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Chemical Crystallography

**Physical Chemistry
Series Two
Volume 11**

**Consultant Editor
AD Buckingham FRS
Volume Editor
JM Robertson CBE FRS**

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Physical Chemistry
Series Two

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Chemical Crystallography

Edited by **J. M. Robertson, C.B.E., F.R.S.**
formerly of the University of Glasgow

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International Review of Science

**Physical Chemistry
Series Two**

Consultant Editor

A. D. Buckingham, F.R.S.

Publisher's Note

The International Review of Science is an important venture in scientific publishing, presented by Butterworths. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. Chemistry was taken first as the problems of literature survey are probably more acute in this subject than in any other. Biochemistry and Physiology followed naturally. As a matter of policy, the authorship of the Review of Science is international and distinguished, the subject coverage is extensive, systematic and critical.

The Review has been conceived within a carefully organised editorial framework. The overall plan was drawn up and the volume editors appointed by seven consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence the 500 or so contributions to the Review of Science come from many countries of the world and provide an authoritative account of progress. The publication of Physical Chemistry Series One was completed in 1973 with thirteen text volumes and one index volume; in accordance with the stated policy of issuing regular reviews to keep the series up to date, volumes of Series Two will be published between the middle of 1975 and early 1976; Series Two of Organic Chemistry will be published at the same time, while Inorganic Chemistry Series Two was published during the first half of 1975. Volume titles are the same as in Series One but the articles themselves either cover recent advances in the same subject or deal with a different aspect of the main theme of the volume. In Series Two an index is incorporated in each volume and there is no separate index volume.

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Consultant Editor's Note

The International Review of Science was conceived as a comprehensive, critical and continuing survey of progress in research. The difficult problem of keeping up with advances on a reasonably broad front makes the idea of the Review especially appealing, and I was grateful to be given the opportunity of helping to plan it.

Physical Chemistry Series One was published in 1972/1973. Its success was assured by the very great distinction of its editors and authors. Our need for critical reviews at a high level has not diminished. In the rather difficult times being experienced in most parts of the world, research workers should seek to broaden the range of their expertise; it is hoped that this Series will be of use in this connection.

Like its forerunner, Series Two consists of thirteen volumes covering Physical and Theoretical Chemistry, Chemical Crystallography and Analytical Chemistry. Each volume has been edited by a distinguished chemist; in several cases the person responsible for Series One has acted again as editor. The editors have assembled a strong team of authors, each of whom has assessed and interpreted recent progress in a specialised field in terms of his own experience. I believe that their efforts have again produced useful and timely articles which will help us in our efforts to keep abreast of progress in research.

It is my pleasure to thank all those who have collaborated in this venture—the volume editors, the authors and the publishers.

Cambridge

A. D. Buckingham

Preface

The field of chemical crystallography is wide and continues to expand rapidly. Several important and comprehensive reviews of recent work have been published within the past year. The first volume in a series of the Chemical Society Specialist Periodical Reports on *Molecular Structure by Diffraction Methods*, compiled by G. A. Sim, L. E. Sutton and others, is available and covers the literature from January 1971 to March 1972. This work runs to over 800 pages and has detailed references and diagrams.

The invaluable classified bibliography of organic and organometallic crystal structures prepared by the Crystallographic Data Centre, Cambridge, continues, and the fifth volume, covering the literature published during 1972–1973 has appeared. Also from the Data Centre in Cambridge, the first volume of an important work on *Molecular Structure and Dimensions* is now available. This gives stereoscopic drawings and all the numerical data for organic and organometallic structures and covers the years 1960–1965. The volume runs to 600 large pages and costs £24.50. A computerised file at the Crystallographic Data Centre contains all this information and about 1500 new entries are added annually. Further numeric volumes for the post-1965 period are planned.

In view of these publications it would be unnecessary as well as impossible to attempt anything like a complete review of chemical crystallography in the present small volume. Instead we have confined our review to a number of special topics. In the field of natural products, a condensed review of alkaloid structures is provided. Another short chapter covers the astonishing molecular rearrangements and transformations of a single sesquiterpene, caryophyllene, while Speakman deals with further aspects of hydrogen bonding. Organotransition metal chemistry continues to be a subject of very rapid development, stimulated by the synthesis of sandwich compounds and the availability of instrumentation which allows their rapid characterisation. This subject is reviewed in an important chapter by Mason and Mingos. The determination of structure, however, is not the only and perhaps not even the most important aspect of modern crystallography. Studies of electron density are of central importance in our understanding of the nature of molecules and solids. As J. R. Platt has said, a theory of chemistry and the chemical bond is primarily a theory of electron density. It was clear from the very beginning that x-ray crystallography was potentially capable of completely defining the distribution of electron density in molecules and solids. However, for significant results the requirements of accuracy in intensity measurements are

extremely stringent and low-angle scattering data must be as complete as possible. Recent advances in experimental techniques have now made some detailed studies of electron distribution feasible, and the review of this subject by Coppens is timely.

Another subject which is substantially non-structural, in the sense that it is not directly concerned with finding the positions of the atoms within a molecule, is covered in the chapter by Dunitz and Burgi on non-bonded interactions. The calculations involved in the study of such interactions are extremely formidable even when all kinds of approximations are made, and this chapter can perhaps be best described as a guide to empirical force field calculations. Applications to small and medium ring cycloalkanes and cyclo-olefins are also described, as well as a number of other topics.

Glasgow

J. M. Robertson

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1

Aspects of Hydrogen Bonding

J. C. SPEAKMAN

University of Glasgow

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1.1 INTRODUCTION

The article on hydrogen bonding in the first volume of this series (hereinafter referred to as HB. 1) included a general elementary review of the subject with special reference to the study of $\text{O}-\text{H}\cdots\text{O}$ bonds by crystallographic methods. There followed a report on some of the results then recently

published, coverage being to the end of 1971 approximately. In this second volume, we shall continue to be selective, concentrating on topics likely to be of more general interest from the literature to November, 1973. Many of the researches are of importance in other fields of chemistry, though they are considered here because they involve hydrogen bonding.

Mention should be made of a new general text: *Hydrogen Bonding* by Vinogradov and Linnell¹. A supplement to Pimentel and McClellan's authoritative book (1960) has also been published² as well as a recent review of the theory of the hydrogen bond³.

As before, we shall give interatomic distances in terms of the ångström: $1 \text{ Å} = 10 \text{ pm}$. Estimated standard deviations of cited results are shown in parentheses; they should be accepted with the usual qualifications.

1.2 POLYMORPHS OF ICE

Definitive papers have now been published describing neutron diffraction (ND) work on the two forms of heavy ice, D_2O (II)⁴ and D_2O (IX)⁵. The former is completely ordered with respect to the deuterons. (Whalley has stated⁶ that were this structure disordered, its higher entropy might render it stable in conditions that could occur terrestrially. As ice (II) is denser than water, disastrous consequences might then ensue.)

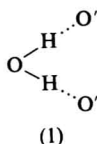
Ice (IX) has now had its structure more precisely determined than that of any other form of ice (see HB. 1, Figure 1.9). It is nearly completely ordered but has perhaps 4% of its deuterons in alternative sites. In general, there is little evidence in any form of ice for notable deviation of the water molecule from its gas-phase geometry, though this is not true for water in crystalline hydrates where experimental studies have been easier and much more numerous (see Section 1.3). In D_2O (IX), however, there is probably a significant lengthening of the hydrogen bonded O—D bonds. After correction for libration (see HB. 1, Section 1.6.4), O—D bond lengths average at $0.982(3) \text{ Å}$ compared with 0.970 Å in the gas. The validity of the lengthening is supported by the O—D stretching frequency which is 2454 cm^{-1} in D_2O (IX) as against 2727 cm^{-1} in gaseous HOD. On the other hand, and more surprisingly, the D—O—D angles are not significantly below 104.5° , the gas-phase value, despite the circumstance that the acceptor angles, $\text{O}^1 \cdots \text{D} - \text{O} - \text{D} \cdots \text{O}^2$, are 98° and 101° for the respective molecules in D_2O (IX).

1.3 THE WATER MOLECULE IN SALT AND OTHER CRYSTALLINE HYDRATES

In salt hydrates, the water molecule engages in one, or more usually both, of two bonding roles: it directs one — sometimes both — of its lone pairs of electrons towards the (usually metallic) cation; or it donates its protons to form hydrogen bonds with the anion, either directly if this is a monatomic ion, or to the oxygen atoms of oxy anions. It may also be hydrogen-bonded to other water molecules. The possibilities have been classified in more detail⁷.

To understand such bonding in hydrates, we need to know the positions

of the hydrogen atoms, preferably by ND but alternatively by less direct inference⁸. Ferraris and Franchini-Angela⁹ have made a detailed statistical survey of some 90 water molecules whose structures have been determined accurately by ND in about 40 different crystalline hydrates. Amongst other features, the geometry of the hydrogen-bonded molecule (1) has been



examined. On an average, the water molecule in a hydrate has the dimensions, $\text{O—H} = 0.96$, $\text{O} \cdots \text{O}' = 2.81$, $\text{H} \cdots \text{O}' = 1.88 \text{ \AA}$, $\text{H—O—H} = 108^\circ$, $\text{O}' \cdots (\text{HOH}) \cdots \text{O}' = 108^\circ$. The molecule itself is not much different from the isolated molecule.

However, the average dimensions have internal standard deviations larger than those of the individual values. The scatter is significant. The interpretation is that the water of hydration is acting as a 'flexible strain-absorber'. It helps to stabilise the interactions between charged ions by relieving any imbalance of bond strengths, in the sense of Pauling's electrostatic valency principles.

One of the correlations published in this paper is a histogram of the frequencies of occurrence of various $\text{O—H} \cdots \text{O}$ angles. As had been found previously, 180° is not the commonest angle: there is a maximum for the range $165\text{--}170^\circ$ which has nearly twice as many examples as has the range $175\text{--}180^\circ$. This has been taken by various commentators as a possible indication of a preference for $\text{O—H} \cdots \text{O}$ bonds that are slightly bent. It has already been suggested (see, e.g. HB. I, Section 1.3) that this deduction may be invalid. In a bond with $\text{O—H} \cdots \text{O} = 180^\circ$, the acceptor atom must lie somewhere on the O—H line produced beyond H. For an angle of (say) 165° , the acceptor has a wider choice: it is merely required to lie somewhere on the surface of the cone generated by rotating $\text{H} \cdots \text{O}$ about O—H . There is more phase-space in the latter situation and this must be taken into account in assessing the meaning of the histogram¹⁰.

The hydrogen bonds occurring in hydrates are fairly weak bonds. For such, the effectiveness of the bonding will not be sensitive to small deviations of $\text{O—H} \cdots \text{O}$ from strict linearity. For stronger bonds, with $\text{O} \cdots \text{O}$ less than 2.5 \AA , linearity is probably more important; but certainly some very short OHO bonds are not exactly linear.

1.4 THE HYDRATED 'HYDROGEN ION'

For over half a century it has been realised that the 'hydrogen ion' of aqueous-solution chemistry must be hydrated, and the formula H_3O^+ has been written, when necessary, to betoken the hydration. This particular entity has been characterised in many crystals. As long ago as 1924, Volmer noticed the similarity between the x-ray powder patterns of ammonium perchlorate and

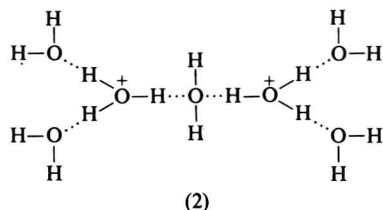
of the hydrate of perchloric acid: as the former was best represented as $\text{NH}_4^+\text{ClO}_4^-$, so $\text{OH}_3^+\text{ClO}_4^-$ was preferable to $\text{HClO}_4\cdot\text{H}_2\text{O}$ for the latter. This suggestion has subsequently been confirmed by more direct experiments. From recent x-ray analyses, examples of crystals containing the 'oxonium ion' are $[\text{H}_3\text{O}^+]_2[\text{O}_3\text{S}\cdot\text{CH}_2\cdot\text{SO}_3^-]$ ¹¹ and $[\text{H}_3\text{O}^+][\text{CF}_3\cdot\text{SO}_3^-]$ ¹².

In early x-ray work, the positions of the hydrogen atoms were merely inferred, and even now they are not accurately found. So there is a lack of firm information about the exact geometry of H_3O^+ in crystals. A recent account of a ND study of the monohydrate of toluene-*p*-sulphonic acid¹³ therefore supplies valuable information. In this compound, the cation has no built-in crystal symmetry; the four atoms are all in general positions. All the same, its structure does not deviate significantly from the ideal of $3m$ (C_{3v}) symmetry. The O—H distances are 1.008, 1.011 and 1.013(8) Å, and the H—O—H angles are 109.2, 110.7 and 111.2(5)°. These results imply that the oxygen atom is 0.322 Å out of the plane of the three hydrogen atoms.

The finding agrees satisfactorily with one's expectations. However, it is fair to point out — as the authors do — that each hydrogen atom takes part in a strong hydrogen bond ($\text{O}\cdots\text{O} = 2.528$ Å, average), and that the acceptor oxygen atoms, belonging to three different sulphonate groups, lie in positions of approximate trigonal symmetry with respect to the oxonium ion. No doubt, in a less favourably symmetrical environment the H_3O^+ ion would be more distorted¹².

More hydrated species of the proton are well documented in the crystallographic literature. We instanced H_5O_2^+ in HB. 1, Section 1.4.4, and a recent example was found in x-ray work on the tetrahydrate of sulphuric acid, where ' $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ ' turn out to be $[\text{H}_5\text{O}_2^+]_2[\text{SO}_4^{2-}]$ ¹⁴.

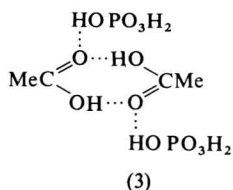
Almlöf, using x-rays¹⁵, has found a complex hydrogen-bonded system in $\text{HClO}_4\cdot 3.5\text{H}_2\text{O}$. In this crystal, two independent H_9O_4^+ units can be recognised, and they share the same water molecule. The entity (2) thus produced



could be regarded as $\text{H}_{16}\text{O}_7^{2+}$, though it does not possess the crystal symmetry suggested by this simplified diagram. The hydrogen bonds to the central water molecule have $\text{O}\cdots\text{O} = 2.68$ and 2.61 Å; the other four bonds are even stronger with $\text{O}\cdots\text{O} = 2.48$ – 2.59 Å.

As is well known (e.g. see HB. 1, Section 1.1.1), acidity in the proton donor and basicity in the acceptor favour hydrogen bonding up to a point, but if they become too strong an ionised structure results. This is illustrated by ND work on the molecular compounds between acetic acid and a range of other acids. With sulphuric acid the crystal is ionic, being made up of $\text{MeC}(\text{OH})_2^+$ and HSO_4^- ¹⁶. With phosphoric acid, the dimeric hydrogen-bonded molecule

(3) is formed¹⁷. The intercarboxyl bonds [$\text{O} \cdots \text{H} \cdots \text{O} = 2.685(3) \text{ \AA}$] are significantly longer than those in a normal carboxylic acid dimer ($\sim 2.64 \text{ \AA}$).



Such weakening is attributable to the acceptance by each carbonyl oxygen atom of a second hydrogen atom from a phosphoric acid molecule.

1.5 SOME ACID SALTS

1.5.1 The bifluoride anion

For many years the FHF^- ion has been regarded as the firmest example — possibly the only sound example — of a symmetrical hydrogen bond. Structurally, it has been studied by particularly careful ND work on the sodium and potassium salts (MHF_2 , where $\text{M} = \text{Na}, \text{K}$; see HB. 1, Section 1.6.2). According to a preliminary report¹⁸, Williams and Schneemeyer have discovered by ND an unsymmetrical FHF^- ion in *p*-toluidinium bifluoride ($\text{M} = \text{C}_7\text{H}_7\text{NH}_3^+$). In this crystal the anion has the geometry $\text{F} \cdots \text{F} = 2.260(4)$, $\text{F} - \text{H} = 1.025(6)$, $\text{F} \cdots \text{H} = 1.235(6) \text{ \AA}$; $\text{F} - \text{H} \cdots \text{F} = 178^\circ$. The distortion here is similar to, but more marked than, that in the intramolecular $\text{O} - \text{H} \cdots \text{O}$ bond reported by Schlemper *et al.*¹⁹ (see HB. 1, Section 1.4.3), and similarly it may be attributed to the asymmetry of the crystal environment. Indeed, in the toluidinium bifluoride the asymmetry can be quantified simply. At each end the $\text{F}(2) - \text{H} \cdots \text{F}(1)$ anion accepts two hydrogen bonds from different $-\text{NH}_3^+$ groups; the $\text{N} - \text{H} \cdots \text{F}$ bonds to $\text{F}(1)$ are stronger than those to $\text{F}(2)$, the $\text{H} \cdots \text{F}$ distances being, respectively, 1.608, 1.675 and 1.777, 2.518 \AA †. The stronger external bonding renders the corresponding internal (half-)bond the weaker, and the longer.

The obvious interpretation is that an isolated bifluoride ion would have its proton moving in a symmetrical, single-minimum* (but flattened) potential well. At a crystallographically symmetrical site, the bond retains its symmetry; at one that lacks symmetry, the point of minimum energy is readily displaced towards one of the fluorine atoms (see HB. 1, Figure 1.5).

Is the symmetry of HF_2^- in the simple alkali bifluorides merely a statistical effect, due to two opposite but equally probable orientations of $\text{F} - \text{H} \cdots \text{F}^-$, itself unsymmetrical and with a geometry like that specified above? This seems improbable. It is true that the ND measurements, considered alone, on NaHF_2 and KHF_2 can equally well be reconciled with a single-minimum potential, or with 'half-protons' vibrating less vigorously about two minima, provided these minima are *close together*. But a minimum 0.10 \AA from the

* Or *effectively* single, and flattened, at the bottom of the well, relative to a parabolic shape.

† The last $\text{H} \cdots \text{F}$ distance is really too long for significant bonding.

mid-point, as found in the toluidinium bifluoride, is rather beyond the limits allowed by the ND measurements, for NaHF_2 in particular. There were, too, other reasons for supposing the anions in these latter salts to be genuinely symmetrical²⁰.

1.5.2 Symmetrical, or nearly symmetrical, OHO bonds

In HB. 1, Sections 1.4.1 and 1.4.2, the type-A acid salts of carboxylic acids were cited as a class of crystalline compounds in which very short, and effectively symmetrical $\text{O}\cdots\text{H}\cdots\text{O}$ bonds have been found. Five more well-authenticated examples are now known to the reviewer. X-ray analyses have been reported on two type-A acid salts (MHX_2 , where M is a univalent cation) of monocarboxylic acids (HX)^{21, 22} and on two type-A₂ acid salts (MHY) of the symmetrically dicarboxylic acids (H_2Y)^{23, 24}. There has also been reported a ND analysis²⁵ of RbHY , where H_2Y is oxydiacetic acid $\text{O}(\text{CH}_2\text{CO}_2\text{H})_2$. Some particulars of the hydrogen bonding in these acid salts are listed in Tables 1.1 and 1.2, which are to supplement Tables HB. 1,

Table 1.1 Intercarboxylic hydrogen bonding in type-A acid salts, MHX_2 .

HX	M	Symmetry of bond	$\text{O}\cdots\text{O}$ /Å	$\text{C}-\text{O}\cdots\text{H}$ /degrees	Ref.
Dichloroacetic	NH_4	$\bar{1}$	2.432(5)	114.8	21
<i>m</i> -Chlorobenzoic	K	$\bar{1}$	2.437(6)	111.6	22

Table 1.2 Intercarboxylic hydrogen bonding in type-A₂ acid salts, MHY

H_2Y	M	Symmetry of bond	$\text{O}\cdots\text{O}$ /Å	$\text{C}-\text{O}\cdots\text{H}$ /degrees	Ref.
Oxalic	N_2H_5	$\bar{1}$	2.457(1)	114.0	23
Acetylene-dicarboxylic	K (<i>a</i> form)	2	2.445(3)	116.2	24
Oxydiacetic	Rb	2	2.450(3)	116.1	25

1.3 and HB. 1, 1.4, respectively. Hydrazinium hydrogen oxalate has already appeared in Table HB. 1, 1.4, but the recent analysis²³ is more precise and to a large extent supersedes the earlier analyses.

The weighted averages for the $\text{O}\cdots\text{O}$ distances (including those from HB.1) are 2.443(2) Å for the monobasic series and 2.454(1) Å for the dibasic. This method of averaging and the resulting standard deviations of the means are based on the unrealistic assumption that all the hydrogen bonds in these different crystals have the same length*, whereas undoubtedly there is a

* The average for the dibasic series of 2.454 Å may have been unduly biased by the heavy weight given to the value for the acid oxalate with its very low standard deviation.