

three secondary I-O distances, which are considerably less than the sum of the van der Waals radii (about 3.5 Å.), and regard them as indicating weak secondary bonds from the I atom. (Copper forms two weak bonds in addition to the four strong coplanar bonds in a number of crystalline cupric compounds (Wells, 1947).) In deciding on the location of the H atoms in HIO_3 , the O-O distances of 2.78 Å. within an IO_3 group are regarded as resulting from the formation by I of three bonds of length 1.8 Å. inclined at angles of about 100° ; they are not considered as possible O-H-O bonds. Equally, however, if the three

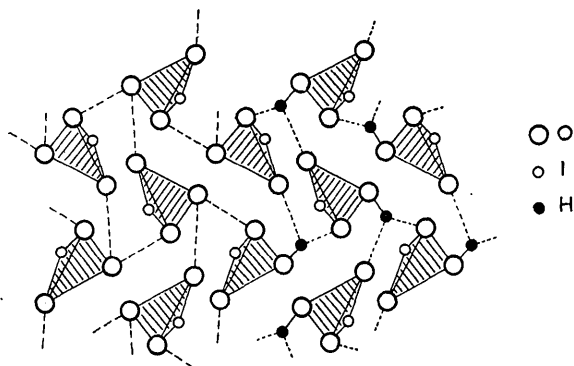


Fig. 1. Projection of the structure of $\alpha\text{-HIO}_3$ on (100). The positions suggested by Rogers & Helmholz for the H atoms are shown on the right.

longer I-O distances are interpreted as indicating the formation of three secondary bonds by the I atom, then it is not justifiable to regard the short length of any edge of this distorted IO_6 group as evidence of hydrogen bonding. In Fig. 2 the six nearest O neighbours are emphasized for one of the I atoms, and the three weaker I-O bonds are indicated by dotted lines. It is found that two of the four 'bifurcated' hydrogen bonds from any IO_3 group are edges of IO_6 co-ordination groups. If these are disregarded, the hydrogen bonding is that shown by the heavy broken lines, two of which join each IO_3 group to neighbouring groups to form infinite chains $-\text{H}-\text{IO}_3-\text{H}-\text{IO}_3-$, etc. In support of this interpretation there is the additional fact that in H_2SeO_3 the Se atom has,

like I in HIO_3 , three more neighbours in addition to its three nearest O atoms which complete a distorted octahedral co-ordination group. The distances to these next nearest neighbours are, however, 3.00, 3.08 and 3.09 Å. (as compared with Se-O, 1.74 Å. (mean) within a SeO_3 group), i.e. considerably greater than the secondary I-O distances in HIO_3 , in spite of the fact that Se is smaller than I. This supports the view that I really is forming bonds additional to the three strong bonds in an IO_3 group. The variation (2.45-2.90 Å.) in the lengths of these weaker bonds is somewhat surprising, but it is well known that it is difficult to locate accurately the lighter atoms in a structure containing much heavier ones, as shown by the large

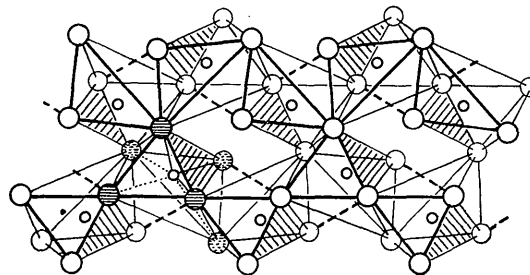


Fig. 2. Projection on (100) of the structure of $\alpha\text{-HIO}_3$ shown as a system of linked, distorted IO_6 octahedra. The O atoms of one octahedron are shaded, and the three weaker I-O bonds are shown as dotted lines. The edges of the uppermost face of each IO_6 octahedron are indicated by heavy lines. The shaded octahedron faces correspond to the shaded IO_3 groups in Fig. 1.

discrepancy between I-O bond lengths found in two recent studies of NaIO_3 , viz. I-O, 1.80 Å. (1) and 1.83 Å. (2) (MacGillavry & van Eck, 1943); and I-O, 2.05 Å. (1) and 2.08 Å. (2) (Náray-Szabó & Neugebauer, 1947).

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Preliminary examination of the crystal structure of l-proline. By BARBARA A. WRIGHT and PETER A. COLE*. *United Shoe Machinery Corporation, Research Division, Beverly, Massachusetts, U.S.A.*

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The hygroscopic character of proline has presented considerable difficulty in the growth of water-free crystals suitable for single-crystal studies. In an atmosphere of high humidity crystal growth takes the form of a fine white powder or feather-like formation with no single crystals of satisfactory size. The powder pattern from this material exhibited marked differences from that of the

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original dry proline powder. Successful single crystals were grown from a solution of the material in ethyl alcohol previously dried over anhydrous copper sulphate. Normal methyl amyl ketone was used to reduce the rate of evaporation. Evaporation took place in a closed container through which a moderate flow of dry air was maintained. This gave needle-shaped transparent birefringent crystals of rectangular cross-section.

Considerable care was required to protect the crystals

from exposure to the atmosphere, as even brief contact with water vapor caused immediate deterioration. Protection was effected by coating the crystals with a very thin layer of cellulose nitrate obtained by dipping the crystal in a 4% neutral amyl acetate solution before mounting. In this way it was possible to preserve the crystals for several days.

Weissenberg photographs were taken of the equator and first and second layer lines with the crystal rotated about the c axis, which was parallel to the long dimension of the crystal. These photographs were obtained through facilities made available by Prof. B. E. Warren of the Massachusetts Institute of Technology. In this laboratory, additional rotation photographs were taken of the crystal

rotated about the a and b axes. It was observed that the a and b axes lie in directions approximately 45° to the crystal faces. The unit cell was found to be orthorhombic with the following dimensions:

$$a = 11.64, \quad b = 9.05, \quad c = 5.18 \text{ \AA.}$$

The following systematic absences were observed: $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd. These indicate that the space group is $P2_12_12_1$. The density of the proline crystals, as determined by flotation in a mixture of p -bromotoluene and n -butyl bromide, was 1.35 g.cm.^{-3} . The number of molecules per unit cell was calculated to be 3.9. This indicates that the unit cell contains four molecules.

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A photoelectric device for the evaluation of structure factors. By H. LIPSON and C. A. TAYLOR. *Physics Department, College of Technology, Manchester 1, England.*

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Introduction

One of the most important needs in structure analysis is a means for the rapid assessment of the correctness or otherwise of a proposed structure. The device described in this note is a first step towards filling this need, and we hope to develop it into a much more versatile instrument.

Theory

Huggins (1945) has described the preparation of masks (for use in photographic Fourier synthesis) in which the transmission of light at any point is proportional to $1 \pm \cos 2\pi(hx + ky)$, the symbols having the usual meanings. If an image of one of these masks, with positive sign, is projected on a template in which small holes have been drilled with centres at (x, y) , the light transmitted will be proportional to $\Sigma A\{1 + \cos 2\pi(hx + ky)\}$, where A is the area of each hole. Thus, if the holes are made to correspond in position to the atoms in a proposed structure, with areas proportional to their scattering factors, the value of the summation is proportional to $F(000) + F(hk0)$.

Experimental test

By means of a film-strip projector, modified to give unit magnification, images of the Huggins' masks were projected on a brass template in which holes of about 1 mm. diameter were drilled to represent the structure of durene (Robertson, 1933) projected on to (010). A barrier-layer photocell was placed immediately behind the template and was connected to a galvanometer, the sensitivity of which was so adjusted that the zero reading corresponded to $-F(000)$ and the reading with no mask in position corresponded to $+F(000)$; then the readings with the various masks in position should be equal to the corresponding structure factors uncorrected for change in scattering factor. The following table gives the result of this test. It will be noted that, although there are a few large discrepancies in magnitude, all the signs are correctly derived:

hkl	$F(\text{calc.})$	$F(\text{from machine})$
000	+148	+148
200	+36	+24
400	-24	-24
600	-33	-50
800	-48	-22
001	+50	+35
002	-65	-52
003	-63	-73
004	-1	-7
005	-5	-5
201	+21	+22
20 $\bar{1}$	+53	+37
202	+8	+30
20 $\bar{2}$	-4	-9
203	-25	-21
20 $\bar{3}$	-62	-32
204	-40	-53
20 $\bar{4}$	-19	-2
401	+3	+12
40 $\bar{1}$	-32	-41
601	-89	-63
60 $\bar{1}$	+12	+17

Sources of error

It is rather difficult to align the image of the mask accurately on the template. Moreover, the method assumes that the photocell has a linear response and that the response is uniform over the whole surface.

These sources of error could be eliminated by allowing a magnified image of the masks to fall on a set of photocells representing atoms; the outputs could be fed through potentiometers, set to allow for different scattering factors. With this device different atomic arrangements could be tried more quickly. Moreover, if the outputs were fed to further potentiometers set to correspond to the appropriate values of $\cos 2\pi lz$ or $\sin 2\pi lz$, values of $F(hkl)$ could also be determined in sets with constant l . This would have great utility in three-dimensional work.

References

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