

Thus the equi-intensity lines around the (200) reciprocal-lattice point in the plane parallel to  $(b^*, c^*)$  are circles. But the intersections of the iso-diffusion surface obtained by Garrido around the (200) reciprocal-lattice point by a plane parallel to  $b^*, c^*$  are not circles; they are of the form shown in Fig. 1.

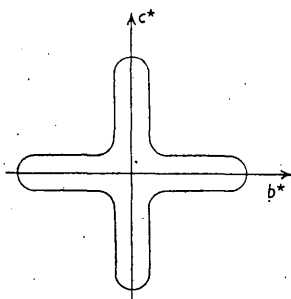


Fig. 1. Section of iso-diffusion surface around (200) reciprocal-lattice point by a plane parallel to  $b^*, c^*$  as observed by Garrido.

The section of the iso-diffusion surface by a plane parallel to  $a^*, b^*$  as observed by Garrido is of the form shown in Fig. 2 (a). The corresponding iso-diffusion lines obtained from Jahn's formula are shown in Fig. 2 (b). In this case the discrepancy between the theoretical and the experimentally observed iso-diffusion surfaces is not so prominent, but there is no appreciable agreement.

In view of the above discrepancies between theoretical and experimental results, it is natural to conclude that the extra reflexions from  $\text{NaClO}_3$  crystals do not owe their origin to the thermal vibrations. In order to ascertain the origin of the extra reflexions in this case a thorough re-investigation of the problem is desirable. Laue photo-

graphs of  $\text{NaClO}_3$  at very low temperature will also provide valuable informations in this matter.

It has also been observed that the disagreement between the experimental and the theoretical sections of the iso-diffusion surface by a plane parallel to  $a^*, b^*$  is even greater when Voigt's (1910) values of the elastic constants

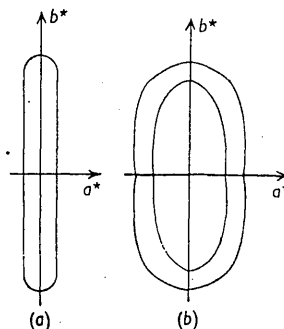


Fig. 2. Section of iso-diffusion surface around (200) reciprocal-lattice point by a plane parallel to  $a^*, b^*$ ; (a) as observed by Garrido, (b) as given by equation (1).

are used. The iso-diffusion surfaces obtained from Jahn's formula, using the values of elastic constants of Mason (1946) and of Bhagavantam & Suryanarayana (1947), are almost of the same shape.

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**Bifurcated hydrogen bonds.** By A. F. WELLS. *Research Laboratories, Imperial Chemical Industries Ltd. (Dyestuffs Division), Hexagon House, Blackley, Manchester 9, England*

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The precise nature of the constitutional differences (if any) between O-H-O bonds of various lengths is not known. The postulation of 'bifurcated' O-H-O bonds in crystals of  $\alpha\text{-HIO}_3$  (Rogers & Helmholtz, 1941) further complicates the general picture of the part played by H in intermolecular binding. The object of this note is to point out that there is an alternative and entirely reasonable interpretation of the interatomic distances in this crystal which obviates the necessity for assuming the existence of bifurcated H bonds. The facts are as follows. Crystals of  $\alpha\text{-HIO}_3$  are orthorhombic (space group  $P2_12_12_1$ ) with four molecules in the unit cell. There are therefore three sets of non-equivalent O atoms ( $O_1$ ,  $O_2$  and  $O_3$ ). The nearest neighbours of atoms are as follows:

I: 3 O (at 1.80, 1.81, 1.89 Å.) forming a pyramidal  $\text{IO}_3$  group;

3 more O (at 2.45, 2.70, 2.90 Å.) completing a distorted octahedral group;

$O_1$ : 3 O at 2.78 Å., others at 2.90 Å. or more;

$O_2$ : 4 O at 2.78 Å., others at 3.10 Å. or more;

$O_3$ : 3 O at 2.78 Å., others at 2.90 Å. or more.

Two of the nearest O neighbours of any O atom are two belonging to its own  $\text{IO}_3$  group, within which O-O is 2.78 Å., the same as the shortest O-O distances between O atoms of different  $\text{IO}_3$  groups. Rogers & Helmholtz regard all the latter (four per  $\text{IO}_3$  group) as hydrogen bonds, and describe them as bifurcated because there are twice as many such bonds as H atoms available. They are shown as broken lines at the left-hand side of Fig. 1, which is a projection of the structure on (100). They then propose positions for the H atoms, as shown to the right in Fig. 1.

There are reasons for regarding this interpretation of the interatomic distances as unsatisfactory. We have determined the crystal structure of the orthorhombic form of selenious acid,  $\text{H}_2\text{SeO}_3$ , and find that the hydrogen bonding is very similar to that in Fig. 1. This type of structural scheme is to be expected for an oxy-acid with H:O ratio of 2:3, but not for a H:O ratio of 1:3. The alternative interpretation of the structure of  $\alpha\text{-HIO}_3$  is as follows.

Rogers & Helmholtz comment on the shortness of the

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  $\text{HIO}_3$ , the O-O distances of 2.78 Å. within an  $\text{IO}_3$  group are regarded as resulting from the formation by I of three bonds of length 1.8 Å. inclined at angles of about  $100^\circ$ ; they are not considered as possible O-H-O bonds. Equally, however, if the three

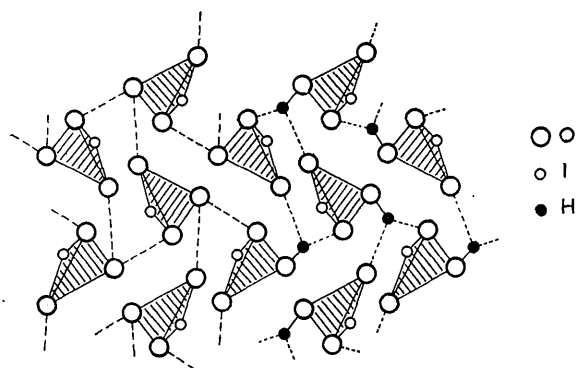


Fig. 1. Projection of the structure of  $\alpha\text{-HIO}_3$  on (100). The positions suggested by Rogers & Helmholz for the H atoms are shown on the right.

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  $\text{IO}_6$  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  $\text{IO}_3$  group are edges of  $\text{IO}_6$  co-ordination groups. If these are disregarded, the hydrogen bonding is that shown by the heavy broken lines, two of which join each  $\text{IO}_3$  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  $\text{H}_2\text{SeO}_3$  the Se atom has,

like I in  $\text{HIO}_3$ , 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  $\text{SeO}_3$  group), i.e. considerably greater than the secondary I-O distances in  $\text{HIO}_3$ , 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  $\text{IO}_3$  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

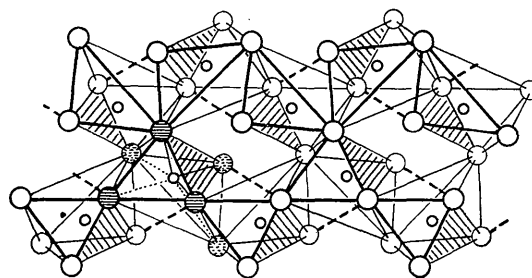


Fig. 2. Projection on (100) of the structure of  $\alpha\text{-HIO}_3$  shown as a system of linked, distorted  $\text{IO}_6$  octahedra. The O atoms of one octahedron are shaded, and the three weaker I-O bonds are shown as dotted lines. The edges of the uppermost face of each  $\text{IO}_6$  octahedron are indicated by heavy lines. The shaded octahedron faces correspond to the shaded  $\text{IO}_3$  groups in Fig. 1.

discrepancy between I-O bond lengths found in two recent studies of  $\text{NaIO}_3$ , 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