The results may be discussed qualitatively in terms of the following scheme. Let the complex be divided into $n$ parts, each part corresponding to the two hydrogen atoms and oxygen atom of a component water molecule. The energy of the complex may then be divided, roughly speaking, into three contributions

$$\mathcal{E}_c = n\mathcal{E}_i + \sum_{i=1}^{n} \mathcal{D}_i \sum_{i=1}^{n} \sum_{j=i+1}^{n} \mathcal{H}_{ij} \tag{1}$$
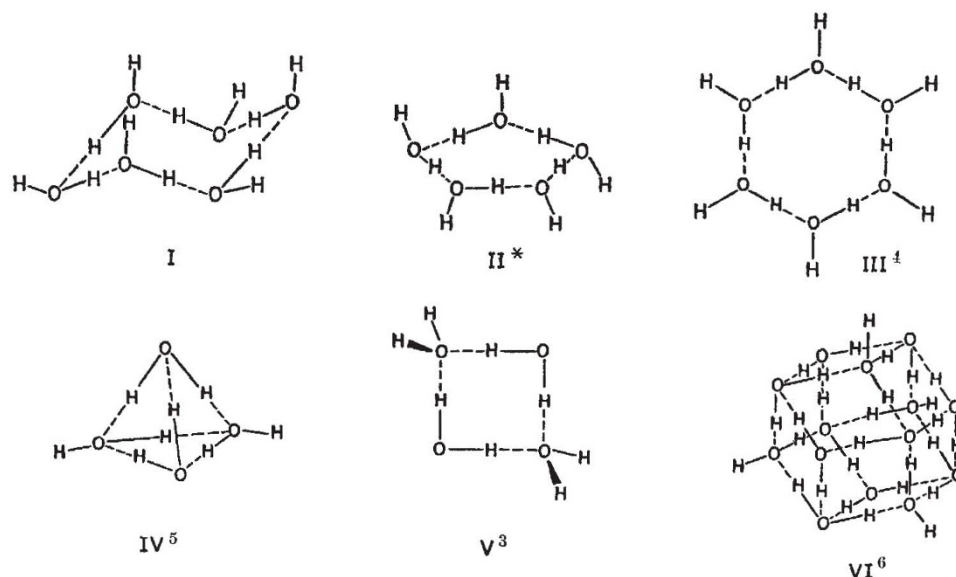


Fig. 1. Proposed structures for oligomeric or polymeric water. * Out-of-plane hydrogen atoms may be individually located either above or below the plane of oxygen atoms.

where $\mathcal{E}_i$ is the energy of an isolated water molecule in its equilibrium conformation, $\mathcal{D}_i$ is the energy required to distort molecule $i$ from its equilibrium conformation into the configuration of the $i$th part of the complex, and $\mathcal{H}_{ij}$ is the interaction energy between the $i$th and $j$th parts of the complex. The complex will be stable if a configuration can be found for which $\mathcal{E}_c - n\mathcal{E}_i < 0$. By definition, $\mathcal{D}_i \geq 0$, whereas $\mathcal{H}_{ij}$ may be positive or negative in the general case.

In the structures I, II and III, $\mathcal{H}_{ij}$ may be considered, to a good approximation, to be the energy of the hydrogen bond between the $i$th and $j$th parts of the complex. Since all parts are equivalent and the number of hydrogen bond interactions equals the number of parts, we may define the quantities $\mathcal{D} \equiv \mathcal{D}_i$ and $\mathcal{H} \equiv \mathcal{H}_{i,i+1}$ (or $\mathcal{H}_{n,1}$). Equation 1 may then be rewritten as

$$\mathcal{E}_c - n\mathcal{E}_i = n(\mathcal{D} + \mathcal{H}) \qquad (2)$$

(In the general case of the extended network this equation becomes

$$\mathcal{E}_c - n\mathcal{E}_i = n(\mathcal{D} + k\mathcal{H}) \qquad (2)$$

where $k$ is 2 for structures I and II and 3/2 for structure III. This change does not, however, alter the qualitative nature of the conclusions drawn in this report.)

Previous calculations on the interaction between water molecules[9] have shown that the hydrogen bond energy $\mathcal{H}$ is greatest when the atoms O′, H and O″ are collinear and the lone pair of atom O″ is pointing directly at the hydrogen. Minimum energy configurations vary with environment but in every case calculated are characterized by an O′–O″ distance $(R)$ exceeding 2·7 Å, a hydrogen position well to one side of the midpoint of the O′–O″ line of centres, and a binding energy of less than 0·2 eV. In structure III one does not see even a binding energy of this magnitude for two reasons. First, the oxygen lone pair does not lie along the OHO bond axis, thus somewhat weakening the interaction. The second and more important reason is that, contrary to structures I and II, the distortion energy $\mathcal{D}$ is substantial. A change of HOH bond angle from the equilibrium value of 104·52° to 120° and an extension of one OH bond length from 0·96 Å to $R/2$ requires an energy investment of 0·5 to 1 eV per molecule depending on $R$, decreasing as $R$ decreases. Below an $R$ of about 2·6 Å, however, the interaction becomes strongly repulsive in every instance calculated. A structure of type III with an $R$ of 2·3 Å as proposed by Lippincott et al.[4] thus seems highly unlikely.

The above description may be applied, albeit somewhat more loosely, to structures IV, V and VI (Fig. 1) as well. In both structures IV and V, but especially IV, the distortion energy $\mathcal{D}$ is substantial. It can be reduced by making the OHO bond non-linear, but only at the cost of reducing $\mathcal{H}$, the interaction energy, as well. In VI, $\mathcal{D}$ is reduced to a minimum but there does not seem to be any reason why $\mathcal{H}$ should be an order of magnitude greater in this structure than it is in either I or II.

Only qualitative significance is attributed to the results reported here. But the IEHT method yields not even a hint of the proposed strong OHO interaction. In view of the reasonable and realistic results of this method when applied to other systems of similar composition, these calculations strongly suggest that the proposed strong OHO bond between water molecules does not exist and, as a corollary, that the observed behaviour of "anomalous water" cannot properly be attributed to polymerization of water molecules.

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# Pearl Chain Formation across Radio Frequency Fields

THAT chains of living or non-living particles (pearl chains) form along the lines of force of electromagnetic fields has been known for many years[1-3], and detailed experimental and theoretical analyses of the phenomenon have been carried out[2,4].

In work related to the analysis of orientation in radio frequency fields[5,6], reproducible formation of pearl chains across field lines has been observed in mixtures of electrically different particles. In this report the conditions under which chains across fields occur are described, and a possible explanation is presented. To distinguish them clearly from conventional pearl chains, which form parallel to the lines of flux (perpendicular to the electrodes), the chains of mixed particles that form perpendicular to (across) the lines of flux (parallel to the electrodes) will be called transverse pearl chains.

The equipment and its use were essentially as described previously[5]. An alternating current at frequencies between 10 and 190 mHz, usually pulsed with 10 per cent duty cycle, was applied at levels below 100 volts, peak to peak, to parallel platinum wire (60 microns in diameter) electrodes[2,7] separated by 0·25 or 0·5 mm. Thus the maximum levels of electric field intensity were 400 or 200 V/mm, respectively. The microscope chamber is described and illustrated in a manuscript on orientation of erythrocytes[7].

In radio frequency fields, the only necessary condition for transverse pearl chains seems to be a requirement for mixed particles with different dielectric constants. Polystyrene spheres (Dow Chemical Company, Midland, Michigan), 7–14 microns in diameter, were included in transverse chains in mixtures with human or avian erythrocytes or the unicellular algae *Chlorella* or *Chlamydomonas*. As in conventional pearl chain formation of homogeneous particles[2], transverse chains formed at all frequencies tested. The formation required fortuitous placement of plastic and biological particles so that they alternated in all transverse chains and such chains were usually short. Where living and non-living particles were not adjacent, conventional chains (with the field) formed containing either all plastic or all biological particles. A single particle could be simultaneously in both transverse and conventional chains, but plastic and biological particles were never mixed in conventional chains with the field. In appropriate conditions, three types of pearl chains were simultaneously present: plastic with field (Fig. 1A); biological with field (Fig. 1B); and mixed alternate particles across the field (Fig. 1C). The lateral attraction between dissimilar particles sometimes caused previously formed conventional biological and plastic chains to move together and lie side by side.

Precise determinations of threshold, such as Sher[2] made for conventional pearl chains, were not carried out, but ciné records showed that the lateral attraction between different types of particles acted over similar distances and about as fast as polar attraction between similar