

wheat seems not to have kept pace with the growth of population. However, Russian wheat statistics are complicated by the change which took place in 1933; prior to that date they were based on the grain actually collected; after that date they are based on the "biological" or unharvested crop, a deduction being made for

"technically inevitable losses in harvesting". In 1933 the deduction was given as 10 per cent, that is, about 1 bushel per acre, but much doubt has been expressed as to whether the losses could be kept as low; the figures for production are taken by Dr. Schiller as maximum figures which certainly have not been exceeded.

THE HYDROGEN BOND

By DR. C. E. H. BAWN,

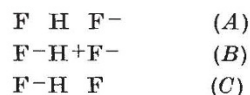
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IT has been recognized for many years that under certain conditions a hydrogen atom can form a connecting link between two other atoms. It may be considered as forming a bond between them, known as the hydrogen bond. Although the hydrogen bond is not strong, recent investigations have shown it to be of very wide occurrence. The concept has been extremely useful in explaining the association of polar liquids like water, the association of carboxylic acids, alcohols, amides, etc., the closure of rings within the molecule, and in interpreting many measurements of structure by X-ray and electron diffraction methods and of the frequency shifts of the infra-red absorption bands of certain known groupings. It was investigations of this type that not only established the existence of this form of bond but also provided information regarding the conditions in which its formation is to be expected, and, in many cases, of the actual energy of the bond. In spite of the enormous amount of experimental data now available, there is still much information which is lacking; the exact mechanism of the bonding power of the hydrogen is not clear, and there are many difficulties with questions of terminology.

With the object of clarifying the situation, a general discussion on "The Hydrogen Bond" was held by the Faraday Society on May 17 at the Imperial College of Science and Technology, London. A number of subjects was discussed in the six papers presented to the meeting, but briefly, the discussion can be considered under two headings: (1) the methods of studying hydrogen bonds by infra-red absorption, X-ray diffraction, and magnetic susceptibility measurements, and a survey of the results obtained; and (2) the occurrence of hydrogen bonds in molecules of biological importance, such as the proteins and carbohydrates.

It follows from the quantum-mechanical theories of valency that hydrogen cannot form more than

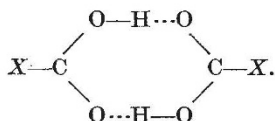
one covalent bond and that the attraction of two atoms as found in hydrogen bond formation must be due to ionic forces. The positive hydrogen ion with no electronic shell around it attracts one anion to its normal internuclear separation, and this could then attract a second anion, namely, $X-H^+Y^-$. As might be expected, the strength of the bond formed should increase with increase in the effective negative charge of the bonded atoms. Thus fluorine, oxygen, nitrogen, and chlorine should form hydrogen bonds of strength decreasing in this order. Perhaps the best example of this type of ionic bonding is the HF_2^- ion; Pauling considers that this ion resonates among three structures:



When we come to consider more complex structures involving intermolecular hydrogen bonds, steric requirements must also be satisfied, that is, the interacting groups must be capable of sufficiently close approach to enable the attractive forces to come into play. When we review the conditions of formation of the hydrogen bond, it is not at all surprising that one meets examples of bonds covering a wide range of interaction, from strong bonds to weak bonds, finally emerging into groups of interaction which we know as due to van der Waals forces. It seems at present that the only means of characterizing the hydrogen bond in the molecule is the energy required to break it.

The most important and useful method for the discovery of hydrogen bonding is infra-red spectroscopy. The main results obtained up to the present time were discussed by Dr. G. B. B. M. Sutherland. Every molecule containing an XH group gives rise to well-marked absorption bands in the near infra-red, which are characteristic of the stretching and contraction of the XH bond.

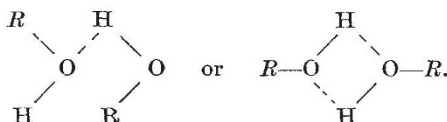
If the hydrogen atom of the XH group becomes subject to the influence of a force other than that which binds it to the X atom, then the frequency of vibration will be altered and the characteristic band will be shifted. The presence of hydrogen bonds in the molecule can therefore be inferred from the perturbation it produces in the normal XH bond. In this way both intermolecular and intramolecular bonds have been determined. As an illustration of the method we may select one of the best-known examples of the hydrogen bond, namely, the dimeric form of the carboxylic acids,



The effect of association is shown by the shift of the OH fundamental frequency at 2.83μ to 3.25μ in the acid, and the change in intensity of the band with temperature can be used as a measure of the degree of dissociation of the dimeric molecule, and hence of the heat of dissociation. The method is equally applicable for the study of hydrogen bonds in solids, solutions and liquids. Thus, the association of the alcohols in carbon tetrachloride is characterized by a band at 2.84μ – 2.88μ , in contrast to the sharp monomeric band at 2.75μ . Dr. J. J. Fox and Dr. A. E. Martin find that the monomeric O-H bond of benzyl alcohol in carbon tetrachloride has two components, 2.750μ and 2.765μ , which seems to indicate two molecular species of the alcohol. At low concentrations this alcohol dimerizes (2.865μ) and an equilibrium

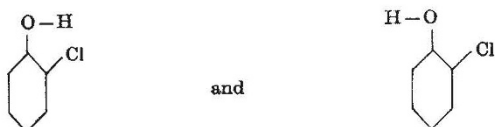


is set up, but it is not possible to decide whether the dimer has the structure,



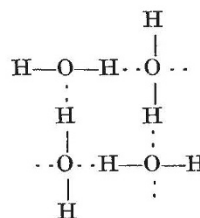
At higher concentrations polymeric association becomes predominant, and this they conclude is in accordance with an equilibrium between dimer and quadruple molecule.

Numerous infra-red investigations have shown the presence of intramolecular hydrogen bonds. The classic example of this group is the two forms of *o*-chlor-phenol,

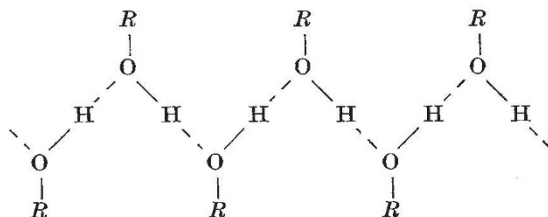


the possibility of *cis-trans* isomerism giving rise to two absorption peaks, one at about $7,050 \text{ cm}^{-1}$ (*trans*-form) and the other at about $6,890 \text{ cm}^{-1}$ (*cis*-form). Many other examples were given in Fox and Martin's paper.

The results obtained by the other powerful method of studying hydrogen bonds was reviewed in a paper by Dr. J. M. Robertson. By this method the distance between the bridged atom or groups forming the hydrogen bond can be directly measured. In this way the presence of hydrogen bonds has been demonstrated in many inorganic and organic structures. Perhaps the most interesting example is that of ice, in which each oxygen is surrounded tetrahedrally by four other oxygen atoms at a distance of 2.76 \AA . The structure is pictured to be of the type



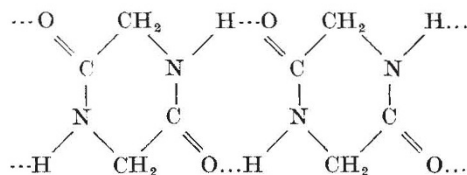
In the crystalline alcohols a similar sort of structure exists, the molecules combining through hydrogen bonds to form indefinitely large structures,



Bernal has suggested that on the basis of results obtained by X-ray analysis, two types of bonds should be distinguished, for which he proposes the names hydrogen and hydroxyl bonds. In the former, hydrogen is attached by equal firmness to two oxygens, $\text{O}-\text{H}\cdots\text{O}$, the energy being about $8,000 \text{ cal}$. and the distance between the oxygens being 2.5 – 2.65 \AA . In the latter, the hydrogen remains unsymmetrically attached to one of the oxygens, $\text{O}-\text{H}-\text{O}$, giving a bond energy of $5,000 \text{ cal}$. and an oxygen–oxygen distance of 2.7 – 2.9 \AA . Since the experimental evidence seems to indicate an almost continuous transition between these two extremes, the necessity for this distinction is not accepted by all.

In a short paper Dr. W. Rogie Angus and W. K. Hill described some preliminary results on a general investigation of diamagnetism and hydrogen bonding. There seems to be every indication that hydrogen bonding should be detectable by susceptibility measurements.

The hydrogen bond may be of great importance biologically, and two papers of the discussion were concerned with the role of hydrogen in determining the structure of the proteins and starch. Our knowledge of the detailed structure of these molecules is still far from complete, and consequently it was not possible to do more than to survey the possible part which hydrogen bonds might take in determining the structure of these substances. In this short summary, one can only restate the conclusion reached by Dr. W. T. Astbury after a critical discussion of the way in which hydrogen bonds may intervene in protein structures, "that whichever way we turn it is impossible to reach a verdict that is really satisfying". However, X-ray analysis of crystalline diketo-piperazine, a substance related to the proteins, shows that the molecules are linked together by hydrogen bonds between their respective oxygen atoms and =NH groups, to form flat continuous chains throughout the structure.



It may be expected that the formation of hydrogen bonds may be important in determining the behaviour of complex molecules containing multiple active hydrogen bond-forming groups, for example, polysaccharides. A critical consideration of this possibility for starch by Prof. E. L. Hirst, Dr. G. T. Young and the present writer shows that the properties of this molecule are inconsistent with those of a structure held together by hydrogen bonds. Analysis of physico-chemical data indicates that the repeating units in starch are held together by normal glucosidic linkages. It is pointed out, however, that the macro-molecules may be associated by hydrogen bonds in native starch.

OBITUARIES

Dr. A. C. Haddon, F.R.S.

ON April 10 there passed away in his eighty-fifth year Dr. Alfred Cort Haddon, the doyen of British anthropologists*. Haddon came of Northamptonshire stock, his grandfather founding the firm of John Haddon and Co., printers and typefounders and also produce brokers. The family business connexion brought people from all parts of the world to Haddon's home, and this may well have influenced his choice of a career. From his mother, who wrote children's books, came an interest in natural history, and young Haddon spent much of his time at the Zoo studying and drawing animals. This led friends to advise his father to send him to Cambridge to study zoology, but the boy was destined for his father's business, which he entered on leaving Mill Hill School.

According to Haddon's own account, it took his father scarcely two years to discover that it might be less costly to send his son to Cambridge than to retain him in the firm. So to Cambridge he went, entering Christ's College at the age of twenty, where he worked at zoology under F. M. Balfour and also came under the influence of Michael Foster. It was the former who inspired his first big book, the "Introduction to Embryology" (1887). He took his B.A. in 1879, and was appointed demonstrator in comparative anatomy almost immediately, holding this post until 1880, when he migrated to Dublin as professor of zoology in the Royal College of Science. The M.A. followed in 1882 and the Sc.D. in 1897; he

* I wish to thank Miss E. S. Fegan for invaluable assistance in the preparation of this notice.

was a fellow of Christ's from 1901 onwards. In 1881 he married Fanny Elizabeth Rose, the sister of his college friend J. Holland Rose (later Harmsworth professor of naval history), by whom he had three children.

In Dublin, Haddon was active in marine biology, being secretary of the Dredging Committee, which did much work off the south-west coast of Ireland, and this led to a series of papers, mostly on the Actinozoa, in the *Proceedings of the Royal Dublin Society* and the *Royal Irish Academy*. For some years he divided his time between Dublin and Cambridge, lecturing in Dublin during the winter and spending the summers at Cambridge.

So far there is little evidence that Haddon was anything more than a zoologist of recognized ability, and it was in this capacity that he was sent to Torres Straits in 1888, where he spent nearly a year, though an early interest in decorative art (he was then twenty-five) is shown by a letter to *NATURE* (23, 9-10; 1880) on the Greek fret. The zoological material brought back from this expedition was published in the *Proceedings of the Royal Society* and in the *Transactions of the Royal Dublin Society*. However significant these results may have been, their importance is entirely eclipsed by the alteration that occurred in the man himself, for it was on this first expedition to Torres Straits that Haddon's interest was largely transferred from marine zoology to anthropology. He would relate how, canoeing with the natives and living very much as they did, he became conscious of the change in their old mode of