flat top is a primary, constructional feature; during each eruptive episode the minute glass fragments (produced either by steam explosions or by thermal shattering) formed suspensions in the water, were dispersed to various extents according to the size of the grains, water currents, and so forth, and subsequently were deposited in well-sorted, nearly horizontal layers. The aforementioned low ratio of height to diameter of base in submarine structures, relative to subaerial ash cones, can also be explained by the fact that the pyroclastics settle more slowly and are dispersed over wider areas when they are ejected and set in suspension in water rather than air.

The evidence in favor of wave truncation for the origin of many oceanic guyots is overwhelming (*1*). Our observations on this Ethiopian guyot, however, support previous suggestions (*2*, *15*) that not all flat-topped seamounts have formed by wave truncation and subsidence of volcanic islands; in some cases they may be primary structures constructed by a particular mechanism of submarine volcanic activity.

ENRICO BONATTI
Institute of Marine and Atmospheric Sciences, University of Miami, Miami, Florida 33149
HAROUN TAZIEFF
15, Quai de Bourbon, Paris IV, France

References and Notes

1. H. H. Hess, *Amer. J. Sci.* **244**, 772 (1946); E. L. Hamilton, *Mem. Geol. Soc. Amer.* **64**, 42 (1956); H. W. Menard, *Marine Geology of the Pacific* (McGraw-Hill, New York, 1964).
2. M. N. Christensen and C. M. Gilbert, *Science* **143**, 240 (1964).
3. The expeditions, led by H. Tazieff and G. Marinelli (University of Pisa), took place during the winter months of 1967 and 1968 under the sponsorship of the Upper Mantle Committee of the International Union of Geology and Geophysics.
4. H. Tazieff, G. Marinelli, F. Barberi, J. Varet, *Bull. Volcanol.*, in press.
5. H. Tazieff, *C. R. Acad. Sci. Paris* **268**, 2657 (1969).
6. E. Bonatti, *Trans. N.Y. Acad. Sci.* **25**, 938 (1963).
7. ———, *Science* **153**, 534 (1966).
8. J. Verhoogen, *Amer. J. Sci.* **249**, 729 (1951).
9. H. Tazieff, *Bull. Soc. Belg. Geol.* **67**, 14 (1958); *Geol. Rundschau* **57**, 955 (1968).
10. S. Thorarinsson, in *Surtsey Res. Progr. Rep.* **1**, 51 (1965).
11. J. Honnorez, *Bull. Soc. Belg. Geol.* **70**, 407 (1961); E. Bonatti, *Bull. Volcanol.* **28**, 257 (1965).
12. A. R. McBirney, *Bull. Volcanol.* **26**, 455 (1963).
13. E. Bonatti, in *Researches in Geochemistry*, P. Abelson, Ed. (Wiley, New York, 1967), vol. 2, p. 453.
14. J. Honnorez and P. Krist, in preparation.
15. Y. R. Nayudu, *Geophys. Monogr. No. 6*, (American Geophysical Union, Washington, D.C., 1962), p. 171.
16. Supported by CNRS (France), CNR (Italy), NSF grant GA-1602, and ONR contract Nonr 4008(02). Contribution No. 1202 from the Institute of Marine and Atmospheric Sciences, University of Miami.

21 January 1970; revised 30 March 1970

Covalent Polymers of Water

Abstract. *A new covalent structural scheme for water polymers is proposed. The observed properties of "polywater" are related to the structures of the suggested homologous series of molecules. Mechanisms of formation are suggested.*

Several groups of investigators have reported (*1–6*) that when water vapor condenses in fine quartz or Pyrex capillaries it sometimes forms a viscous liquid of abnormally high density and refractive index. At low temperatures the liquid separates into two phases (*3*). It has a lower vapor pressure, a lower freezing point, and a higher boiling point than normal water. While no differences from ordinary water could be detected in the viscous liquid (*4*) by mass spectrometric and nuclear magnetic resonance techniques, other techniques revealed infrared and Raman spectra very different from those of water and ice and showed that these spectra are not associated with impurities which were sought and identified at negligible concentrations (*5*, *6*).

To chemists and physicists familiar with the molecular properties of water and its solutions, and with theories of their structure and properties, these reports have been very surprising. They bring to mind earlier studies of some properties of colloidal systems for which it has been suggested that there may be exceptionally long-range ordering forces extending many water molecule diameters from surfaces into the solvent. These proposals have been examined and are inconsistent with other properties (*7*). Furthermore, the unusual features of the "anomalous water" are retained when the liquid is removed from the capillaries for spectral studies (*6*).

It was first suggested (*2*) that the observations could be explained in terms of the existence of an allotropic form of liquid water. Measurements of thermal expansion in fine capillaries, as a function of temperature, demonstrated that the liquid possessed properties quite different from those of ordinary water (*3*). Supercooling to near −50°C was accompanied by the development of turbidity and a separation into two liquid phases. Deryagin *et al.* (*3*) cited acetaldehyde trimerization

$$3\,(C_2H_4O) \rightarrow (C_2H_4O)_3$$

as a similar example of a liquid with two phases, described earlier as a "pseudo-one-component" system, and referred to the "two-component behavior of water" as "evidently an indication of the existence either of isomers of water or of dimers, the transitions of which are frozen." They observed that evaporation from a column produces a condensate of decreased "anomalousness."

The well-established Gibbs phase rule states that

$$f = c - p + 2$$

where f is the number of degrees of freedom, c is the number of components, and p is the number of phases in equilibrium. This rule asserts that an allotropic liquid form of water in equilibrium with ordinary water is not possible in a one-component system. However, if a covalent polymer is formed with the aid of a catalyst, which is then removed, the polymer would not be in dynamic equilibrium with the monomer and thus should be considered as a separate component. With $c = 2$, we may have two liquid phases in which each component in a given liquid phase is in equilibrium with the same component in the other liquid phase, although the components in the same liquid phase are not in equilibrium with each other. If there were more components, for example, oligomers of lower molecular weight, this increase would allow for the existence of more liquid phases for the system. Thus, the two liquid phases reported are entirely consistent with the Gibbs phase rule if we assume the formation of a covalently bonded polymer which can be counted as a separate component because of "freezing" or stopping of the conversion process.

Although only submicrogram quantities of "anomalous water" were available, Raman and infrared studies with sensitive instrumentation showed spectra far different from those of water and ice (*6*) and supported the indications of an earlier study (*5*). Proposals were made that the anomalous properties are due to the formation of a new substance, "polywater" (*5*), consisting of tetrahedral (*8*) or square (*5*) tetramers, or of long chains of water molecules or hexagonal planar nets with symmetrical O–H–O bonds (*5*). These structural proposals have unattractive features. Why should the O–H–O bonds of water become symmetrical when they are normally much more stable in unsymmetrical states? Moreover, comparisons with crystallographic data on substances with symmetrical O–H–O bonds suggest (9) that the O–H–O distances in the proposed structures would have to be less than distances that seem likely to give the observed maximum density of 1.4 g/cm^3 (10), even if the single minimum did exist. A rhombic dodecahedral structure of symmetric O–H–O bonds was considered less unattractive (9). However, this structure, along with most of the others, implies a low volatility. These structures either are ionic forms or contain large clusters, or both, and thus are expected to have extremely low vapor pressures. This requirement is unsatisfactory because oligomers of low molecular weight and considerable volatility have been distilled and studied (5). A more exotic structure, involving fundamental changes in valence states, would appear to be required.

No satisfactory bonding scheme could be found based on a valence-bond approach by itself. Then I arrived at a symmetrical new structure with the aid of directed valence and molecular orbital concepts, and the idea of σ-π separability. The structure (Fig. 1) consists of a linear array of oxygen-to-oxygen σ-bonds, with pairs of hydrogen atoms in symmetrical bridges, each pair being involved with two oxygen atoms in π-type bonds.

The use of hydrogen bridges, which can account for the disappearance of most of the infrared O–H stretch absorption, is a feature normally associated only with electron-deficient molecules (11). The water molecule, with its two lone pairs of electrons, is an electron-rich system. However, the electrons can all be accommodated, for any degree of polymerization, within the framework of a molecular orbital description.

By reference to the coordinates shown in Fig. 1, the bonding may be described as a linear σ skeleton made of sp_z hybrid orbitals that consist of two electrons from each oxygen and the two $1s$ orbitals and electrons of the terminal hydrogens, along with a set of $(n-1)$ four-center molecular orbitals $(\pi_x{}^{H}, \pi_y{}^{H}, \ldots)$, where n is the degree of polymerization. For an isolated four-center π-system there would be four atomic orbitals and four possible molecular orbitals, into which may be placed six electrons—two from each oxygen and one from each bridge hydrogen. Each inner O atom will be involved with three atoms to its left and three to its right, the two sets lying in mutually perpendicular planes, and will have nearly tetrahedral symmetry. There will be a lone pair on each terminal oxygen.

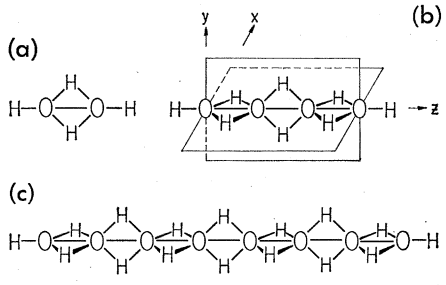

Fig. 1. Oligomers of water: (a) dimer; (b) tetramer; (c) octamer.

The unconventional number of bonds to oxygen shown in Fig. 1 should be regarded as schematic, since one bond arrangement cannot adequately portray a full molecular orbital description (12). The question of the relative importance of various overlap terms, for example, the one for the O–O orbitals, must await further quantitative investigations. Nevertheless, the bonding scheme has a hint of aromatic character and suggests electronic spectra markedly different from those of ordinary water and ice structures.

The facts that polywater is synthesized slowly and not very reproducibly suggest a catalytic polymerization mechanism, which would be expected to produce a distribution of molecular weights, and possibly the oligomers of lower molecular weight. Since the molecular weights of the species studied spectroscopically (5, 6) were not specified, detailed analyses of those data would seem premature. However, it is expected that the transverse vibrations of the oxygen atoms may be responsible for the intense band seen near 620 cm^{-1} (6). The large axial polarizability expected in this structure would lead to a high optical anisotropy which can be checked by measurements of light scattering or the Kerr effect (13).

In the oligomers of higher molecular weight the population of terminal O–H bonds would become relatively small; this reduction can account for the reported disappearance (6) of the O–H stretch bands in the infrared region, since they could be easily lost in the broad region of O–H absorption of normal water. The terminal O–H stretch and bend frequencies should, of course, be shifted by the changes of hybridization and structure.

All but the terminal hydrogens in this structure would be expected to be relatively neutral, in analogy with the bridge hydrogens of diborane. Such molecules would tend to pack closely, thus avoiding the ice-like network of hydrogen-bonded tetrahedrally arranged neighbors that is relatively open and is thus responsible for the low density of normal ice and water. This close packing would be expected to produce a relatively high density and a high refractive index in both liquid and crystalline phases. The molecules of this homologous series are uncharged so that the oligomers of lower molecular weight should be quite volatile. The polymer chains, like those of some biopolymers, are expected to be rather rigid and extended, thus giving high intrinsic viscosities, and would be expected to interact in parallel bundles to form anisotropic clusters which probably would lead to the formation of liquid crystals and gels.

The lone pair repulsion in the water dimer might make it less stable than oligomers of high molecular weight; the dimer may in fact turn out to be unstable with respect to normal water and higher polymers. It may be learned from quantum mechanical calculations whether or not reasonable stabilities can be expected for the proposed structures.

The polyalcohols (2) and other polymers can be fitted into this structural scheme, with the bridge positions occupied by the carbon atoms of alkyl groups. A similar alkyl bridged structure has been found for beryllium dimethyl polymer (14), and another was suggested as an unstable intermediate in reactions of trialkylboranes and B_2H_6 (15). Alcohols or acids could make similar copolymers with water. With mixed occupancy (alkyl groups, acyl groups, or hydrogen atoms) of the bridge positions, various stereoisomers, including helical and zigzag configurations, could exist. These might be important in biological systems, perhaps as metastable species.

Once some idea of the possible components of polywater has been developed, explanations for some other observations can be proposed. When vapor molecules arrive at rare catalytic sites at the surface of Pyrex or quartz, they begin to polymerize, thus forming the bridged structure in a growing chain. After a monolayer or more of polymer is formed, it may nucleate the condensation of ordinary liquid water at less than 100 percent relative humidity to form a polymer solution. A liquid column of this solution may grow until dilution of polymer raises the vapor pressure of ordinary water to the prevailing humidity. At low temperatures the solution may separate into two phases, as other macromolecular solutions do (*16*). This process is in accord with observations (*1–6*).

After ordinary water condenses, there would be occurring simultaneously the processes of physical absorption of ordinary water by the solution, diffusion of water and of oligomers of low molecular weight into vapor, and diffusion of water, oligomers, and polymer in the solution. Condensation of ordinary water around the polymer molecules probably terminates or inhibits the growth of the polymer chain. This is suggested by the fact that vapor must be allowed to diffuse to a capillary wall in order to produce polywater. For example, an activated complex consisting of the growing polymer chain, a water molecule, and ions may be important kinetically in a polywater (nonpolar) environment but may be energetically less favored in ordinary water because of the relatively high dielectric constant. Alternatively, site poisoning or termination of chain propagation by water-soluble impurities might occur. The role of ordinary water in inhibiting its own conversion from liquid polymer thus becomes explicable if the polywater has markedly different solvent properties from those of ordinary water; this inhibition would account for the fact that all water does not convert to polywater, although, because of the spontaneous formation, one may conclude that the free energy of the polymer is lower than that of ordinary water.

Since submission of this report, several physical measurements of polywater that are qualitatively consistent with the above proposals have been reported. These include a proton resonance spectrum consisting of a single broad line (*17*), a very low microwave dielectric constant (*18*), and sharp x-ray diffraction rings characteristic of liquid crystals (*19*).

Note added in proof: This report was submitted before the article by Allen and Kollman (*20*) became available. Although CNDO/2 molecular orbital computations on a bridged structure were included in that study, the structure calculated was the diprotonated tetramer, $H_{10}O_4{}^{2+}$, so the results are not applicable to the present discussion.

CHESTER T. O'KONSKI
Department of Chemistry, University of California, Berkeley 94720

References and Notes

1. N. N. Fedyakin, *Kolloid. Zh.* **24**, 497 (1962), translated in *Colloid J. USSR Engl. Transl.* **24**, 425 (1962); B. V. Deryagin and N. N. Fedyakin, *Dokl. Akad. Nauk SSSR* **147**, 402 (1962); N. N. Fedyakin, B. V. Deryagin, A. V. Novikova, M. V. Talaev, *ibid.* **165**, 878 (1965); *Proc. Acad. Sci. USSR Phys. Chem. Sect. Engl. Transl.* **165**, 862 (1965); V. I. Anisimova, B. V. Deryagin, I. G. Ershova, D. S. Lychnikov, Ya. I. Rabinovich, V. Kh. Simonova, N. V. Churaev, *Russ. J. Phys. Chem. Engl. Transl.* **41**, 1282 (1967).
2. B. V. Deryagin, M. V. Talaev, N. N. Fedyakin, *Dokl. Akad. Nauk SSSR* **165**, 597 (1965); *Proc. Acad. Sci. USSR Phys. Chem. Sect. Engl. Transl.* **165**, 807 (1965).
3. B. V. Deryagin, N. V. Churaev, N. N. Fedyakin, M. V. Talaev, I. G. Ershova, *Izv. Akad. Nauk SSSR* **10**, 2178 (1967); *Bull. Acad. Sci. USSR Div. Chem. Sci. Engl. Transl.* **1967**, 2095 (1967).
4. E. Willis, G. K. Rennie, C. Smart, B. A. Pethica, *Nature* **222**, 159 (1969).
5. L. J. Bellamy, A. R. Osborn, E. R. Lippincott, A. R. Bandy, *Chem. Ind. London* **1969**, 686 (1969).
6. E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969).
7. J. C. Henniker, *Rev. Mod. Phys.* **21**, 322 (1949); C. T. O'Konski and A. J. Haltner, *J. Amer. Chem. Soc.* **79**, 5634 (1957).
8. R. W. Bolander, J. L. Kassner, Jr., J. T. Zung, *Nature* **221**, 1233 (1969).
9. J. Donohue, *Science* **166**, 1000 (1969).
10. B. V. Deryagin and N. V. Churaev, *Priroda (Moskva) No. 4* (1968), p. 16; *Joint Publ. Res. Serv. No. 45* (1968), p. 989; excerpted in *Saturday Review* (6 September 1969), p. 54.
11. K. S. Pitzer, *J. Amer. Chem. Soc.* **67**, 1126 (1946); W. N. Lipscomb, *Boron Hydrides* (Benjamin, New York, 1963); W. C. Hamilton, *Proc. Roy. Soc. London Ser. A Math. Phys. Sci.* **235**, 395 (1956); *J. Chem. Phys.* **29**, 460 (1958); M. Yamazaki, *ibid.* **27**, 1401 (1957); G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, H. I. Schlesinger, *J. Amer. Chem. Soc.* **73**, 4585 (1951); E. Wiberg and R. Bauer, *Z. Naturforsch.* **66**, 171 (1951).
12. R. S. Mulliken, *J. Chim. Phys.* **46**, 497 (1949); *ibid.*, p. 675.
13. C. T. O'Konski, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark *et al.*, Eds. (Interscience, New York, 1968), vol. 9, p. 551.
14. A. I. Snow and R. E. Rundle, *Acta Crystallogr.* **4**, 348 (1951).
15. E. L. Muetterties, *The Chemistry of Boron and Its Compounds* (Wiley, New York, 1967), p. 249.
16. E. J. W. Verwey and J. Th. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948); L. Onsager, *Phys. Rev.* **62**, 558 (1942); *Ann. N.Y. Acad. Sci.* **51**, 627 (1949).
17. T. F. Page, Jr., R. J. Jakobsen, E. R. Lippincott, *Science* **167**, 51 (1970); G. A. Petsko, *ibid.*, p. 171.
18. P. Hoekstra, G. Swinzow, S. Ackley, W. T. Doyle, *J. Colloid Interface Sci.*, in press.
19. G. A. Petsko, personal communication.
20. L. C. Allen and P. A. Kollman, *Science* **167**, 1443 (1970).

21. I thank H. Heck, B. Houseman, A. Streitwieser, and two referees who have read the manuscript for helpful comments.

11 December 1969; revised 6 March 1970 ■

Solution Conformation of Valinomycin–Potassium Ion Complex

Abstract. *The complete conformation of the valinomycin–potassium ion complex in methanol is presented. Extension from the reported secondary structure requires arguments and data relating to ester orientation, direction of coiling, side-chain orientation, and conformational stability. Conformation of the valinomycin–potassium ion complex provides a clear-cut example in which elucidation of conformation is sufficient to gain an understanding of molecular function which, in this case, is selective ion transport by a carrier mechanism.*

Knowledge of primary structure of polypeptides and proteins has afforded limited information concerning the mechanism whereby a biomolecule functions. Certain biomolecules facilitate ion permeation of membranes with a high degree of selectivity of, say, potassium ion over sodium ion. One example is valinomycin, which selectively binds potassium. The solution conformation of the valinomycin–potassium ion complex shows that the potassium ion is held in a polar core of proper dimensions for binding the nonhydrated ion, while at the same time the complex presents a nonpolar exterior to the surrounding

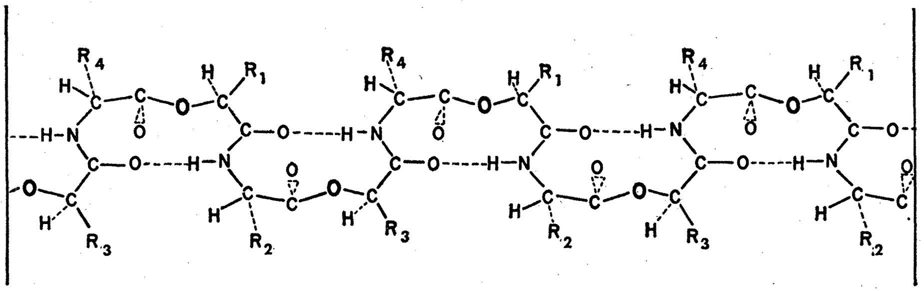

Fig. 1. Secondary structure of the valinomycin–potassium ion complex in methanol solution. The vertical bars at left and right should be brought together by curving the plane of the paper away from the observer. $R_1 = CH_3$; and $R_2 = R_3 = R_4 = CH(CH_3)_2$. The acyl oxygens of the ester moiety are pointing into the paper in accordance with the beta-turn considerations.