G. G. Malenkov

1961

SovietRxiv

Fig. 1. *a*—centrosymmetric (trans) connection of tetrahedra; *b*—mirror-symmetric (cis) connection of tetrahedra

Figure 1: Fig. 1. *a*—centrosymmetric (trans) connection of tetrahedra; *b*—mirror-symmetric (cis) connection of tetrahedra

Abstract

Full Text

CRYSTALLOGRAPHY

G. G. Malenkov

ON THE STRUCTURE OF LIQUID WATER

(Presented by Academician N. V. Belov, December 6, 1960)

It is assumed that the difference between the solid and liquid states is exclusively kinetic in character. It is assumed that the mutual arrangement of particles in a liquid does not differ fundamentally from their arrangement in a solid; at the same time it is usually stipulated that the structure of a liquid is a disordered variant of the structure of the corresponding crystal, and that only "short-range order" is preserved in a liquid.

In a number of papers by J. Bernal [1–3] it is emphasized that, from the structural, geometrical point of view as well, liquids differ sharply from crystalline bodies, and that different principles underlie the construction of the structures of substances in these two states.

Pauling [4] proposed a structural scheme for liquid water that likewise does not proceed from the structure of the known modifications of ice. This scheme is based on the concept of dodecahedral arrangements of water molecules. According to Pauling, the crystalline "prototype" of liquid water is provided by the hydrates of certain gases and liquids. Pauling' s scheme is confirmed by our attempt to derive the structure of liquid water from entirely different premises.

Fig. 1. *a*—centrosymmetric (trans) connection of tetrahedra; *b*—mirror-symmetric (cis) connection of tetrahedra.

As is known, in the structure of ordinary hexagonal ice there are hydrogen bonds of two types: mirror-symmetric (all bonds parallel to the c axis, altogether 1/4 of the total number of bonds) and centrosymmetric (all the remaining bonds). Following the usual stereochemical tradition, we shall henceforth call the former cis-bonds and the latter trans-bonds. These two types of bonds are shown in Fig. 1, the water molecules being represented as tetrahedra whose centers coincide with the centers of the molecules, and whose vertices coincide with the midpoints of the hydrogen bonds. In such a representation the distinction between cis- and trans-bonds becomes clearer. In the structure of ice [5], cis-bonds are 0.5% shorter than trans-bonds, which testifies to the greater strength of the former. This circumstance is also pointed out by Berrum [6]. The very existence of ice in the hexagonal modification is evidence of the greater strength of cis-bonds, since in its structure their number is maximal in comparison with other simple structures formed by tetrahedral bonds and satisfying the first two of the conditions given below.

We shall construct the structure of water on the basis of the following premises:

1) Hydrogen bonds must be rectilinear, and their length may vary only within narrow limits.

2) Each water molecule forms 4 bonds, the angles between which must differ minimally from tetrahedral angles.

3) The number of cis-bonds must be maximal.

5 molecules connected in a "cis-fashion" will be at the vertices of a regular pentagon, and 20 at the vertices of a dodecahedron (Fig. 2). The angles between bonds will be equal to 108°, i.e., will be only slightly smaller than the tetrahedral angle. Filling space with regular dodecahedra without gaps, as is known, is impossible. But, allowing angular fluctuations within the limits 112–107°*, small changes in bond lengths, and also a slightly non-coplanar arrangement of the molecules forming a pentagon, it is possible to fill an arbitrarily large space with molecules connected only in the cis-fashion. The resulting structure will not, in general, possess three-dimensional periodicity and, consequently, cannot be realized in a crystalline solid. In the mentioned structures of gas hydrates ([7], [8]), in order to achieve periodicity, 12-hedra regularly alternate with 14- or 16-hedra containing hexagonal faces along with pentagonal ones.

The density of water possessing the resulting cis-structure should be approximately 0.9 g/cm^3. The radial distribution of particles in it is as follows:

R, Å	2.8	4.5	6.3	7.2
n	4	12	24	12

Here R is the distance from an arbitrarily chosen particle; n is the number of particles separated from the chosen one by this distance. The length of the H_2O—H_2O bond is taken to be, on average, 2.8 Å. This radial distribution is in complete agreement with the experimental data for liquid water. The maxima of the experimental radial-distribution function for water occur at 2.9 and 4.5 Å, and at 6.6 Å an inflection is observed in the plot of the function ([9], [10]).

Fig. 2. Framework of water molecules connected only in the cis-fashion; some of the molecules are shown as tetrahedra; only the molecules forming the front faces of the dodecahedron are shown.

Fig. 2. Framework of water molecules connected only in the cis-fashion; some of the molecules are shown as tetrahedra; only the molecules forming the front faces of the dodecahedron are shown.

Figure 2: Fig. 2. Framework of water molecules connected only in the cis-fashion; some of the molecules are shown as tetrahedra; only the molecules forming the front faces of the dodecahedron are shown.

In order for the density to be equal to 1 g/cm^3, it is necessary to allow the introduction of molecules into part of the dodecahedral voids. In view of the absence in the experimental function of a maximum at 3.7 Å (the distance to the center of the dodecahedron), these molecules are apparently not located at the centers of the voids. To attain a density of 1 g/cm^3, it is necessary to fill about 2/3 of the voids; in this case the mean coordination number of a water molecule will be approximately 4.5, which is in agreement with the experimental data.

Thus, the structure of liquid water obtained from the assumption of the cis-character of the bonds between molecules is in good agreement with Pauling’ s results and also leads to the conclusion that dodecahedral formations of water molecules exist.

All-Union Scientific Research Institute
of Transport Construction

Received
30 XI 1960

REFERENCES CITED

1. J. Bernal, *Nature*, **183**, 141 (1959).
2. J. Bernal, *Proc. Roy. Inst. Gr. Brit.*, **37**, No. 4, 355 (1959).
3. J. Bernal, *Sci. Am.*, **203**, No. 2 (1960).
4. L. Pauling, *The Hydrogen Bonding*, London, 1959, p. 3.
5. P. O. Owston, *Adv. of Phys.*, **7**, No. 26 (1958).
6. N. Bjerrum, *Dan. Mat. Fys. Medd.*, **27**, No. 1 (1951).
7. L. Pauling, R. Marsh, *Proc. Nat. Acad. Sci. USA*, **38**, 112 (1952).
8. W. Claussen, *J. Chem. Phys.*, **19**, 259, 662, 1425 (1951).

9. J. Morgan, B. Warren, *J. Chem. Phys.*, **6**, 666 (1938).
10. W. Brady, W. Romanow, *J. Chem. Phys.*, **32**, No. 1, 306 (1960).

* A bond situated symmetrically with respect to three edges of a dodecahedron meeting at one vertex forms angles of 110°54′ with them.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.