

The Crystal Structures of Two Oxy-Acids of Iodine

I. A Study of Orthoperiodic Acid, H_5IO_6 , by Neutron Diffraction*

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Ortho-periodic acid, H_5IO_6 , crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 5.28 \pm 0.02$, $b = 18.35 \pm 0.06$, $c = 4.95 \pm 0.02$ Å, $\beta = 111.4 \pm 0.2^\circ$, $Z = 4$. The structure has been determined from the intensities of 124 and 127 independent reflexions $0kl$ and $hk0$ respectively, which were obtained by neutron diffraction. Anisotropic refinement by least-squares analysis decreased R to 0.064.

The molecule of H_5IO_6 consists of a slightly deformed IO_6 octahedron, five of the oxygen atoms of which are directly linked to hydrogen. For these five oxygen atoms the distance to the central iodine atom is 1.89 Å. For the remaining oxygen atom, O(2), the distance is shorter, 1.78 Å, e.s.d. 0.02 Å. The O–H distances average 0.96 Å. Each IO_6 octahedron is linked to neighbouring IO_6 octahedra by ten hydrogen bonds. In the three-dimensional network which is thus formed, five independent hydrogen bonds may be distinguished. The two bonds in which O(2) is involved are 2.60 Å, the remaining bonds are 2.78 Å, e.s.d. in the individual bonds 0.03 Å.

Introduction

Until recently little was known with certainty of the crystal structures of the oxy-acids of iodine. Only the structure of $\alpha\text{-HIO}_3$ had been investigated by X-ray and neutron diffraction (Rogers & Helmholz, 1941; Garrett, 1954). In this paper a two-dimensional neutron diffraction study of ortho-periodic acid, H_5IO_6 , is described. The next paper deals with the structure determination of anhydro-iodic acid HI_3O_8 by three-dimensional X-ray methods (Feikema & Vos, 1966).

The crystal structure of H_5IO_6 was studied in order to obtain more accurate information of the configuration of the IO_6 octahedra, first observed in the structure by infrared methods (van Arkel & Fritzius, 1931; Natalis, 1959; Siebert, 1960). Although the IO_6 group had been investigated in some other compounds, no accurate values were available for the bond lengths and angles. The X-ray studies of $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ (Helmholz, 1937) and $\text{Ag}_2\text{H}_3\text{IO}_6$ (Ferrari, Curti & Cavalca, 1944) are presumably rather approximate.

A related point of interest is the linkage of the IO_6 groups by hydrogen bonds. For the examination of these hydrogen bonds the application of neutron diffraction after the previous X-ray work (Feikema, 1961) seemed desirable.

Experimental

The dimensions of the monoclinic unit cell (Feikema, 1961) were redetermined from the θ values of high order X-ray reflexions recorded by the back-reflexion method. With $\lambda(\text{Cu } K\alpha_1) = 1.5405$ and $\lambda(\text{Cu } K\alpha_2) =$

1.5443 Å we obtained $a = 5.28 \pm 0.02$, $b = 18.35 \pm 0.06$, $c = 4.95 \pm 0.02$ Å, $\beta = 111.4 \pm 0.2^\circ$.

In all neutron diffraction experiments the wavelength was 1.05 Å. Only reflexions with $\sin \theta \leq 0.7$ could be measured. First 124 $0kl$ reflexions were obtained from a crystal measuring 0.8 cm along the a axis and 0.4×0.4 cm² perpendicular to this axis. Then the crystal was divided into two equal parts of $0.4 \times 0.4 \times 0.4$ cm³; from one of these 127 $hk0$ reflexions were measured. The intensities were corrected for the Lorentz effect. During the refinement it appeared to be necessary to correct the strong reflexions 080, 040 and 082 for extinction. This was done by regarding the (secondary) extinction as an absorption with absorption coefficient gQ (James, 1958); g was determined by a comparison of the calculated and observed structure factors.

Owing to the large value of b , it was not possible to obtain the $h0l$ reflexions separate from the $h1l$ and $h\bar{1}l$ reflexions with the diffractometer available.

Positions of the hydrogen atoms

The positions of the hydrogen atoms were determined in [100] projection first. With the coordinates from the X-ray investigation (Table 2) the contribution of the oxygen and iodine atoms to the $0kl$ structure factors was calculated. For 63 reflexions this contribution was assumed to be large enough to determine the sign of the structure factor; except in one case the assumed signs proved to be correct later on. The Fourier synthesis of these 63 reflexions only showed four instead of five wells representing hydrogen atoms. The fifth well, corresponding to H(3), did not appear because of overlap with the iodine atom, as is seen in Fig. 1. Its presence was concluded from the relatively small height of the maximum near the iodine atom and the shift of this maximum from the position obtained for the iodine atom by X-ray diffraction.

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After determination of the y and z coordinates, approximate values for the x coordinates were obtained by assuming that the hydrogen bonds $\text{O}-\text{H}\cdots\text{O}$ are linear. In the [001] Fourier synthesis, shown in Fig. 2, all five hydrogen wells were found at the expected positions.

The hydrogen atoms are located between non-centrosymmetrically related oxygen atoms of neighbouring IO_6 groups, the distances $\text{O}-\text{H}\cdots\text{O}$ are 2.59–2.81 Å. Further $\text{O}\cdots\text{O}$ contacts between non-centrosymmetrically related oxygen atoms of different IO_6 groups are larger than 3 Å. Therefore even after the X-ray investigation indirect evidence on the location of the hydrogen bonds could be obtained from the $\text{O}\cdots\text{O}$ distances.

Table 1. Final coordinates and thermal parameters U_{ij} (Å²)

[001] projection					
Atom	x	y	U_{11}	U_{12}	U_{22}
H(1)	0.1472	0.0598	0.0351	-0.0021	0.0362
H(2)	0.4699	0.1870	0.0347	-0.0014	0.0350
H(3)	0.8745	0.1343	0.0226	-0.0010	0.0334
H(4)	0.3428	0.0019	0.0390	0.0032	0.0316
H(5)	0.2195	0.2375	0.0512	0.0051	0.0334
I	0.3300	0.1208	0.0124	-0.0023	0.0157
O(1)	0.3071	0.0500	0.0257	-0.0063	0.0220
O(2)	0.6208	0.0812	0.0163	-0.0023	0.0188
O(3)	0.0867	0.0648	0.0226	-0.0056	0.0235
O(4)	0.3386	0.1968	0.0269	0.0034	0.0186
O(5)	0.0300	0.1687	0.0195	0.0014	0.0198
O(6)	0.5464	0.1816	0.0253	-0.0043	0.0201

[100] projection					
Atom	y	z	U_{22}	U_{23}	U_{33}
H(1)	0.0583	0.9993	0.0416	-0.0123	0.0367
H(2)	0.1886	0.9162	0.0361	-0.0084	0.0309
H(3)	0.1378	0.4770	0.0290	-0.0031	0.0303
H(4)	0.0031	0.6804	0.0334	0.0090	0.0347
H(5)	0.2356	0.2172	0.0372	0.0036	0.0594
I	0.1215	0.4677	0.0186	-0.0025	0.0118
O(1)	0.0511	0.7312	0.0188	-0.0012	0.0152
O(2)	0.0815	0.4251	0.0160	-0.0066	0.0237
O(3)	0.0651	0.1573	0.0217	-0.0042	0.0164
O(4)	0.1965	0.2051	0.0160	0.0045	0.0196
O(5)	0.1670	0.5048	0.0177	0.0027	0.0288
O(6)	0.1808	0.7744	0.0188	-0.0023	0.0185

Table 2. Comparison of the final coordinates of the X-ray and neutron diffraction investigation

Atom	X-ray diffraction			Neutron diffraction		
	x	y	z	x	y	z
H(1)				0.1472	0.0591	0.9993
H(2)				0.4699	0.1878	0.9162
H(3)				0.8745	0.1360	0.4770
H(4)				0.3428	0.0025	0.6803
H(5)				0.2195	0.2366	0.2170
I	0.3278	0.1210	0.4632	0.3300	0.1212	0.4677
O(1)	0.299	0.051	0.722	0.3071	0.0505	0.7312
O(2)	0.606	0.082	0.419	0.6208	0.0814	0.4251
O(3)	0.090	0.060	0.162	0.0867	0.0650	0.1573
O(4)	0.339	0.196	0.208	0.3386	0.1967	0.2051
O(5)	0.038	0.168	0.504	0.0300	0.1678	0.5048
O(6)	0.543	0.182	0.771	0.5464	0.1812	0.7744

Refinement

The [100] and [001] projections were refined independently with the least-squares refinement program of Curtis (1959) on a Ferranti Mercury computer. The scattering lengths given by Shull & Wollan (1959) were used. The weighting scheme was $w = 64|F_m|^2/|F_o|^2$ with $|F_m| = 0.5$ (in units of 10^{-13} cm). Isotropic refinement decreased the residual R to 0.104 for the $0kl$ reflexions and to 0.082 for the hkl reflexions. Subsequent difference Fourier syntheses showed a considerably anisotropic thermal motion. Refinement with anisotropic temperature factors gave $R(hkl) = 0.064$ and $R(0kl) =$

Table 3. Observed and calculated structure factors

The scattering lengths are in units of 10^{-13} cm.

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0	22	21	0	19	2	3	5	0	13	5	8	7
4	0	0	10	11	0	20	2	39	39	0	14	5	11	12
6	0	0	10	11	0	21	2	33	32	0	15	5	24	26
0	4	0	52	52	0	22	2	25	25	0	2	6	17	17
0	4	0	6	9	0	23	2	11	10	0	3	6	11	10
0	8	0	93	92	0	24	2	45	44	0	4	6	8	8
0	10	0	5	4	0	1	3	55	57	0	5	6	8	8
0	12	0	4	3	0	2	3	51	49	0	6	6	6	6
0	14	0	24	26	0	3	3	22	19	1	1	0	15	15
0	16	0	19	15	0	3	3	24	23	1	2	1	34	34
0	18	0	11	10	0	4	3	17	16	1	3	0	17	16
0	20	0	27	29	0	6	3	20	20	1	4	0	5	4
0	22	0	18	16	0	7	3	12	12	1	5	0	22	22
0	24	0	24	24	0	8	3	9	7	1	6	0	7	4
0	2	0	33	31	0	9	3	25	27	1	7	0	18	18
0	0	4	33	34	0	10	3	29	29	1	8	0	22	21
0	0	6	7	7	0	11	3	37	37	1	9	0	18	18
0	1	1	37	34	0	12	3	7	4	1	10	0	24	25
0	2	1	11	10	0	13	3	6	6	1	11	0	14	14
0	3	1	30	29	0	15	3	23	23	1	12	0	4	4
0	4	1	8	7	0	16	3	23	22	1	13	0	30	29
0	5	1	16	15	0	17	3	38	39	1	14	0	60	63
0	6	1	16	3	0	18	3	32	29	1	15	0	15	15
0	7	1	19	19	0	19	3	7	5	1	16	0	6	6
0	8	1	32	31	0	20	3	18	18	1	17	0	13	14
0	9	1	19	17	0	21	3	28	28	1	18	0	5	7
0	10	1	15	13	0	22	3	12	12	1	19	0	31	28
0	11	1	17	15	0	23	3	10	12	1	20	0	19	18
0	12	1	13	13	0	24	3	24	22	1	21	0	17	16
0	14	1	11	11	0	3	4	42	42	1	22	0	4	3
0	15	1	26	26	0	4	4	8	6	1	23	0	10	9
0	16	1	56	61	0	5	4	29	29	2	1	0	9	8
0	17	1	18	18	0	6	4	35	45	2	2	0	17	16
0	18	1	5	5	0	7	4	7	10	2	3	0	23	22
0	19	1	5	6	0	8	4	20	20	2	4	0	9	7
0	20	1	14	14	0	9	4	21	19	2	5	0	16	15
0	21	1	28	28	0	10	4	25	15	2	6	0	15	12
0	23	1	19	18	0	11	4	6	14	2	7	0	3	3
0	24	1	36	36	0	12	4	13	13	2	8	0	13	13
0	25	1	29	28	0	13	4	31	31	2	9	0	25	24
0	1	2	11	11	0	14	4	36	37	2	10	0	16	15
0	2	2	6	4	0	15	4	5	3	2	11	0	41	43
0	3	2	6	4	0	16	4	11	11	2	12	0	39	39
0	4	2	13	11	0	17	4	14	14	2	13	0	32	28
0	5	2	8	8	0	18	4	22	21	2	15	0	37	37
0	6	2	10	10	0	1	5	7	5	2	16	0	6	5
0	7	2	33	35	0	2	5	5	8	2	17	0	22	22
0	8	2	15	14	0	3	5	15	16	2	18	0	14	14
0	9	2	15	14	0	4	5	8	10	2	19	0	12	12
0	10	2	14	13	0	5	5	22	23	2	20	0	26	22
0	11	2	6	6	0	6	5	32	31	2	21	0	29	29
0	12	2	24	24	0	7	5	14	11	3	1	0	59	59
0	13	2	28	27	0	8	5	22	22	3	2	0	7	4
0	15	2	22	21	0	9	5	10	10	3	3	0	45	46
0	16	2	34	37	0	10	5	22	20	3	4	0	3	6
0	17	2	11	12	0	11	5	36	37	3	5	0	12	15
0	18	2	15	15	0	12	5	19	18	3	6	0	13	12

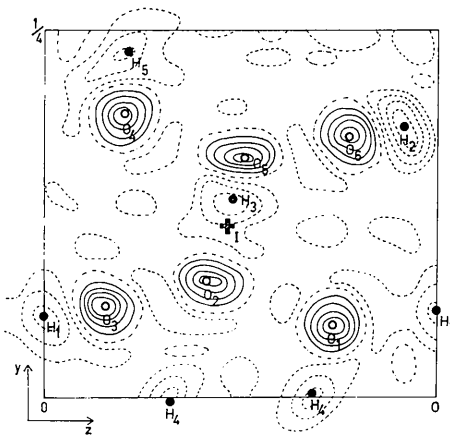


Fig. 1. F_0 -synthesis, without the iodine atom, of the [100] projection. Contours are at equal intervals of arbitrary scale. The dotted lines indicate negative areas.

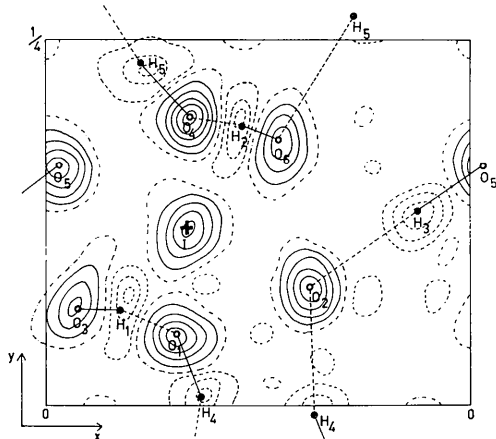


Fig. 2. F_0 -synthesis of the [001] projection. Contours are at equal intervals of arbitrary scale. The dotted lines indicate negative areas.

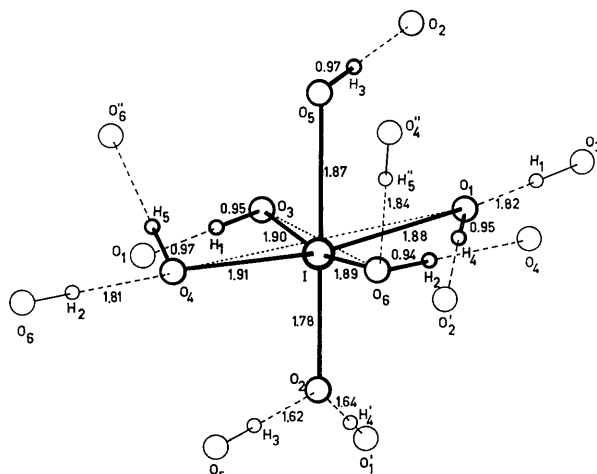


Fig. 3. Molecule of H_5IO_6 and its environment.

0.061. The final coordinates and the thermal parameters U_{ij} (Cruickshank, 1956) are listed in Table 1. It may be noted that the thermal motion of the atoms is rather low; the 'best fit' parameters of the isotropic temperature factors are 1.05, 1.65 and 2.80 \AA^2 for iodine, oxygen and hydrogen respectively. In Table 2 the final coordinates of the X-ray and neutron diffraction investigation are compared. The observed and calculated structure factors are listed in Table 3.

An estimate of the accuracy of the thermal parameters could be obtained by comparing the two sets of independently obtained U_{22} values. The r.m.s. value $\langle(\Delta U_{22})^2\rangle^{\frac{1}{2}}$ is 0.0032 \AA^2 for hydrogen and 0.0022 \AA^2 for oxygen, corresponding to errors 0.26 and 0.18 \AA^2 respectively in B . The errors in the coordinates were estimated by comparing the two sets of values obtained for the y coordinates. In calculating the r.m.s. value $\langle(\Delta y)^2\rangle^{\frac{1}{2}}$ the y coordinates of oxygen and iodine were taken together, as the scattering lengths of these atoms have about the same magnitude. From the calculated r.m.s. values, 0.039 \AA for hydrogen and 0.017 \AA for oxygen and iodine, the errors in the individual coordinates were estimated at 0.028 and 0.011 \AA respectively. These values are slightly larger than the standard deviations calculated with Cruickshank's formula (Cruickshank, 1949). The inaccuracy in the cell constants was estimated at 0.4%.

With the assumption that the errors are equal for all directions, standard deviations of 0.02 and 0.03 \AA were calculated for the I-O and O-H bond lengths respectively. The s.d. in the angles are 0.7° for O-I-O and 1.8° for I-O-H.

Description of the structure

The H_5IO_6 molecule

The structure of ortho-periodic acid consists of slightly deformed oxygen octahedra with iodine near the centre. The octahedra are mutually linked by hydrogen bonds. A molecule of H_5IO_6 and its environment are shown in Fig. 3, the valence angles are listed in Table 4. Atom O(2) which is not directly linked to a hydrogen atom, is closer to the iodine atom than the remaining oxygen atoms. The longer I-O bonds are 1.89 \AA on the average, the distance I-O(2) is 0.11 \AA shorter.

The bonds in the molecule may be described as covalent. After promotion of two of the outer electrons of the iodine atom to $5d$ orbitals, $5s$, $5p$ and $5d$ orbitals of the iodine atom may be used for the bonding. These orbitals can combine to give six equivalent sp^3d^2 orbitals pointing from the iodine atom in the centre to the corners of a regular octahedron. Five out of the seven valence electrons of iodine may be used to form single (σ) bonds with the five OH groups, whereas the remaining lone pair on the iodine atom may give a coordinate (σ) bond with the oxygen atom O(2) such as to form $(HO)_5I^+-O(2)^-$. The relatively small distance I-O(2) indicates, however, that additional π -bonding

occurs by overlap of the orbitals of the lone pair electrons on O(2) with d orbitals of the iodine atom. The electron distribution in the iodine(VII) compound H_5IO_6 is thus better described by the formula $(\text{HO})_5\text{I}=\text{O}(2)$. It is likely that the lone pair electrons on the remaining oxygen atoms cause some π -bonding also, as the bonds $\text{I}-\text{O}(\text{H})$ are approximately 0.1 \AA shorter than the length 1.99 \AA estimated for a single $\text{I}-\text{O}$ bond from the sum of the covalent radii and the difference in electronegativity of oxygen and iodine (Pauling, 1960, p.229; Schomaker & Stevenson, 1941).

In the paper on HI_3O_8 (Feikema & Vos, 1966) the $\text{I}-\text{O}$ bonds will be further discussed.

Hydrogen bonds

Owing to the large H to O ratio the number of hydrogen bonds in H_5IO_6 is large. Each IO_6 group is connected to neighbouring octahedra by ten hydrogen bonds. As is shown in Fig. 3, both O(3) and O(5) are involved in one hydrogen bond only, whereas each of the remaining oxygen atoms takes part in two hydrogen bonds. In this way the three-dimensional network shown in Fig. 4 is formed. For I^*O_6 in the middle of the figure all ten hydrogen bonds are shown. There are two bonds to each of its neighbours in the z -direction and one bond to each of the neighbouring octahedra in the x -direction. In addition there are two bonds directed to the centrosymmetrically related neighbour shown in the lower part of the figure and one bond to each of the octahedra related to I^*O_6 by the n -glide plane operation, which are illustrated in the upper part of the figure. The latter hydrogen bonds give rise to twelve-membered rings: $\text{I}^*-\text{O}(4) \cdots \text{H}(2)-\text{O}(6) \cdots \text{H}(5'')-\text{O}(4'')-\text{I}''-\text{O}(6'')-\text{H}(2'') \cdots \text{O}(4'')-\text{H}(5'') \cdots \text{O}(6)-\text{I}^*$. Bonds in neighbouring rings with $\Delta x=1$ are represented by thin and bold lines, slightly shifted relative to each other. Neighbouring rings along the a axis are connected by bonds $\text{O}(4)-\text{H}(5) \cdots \text{O}(6')$ [$\text{O}(6')$ one cell below $\text{O}(6'')$]. In this way spirals along the a axis with alternating left and right pitch are formed.

The hydrogen bonds have different lengths. Two relatively short bonds, 2.60 \AA , are observed at O(2) (Fig. 3); the remaining bonds are equal within experimental error and have an average length 2.78 \AA . The $\text{O}-\text{H}$ distances average 0.96 \AA . This value for $\text{O}-\text{H}$ has also been found in some other compounds (for a review

of neutron diffraction data, see Hamilton, 1962). In the review by Hamilton lengths varying from 2.60 to 2.78 \AA are quoted for asymmetric hydrogen bonds.

The three-dimensional network described above accounts for the small thermal motion of the iodine and oxygen atoms. The difference maps of the two projections suggest that thermal motion of the hydrogen atoms is largest perpendicular to the hydrogen bonds. For H(2) and H(5) this is shown in Fig. 1; the hydrogen bonds $\text{O}(6)-\text{H}(2) \cdots \text{O}(4)$ and $\text{O}(4)-\text{H}(5) \cdots \text{O}(6)$ are nearly parallel to the c and b axis respectively.

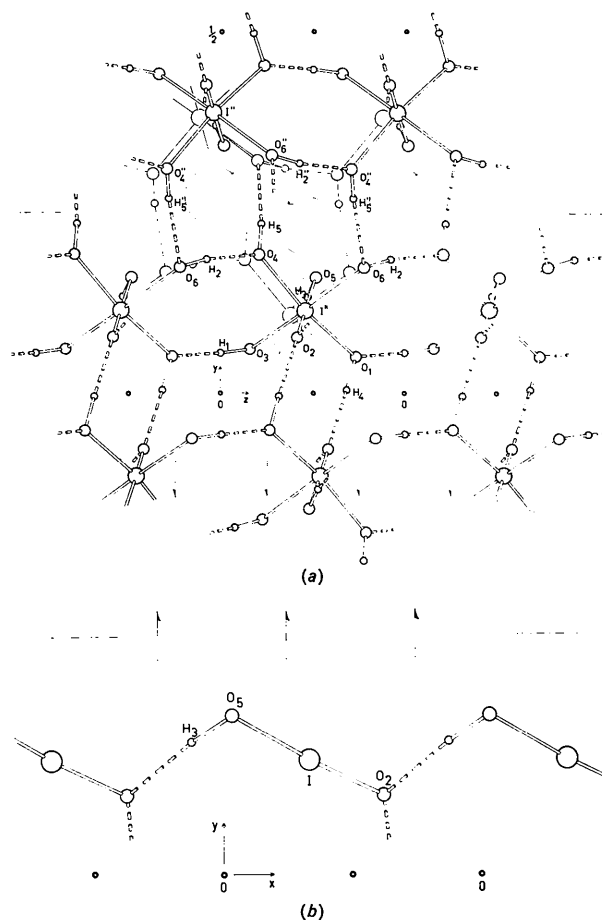


Fig. 4. (a) Three-dimensional network of hydrogen bonds viewed along the a axis. The bonds within the circle around I^* are illustrated in (b). (b) Hydrogen bonds in the direction of the a axis.

Table 4. Valence angles

$\text{O}(1)-\text{I}-\text{O}(3)$	90°	$\text{O}(5)-\text{I}-\text{O}(6)$	87°	$\text{H}(5) \cdots \text{O}(6)-\text{I}$	123°
$\text{O}(1)-\text{I}-\text{O}(6)$	91	$\text{H}(1)-\text{O}(3)-\text{I}$	113	$\text{H}(1) \cdots \text{O}(1)-\text{H}(4)$	118
$\text{O}(2)-\text{I}-\text{O}(1)$	95	$\text{H}(2)-\text{O}(6)-\text{I}$	112	$\text{H}(2) \cdots \text{O}(5)-\text{H}(4)$	124
$\text{O}(2)-\text{I}-\text{O}(3)$	92	$\text{H}(3)-\text{O}(5)-\text{I}$	115	$\text{H}(5) \cdots \text{O}(6)-\text{H}(2)$	113
$\text{O}(2)-\text{I}-\text{O}(4)$	89	$\text{H}(4)-\text{O}(1)-\text{I}$	113	$\text{H}(3) \cdots \text{O}(2) \cdots \text{H}(4)$	116
$\text{O}(2)-\text{I}-\text{O}(6)$	93	$\text{H}(5)-\text{O}(4)-\text{I}$	109	$\text{O}(1) \cdots \text{H}(1)-\text{O}(3)$	173
$\text{O}(4)-\text{I}-\text{O}(3)$	91	$\text{H}(1) \cdots \text{O}(1)-\text{I}$	128	$\text{O}(2) \cdots \text{H}(3)-\text{O}(5)$	178
$\text{O}(4)-\text{I}-\text{O}(6)$	88	$\text{H}(2) \cdots \text{O}(4)-\text{I}$	126	$\text{O}(2) \cdots \text{H}(4)-\text{O}(1)$	176
$\text{O}(5)-\text{I}-\text{O}(1)$	89	$\text{H}(3) \cdots \text{O}(2)-\text{I}$	116	$\text{O}(4) \cdots \text{H}(2)-\text{O}(6)$	171
$\text{O}(5)-\text{I}-\text{O}(3)$	89	$\text{H}(4) \cdots \text{O}(2)-\text{I}$	128	$\text{O}(6) \cdots \text{H}(5)-\text{O}(4)$	171
$\text{O}(5)-\text{I}-\text{O}(4)$	88				

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The Crystal Structures of Two Oxy-Acids of Iodine. II. An X-ray Diffraction Study of Anhydro-iodic Acid, HI₃O₈

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Anhydro-iodic acid, HI₃O₈, crystallizes in the monoclinic system, space group $P2_1/n$. The cell dimensions are $a = 7.55 \pm 0.01$, $b = 7.68 \pm 0.01$, $c = 11.40 \pm 0.015$ Å, $\beta = 90.1 \pm 0.1^\circ$. There are four units of HI₃O₈ per cell.

Refinement has been carried out by the method of least squares with allowance for anisotropic vibration for the iodine atoms. R decreased to 0.056 for 2412 independent hkl reflexions obtained by X-ray diffraction. The structure consists of units HIO₃ and I₂O₅ which show a strong intermolecular interaction. Many intermolecular I...O distances are as short as 2.6 Å; the thermal motion of the atoms is small. The I₂O₅ group with structure O₂I-O*-IO₂ has four 'double' bonds of 1.79 Å and two single bonds (I-O*) of 1.96 Å, e.s.d. 0.013 Å. The length of the two 'double' bonds in the HO'-IO₂ group is 1.80 Å, the distance I-O' is 1.90 Å. Indirect evidence for the position of the hydrogen atom was obtained.

Introduction

It has been concluded from infrared spectra of HI₃O₈ and I₂O₅ that HI₃O₈ is an addition compound of I₂O₅ and HIO₃ (Dupuis & Lecomte, 1961), and that solid I₂O₅ consists of molecules O₂I-O-IO₂ (Duval & Lecomte, 1960). It was thought to be worth while to verify these conclusions and to determine bond lengths and valence angles in the I₂O₅ and HIO₃ groups by X-ray analysis. The configuration of the HIO₃ molecules in solid α -iodic acid has been determined by neutron diffraction (Garrett, 1954).

Experimental

Anhydro-iodic acid was obtained by dehydration of iodic acid at 110°C (Brauer, 1960, p. 281) and by oxida-

tion of iodine with fuming nitric acid (Moles & Parts, 1935). The acid was purified by recrystallizing it from a 55% solution of nitric acid in water. The composition HI₃O₈ was checked by chemical analysis. Crystals with diameters ≤ 0.2 mm perpendicular to the axis of rotation were used during the X-ray work.

The crystallographic data are listed in Table 1. The dimensions of the monoclinic unit cell were determined from a diffractogram of a flat powder specimen; powder lines of CaF₂ were used as a reference.

Table 1. *Crystallographic data*

Monoclinic, space group $P2_1/n$
 $\lambda(\text{Cu } K\alpha) = 1.5418$ Å
 $a = 7.548 \pm 0.01$ Å
 $b = 7.680 \pm 0.01$
 $c = 11.402 \pm 0.015$
 $\beta = 90.1 \pm 0.1^\circ$
 Four units HI₃O₈ per cell
 $d(\text{calc}) = 5.04$, $d(\text{obs}) = 4.97$ g.cm⁻³.

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