

Iodine Oxides

Part III.* The Crystal Structure of I_2O_5

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I_2O_5 crystallizes monoclinically with $a=11.036(3)$ Å, $b=5.063(1)$ Å, $c=8.135(2)$ Å, $\beta=107.18(2)^\circ$. (Standard deviations are appended in brackets.) The space group is $P2_1/c$ and the unit cell contains 2×4 I and 5×4 O in position 4(e). The following values were found for the positional parameters: I(1) $x=0.1260(2)$, $y=0.1143(6)$, $z=0.2136(3)$; I(2) $x=0.3730(2)$, $y=0.6825(5)$, $z=0.1597(3)$; O(1) $x=0.015(3)$, $y=0.850(7)$, $z=0.154(3)$; O(2) $x=0.193(2)$, $y=0.041(7)$, $z=0.434(3)$; O(3) $x=0.486(2)$, $y=0.862(6)$, $z=0.333(3)$; O(4) $x=0.309(2)$, $y=0.492(6)$, $z=0.300(3)$; O(5) $x=0.250(2)$, $y=0.968(6)$, $z=0.116(3)$. The iodine atoms exhibit anisotropic thermal motions, whereas isotropic temperature factors were adequate for the oxygen atoms.

Molecular I_2O_5 units are distinguishable in the structure, although fairly strong intermolecular forces are present in the lattice as clearly evidenced by the occurrence of intermolecular I—O distances as short as $2.23(3)$ Å. The I_2O_5 structure is briefly compared with that of $HI_2O_5 \equiv HIO_3 \cdot I_2O_5$ and a tentative discussion of the chemical bonding is presented.

In the fifth period of the Periodic System there exists a consecutive series of binary oxides in which the oxidation state of the other component is $N-2$ (N =Group number), *i.e.* SnO , Sb_2O_3 , TeO_2 , I_2O_5 , and XeO_3 . With the notable exception of I_2O_5 , the crystal structure of at least one modification of each of these compounds is known. The crystal (and molecular) structure of (di)iodine pentoxide represents a challenging lack of knowledge and this deficiency ought to be corrected for *inter alia* the following reasons.

Two crystalline modifications are known for SnO ,^{1,2} the stable form being a typical layer structure of the PbO type. In the cubic form of Sb_2O_3 ,³ there occur discrete Sb_4O_6 molecules, whereas molecular units are indistinguishable in the orthorhombic modification,⁴ which consists of infinite double chains. One of the modifications of TeO_2 is commonly assumed (*cf.*, *e.g.*, Refs. 5, 6) to crystallize with the TiO_2 -rutile type structure and its chemical bonding has consequently been interpreted as ionic. However, later work^{7,8} suggests very strongly that this structure is only related to, rather than isostructural

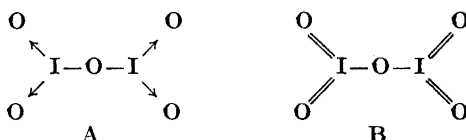
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with, that of TiO_2 -rutile and that its bondings are in fact essentially covalent. The latter interpretation applies apparently also to the second form⁹ of TeO_2 which takes a TiO_2 -brookite like structure. The crystal structure of XeO_3 ¹⁰ is composed of discrete molecules corresponding to the formula.

Considering oxides with the same stoichiometry as I_2O_5 it may be mentioned that the stable crystal structure of N_2O_5 ¹¹ consists of NO_2^+ and NO_3^- ions. The bonding in the three crystalline forms of P_2O_5 is on the other hand definitely covalent. The metastable rhombohedral form¹² preserves the P_4O_{10} molecules of the vapour, the stable orthorhombic modification¹³ arranges linked PO_4 tetrahedra in a three-dimensional network, and a third, orthorhombic modification¹⁴ consists of infinite corrugated sheets of interlocking rings based on PO_4 tetrahedra.

On this basis there are accordingly several possibilities for the hypothetical crystal structure of I_2O_5 , ranging from discrete single molecules, through various kinds of polymerized molecules to a giant three-dimensional molecule or even the other extreme, an ionic lattice.

Provided the I_2O_5 structure turns out to be of the simple molecular type it is of interest to test the two schematic descriptions of the molecule



which often are found in textbooks. In the extreme of case A each atom would obtain complete octets, whereas expanded octets on the iodine atoms are implied in case B. Although essentially different in the starting-points, the cases A and B may be united by assuming a degree of double bond character in relevant parts of the molecule. This may be specified as π back-bonding from a filled p -orbital on the end oxygens to an empty d - (or f -) orbital on the iodines in addition to the regular σ -bonds.

The crystal structure of anhydro iodic acid¹⁵ ($\text{HI}_3\text{O}_8 \equiv \text{HIO}_3 \cdot \text{I}_2\text{O}_5$) has already shed some light on the problem. In this structure molecular units of I_2O_5 are distinguishable and the interpretation of the bond distances within the I_2O_5 unit suggests that the π -character of the bonding of the end oxygens to iodine must be appreciable.

The hitherto available information on the molecular structure of I_2O_5 itself is due to Duval and Lecomte,¹⁶ who concluded that the solid phase contains molecular units of the type A or B above on the basis of infra-red spectroscopic data. Regarding the symmetry of the I_2O_5 molecule they suggested C_{2v} , *i.e.* that two mutually perpendicular mirror planes pass through the oxygen atom bridging the two IO_2 groups. If this is the case the symmetry of the molecule in I_2O_5 itself would indeed be very different from that of the corresponding unit in HI_3O_8 .¹⁵

Methods for the preparation of pure I_2O_5 and some of its crystallographic data are previously reported by the present authors.¹⁷

EXPERIMENTAL

Single crystals of I_2O_5 were obtained by sublimation from powdered I_2O_5 at 250°C.¹⁷ Due to their hygroscopic properties the crystals were mounted and sealed in thin-walled boron-lithium-glass capillaries.

Single crystal X-ray photographs were taken in an integrating Weissenberg camera of 57.3 mm diameter with Zr-filtered $MoK\alpha$ -radiation using the multiple-film technique. Three-dimensional data of, in all, 1127 reflections (313 with zero intensity) were collected from the layers $h0l$ to $h3l$.

The intensity measurements were carried out microphotometrically except for the weakest reflections which were estimated visually by comparison with a standard scale. The intensities of the reflections from different layers were as a first approximation assumed to be on the same scale. The true scale factors were determined during the least squares refinements.

The intensities were corrected for the combined Lorentz and polarization factors, and for absorption (crystal shape approximated to a cylinder; $\mu R=1.1$) and secondary extinction.

The computational work, including corrections, data reductions, scalings, and full matrix least squares refinements of the structure factors, and calculations of interatomic distances and angles, was performed on the electronic computer CDC 3300 using in most cases programmes by Dahl *et al.*¹⁸

The atomic scattering factors used in the calculations of F_c -values were taken from Hanson *et al.*¹⁹ The unobserved reflections were omitted from the least squares refinements, and were not included in the calculations of the reliability factors ($R = \sum |F_o| - |F_c| / \sum |F_o|$).

Anisotropic and isotropic thermal vibrations of the atoms were considered, using the expressions:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \\ \exp[-B \sin^2\theta/\lambda^2]$$

Throughout this paper the calculated standard deviations are appended in brackets behind the corresponding parameter values, only the last digit(s) being given in each case.

CRYSTAL DATA

I_2O_5 , $M = 333.81$.

Needle shaped single crystals with diad axis along the needle axis.

Monoclinic.

$a = 11.036(3)$ Å, $b = 5.063(1)$ Å,

$c = 8.135(2)$ Å, $\beta = 107.18(2)^\circ$.

Unit cell volume: 434.3(2) Å³.

Observed density: 5.08 gcm⁻³ at 25.00°C.

Unit cell content: 4($Z_c = 3.98$) I_2O_5 groups.

Systematic extinctions:

$h0l$ absent when $l = 2n + 1$,

$0k0$ absent when $k = 2n + 1$ (experimental verification somewhat uncertain).

Space group: $P2_1/c$ (the possible space groups Pc and $P2/c$ were excluded as a result of the structure determination).

(The above data are mostly taken from the preceding paper.¹⁷)

STRUCTURE DETERMINATION AND REFINEMENT

The approximate positions of the two crystallographically independent iodine atoms were easily deduced from a three-dimensional Patterson synthesis. A reasonable interpretation of the Patterson map could only be obtained in

terms of space group $P2_1/c$ and the (possible, but unlikely) space groups Pc and $P2/c$ were accordingly eliminated at this stage.

After a preliminary refinement of the atomic coordinates of iodine (giving $R=0.18$), the positions of the oxygen atoms were expected to appear in a three-dimensional Fourier map based on these parameters for the two iodine atoms only. However, the interpretation of the Fourier synthesis was disturbed by the occurrence of a number of false peaks around each iodine at distances corresponding to the expected I—O bond lengths. The false peaks were clearly caused by termination errors in the Fourier series, the same problem being also encountered in the structure determinations of HI_3O_8 ¹⁵ and $\alpha\text{-HIO}_3$.²⁰ After some confusion, five probable peaks of approximately equal heights were picked out for the oxygen atoms, which would give an I_2O_5 molecule with similar geometry (*viz.* comparable bond distances and angles) to that of the I_2O_5 unit in the structure of HI_3O_8 .¹⁵

A subsequent Fourier synthesis with the five oxygen atoms included lead to confidence in the proposed structure and least squares refinement was accordingly started. The first refinement cycles were performed with isotropic temperature factors for all atoms. On the assumption that the observed intensities on the different layers were on the same scale an R -value of 0.14 was obtained, which was improved to $R=0.12$ after the first scaling and subsequent refinement. After a second scaling and correction for secondary extinction, anisotropic temperature factors were introduced for the iodine atoms, giving $R=0.091$. A third scaling and further iterations by the method of least squares gave $R=0.089$, which proved to be the termination of the refinement. The correctness of the proposed structure was at this stage ascertained by a difference Fourier synthesis. The allowance for anisotropic thermal motion of the oxygen atoms gave only insignificant improvement in R (and virtually identical positional parameters) and this possibility is, for example, strongly rejected by application of the Hamilton²¹ test.

The final positional and thermal parameters (with standard deviations) are listed in Table 1 and a comparison of observed and calculated structure factors is presented in Table 2.

Table 1. Final positional and thermal parameters for the crystal structure of I_2O_5 . (All atoms in position 4(e): $\pm(x,y,z; x, \frac{1}{2}-y, \frac{1}{2}+z)$ of space group $P2_1/c$.)

	I(1)	I(2)	O(1)	O(2)	O(3)	O(4)	O(5)
x	0.1260(2)	0.3730(2)	0.015(3)	0.193(2)	0.486(2)	0.309(2)	0.250(2)
y	0.1143(6)	0.6825(5)	0.850(7)	0.041(7)	0.862(6)	0.492(6)	0.968(6)
z	0.2136(3)	0.1597(3)	0.154(3)	0.434(3)	0.333(3)	0.300(3)	0.116(3)
B	—	—	1.7(4)	1.2(4)	1.2(4)	0.9(3)	1.1(3)
β_{11}	0.0011(2)	0.0015(2)	—	—	—	—	—
β_{22}	0.0075(17)	0.0073(17)	—	—	—	—	—
β_{33}	0.0043(3)	0.0048(3)	—	—	—	—	—
$2\beta_{12}$	-0.0009(5)	-0.0012(6)	—	—	—	—	—
$2\beta_{13}$	0.0021(3)	0.0029(3)	—	—	—	—	—
$2\beta_{23}$	0.0005(8)	-0.0012(8)	—	—	—	—	—

Table 2. Observed and calculated structure factors for I₂O₅. The five numbers in each column represent respectively h, k, l, 10|F_o|, and 10F_c. (U=unobserved.)

Table with 5 columns of data (h, k, l, 10|F_o|, 10F_c) and multiple rows of numerical values. Some values are marked with 'U' for unobserved. The table is organized into several vertical columns of data points.

Table 2. Continued.

Table with 13 columns of numerical data. The data is organized in three vertical columns. The first column contains values ranging from 5 3 -3 to 7 1 -11. The second column contains values ranging from 7 1 -10 to 7 1 -11. The third column contains values ranging from 8 2 0 to 10 0 -4. The fourth column contains values ranging from 8 2 0 to 10 0 -4. The fifth column contains values ranging from 10 0 -4 to 10 0 -4. The sixth column contains values ranging from 10 0 -4 to 10 0 -4. The seventh column contains values ranging from 10 0 -4 to 10 0 -4. The eighth column contains values ranging from 10 0 -4 to 10 0 -4. The ninth column contains values ranging from 10 0 -4 to 10 0 -4. The tenth column contains values ranging from 10 0 -4 to 10 0 -4. The eleventh column contains values ranging from 10 0 -4 to 10 0 -4. The twelfth column contains values ranging from 10 0 -4 to 10 0 -4. The thirteenth column contains values ranging from 10 0 -4 to 10 0 -4.

Table 2. Continued.

11	2	3	230	161	12	2	2	117	7	13	3	-7	512	-464	15	0	-6	884	-974	
11	2	4	120	26 U	12	2	3	514	-465	13	3	-6	212	-270	15	0	-4	1306	1409	
11	2	5	124	39 U	12	2	4	249	-320	13	3	-5	1060	1092	15	0	-2	748	-788	
11	2	6	258	-361	12	2	5	120	-113 U	13	3	-4	467	7	15	0	-8	345	1	
11	2	7	133	-14 U	12	2	6	265	252	13	3	-3	894	-673	15	0	-2	150	266 U	
11	3	-11	495	-583	12	3	-11	6	225	-237	13	3	-2	634	-590	15	1	-8	149	106 U
11	3	-10	440	-459	12	3	-10	122	-211 U	13	3	-1	110	167 U	15	1	-7	147	-18 U	
11	3	-9	115	60 U	12	3	-9	700	789	13	3	0	649	682	15	1	-6	144	-139 U	
11	3	-8	609	671	12	3	-8	356	372	13	3	1	364	444	15	1	-5	143	193 U	
11	3	-7	400	400	12	3	-7	782	-748	13	3	2	233	-343	15	1	-4	242	-283 U	
11	3	-6	510	-533	12	3	-6	592	-556	13	3	3	120	-226 U	15	1	-3	263	192 U	
11	3	-5	161	-37 U	12	3	-5	196	68 U	13	3	4	123	-200	15	1	-2	348	440	
11	3	-4	99	77 U	12	3	-4	647	774	14	0	-10	745	-114	15	1	-1	143	21 U	
11	3	-3	448	-449	12	3	-3	443	435	14	0	-8	1259	1331	15	1	0	145	21 U	
11	3	-2	393	346	12	3	-2	967	-562	14	0	-6	783	-814	15	1	1	296	364	
11	3	-1	280	312	12	3	-1	173	-97 U	14	0	-4	135	61 U	15	1	2	684	-614 U	
11	3	0	553	-580	12	3	0	164	-33 U	14	0	-2	271	277	15	2	-6	130	161 U	
11	3	1	350	332	12	3	1	376	-361	14	0	0	139	126 U	15	2	-7	642	-435	
11	3	2	427	437	12	3	2	307	376	14	0	2	290	-467	15	2	-8	251	205	
11	3	3	749	-819	12	3	3	230	355	14	0	4	152	-94 U	15	2	-5	1039	1114	
11	3	4	280	-325	12	3	4	291	-410	14	1	-10	153	-110 U	15	2	-4	349	-366	
11	3	5	531	583	12	3	5	123	120 U	14	1	-8	291	-362	15	2	-3	928	-1021	
11	3	6	340	374	12	3	6	226	284	14	1	-7	264	-356	15	2	-2	124	-4 U	
11	3	7	127	-85 U	13	0	-10	421	-502	14	1	-6	557	585	15	2	0	350	409	
12	0	-10	144	-9 U	13	0	-9	140	11 U	14	1	-5	137	63 U	15	2	1	129	16 U	
12	0	-8	927	580	13	0	-8	133	87 U	14	1	-4	137	-58 U	15	2	2	231	-292	
12	0	-6	679	-694	13	0	-6	448	444	14	1	-3	470	477	15	3	-8	666	-642	
12	0	-4	628	-327	13	0	-2	619	-632	14	1	-2	882	-806	15	3	-7	243	-275	
12	0	-2	1399	1376	13	0	0	132	-91 U	14	1	-1	851	-909	15	3	-6	416	491	
12	0	0	1653	-1636	13	0	2	980	671	14	1	0	1081	1097	15	3	-5	119	73 U	
12	0	2	881	844	13	0	4	1063	-1136	14	1	1	697	740	15	3	-4	110	-4 U	
12	0	4	162	72 U	13	1	-10	519	500	14	1	2	542	-531	15	3	-3	333	370	
12	0	6	283	-266	13	1	-9	145	121 U	14	1	3	250	-267	15	3	-2	237	-315	
12	1	-11	282	243	13	1	-8	161	-93 U	14	2	-10	133	170 U	15	3	-1	338	-420	
12	1	-10	696	-680	13	1	-7	230	296	14	2	-9	755	695	15	3	0	245	483	
12	1	-9	650	-712	13	1	-6	702	-803	14	2	-8	310	-318	15	3	1	123	-220 U	
12	1	-8	1681	1122	13	1	-5	950	-912	14	2	-7	856	-954	15	3	2	250	-290	
12	1	-7	840	846	13	1	-4	1222	1247	14	2	-6	121	-76 U	16	0	-6	593	556	
12	1	-6	606	-618	13	1	-3	898	885	14	2	-5	561	489	16	0	-4	146	-66 U	
12	1	-5	579	-517	13	1	-2	642	-724	14	2	-4	649	647	16	0	-2	770	-913	
12	1	-4	124	-209 U	13	1	-1	262	-308	14	2	-3	110	-49 U	16	0	0	1104	1301	
12	1	-3	123	131 U	13	1	0	133	-87 U	14	2	-2	411	-453	16	1	-6	517	466	
12	1	-2	349	363	13	1	1	136	99 U	14	2	-1	126	21 U	16	1	-5	362	493	
12	1	-1	125	73 U	13	1	2	395	324	14	2	0	121	-141 U	16	1	-4	147	128 U	
12	1	0	127	139 U	13	1	3	144	-47 U	14	2	1	124	-181 U	16	1	-3	147	-154 U	
12	1	1	136	95 U	13	1	4	140	-44 U	14	2	2	253	398	16	1	-2	140	-230 U	
12	1	2	378	-432 U	13	2	-10	130	5 U	14	2	3	130	-5 U	16	1	-1	149	80 U	
12	1	3	130	24 U	13	2	-9	430	401	14	2	4	357	-414	16	1	0	151	-149 U	
12	1	4	143	34 U	13	2	-8	521	440	14	2	5	123	-45 U	16	2	-6	259	-408 U	
12	1	5	418	-419	13	2	-7	120	-11 U	14	3	-8	121	-132 U	16	2	-5	129	-162 U	
12	1	6	432	-480	13	2	-6	430	-450	14	3	-7	473	467	16	2	-4	128	176 U	
12	2	-11	132	-42 U	13	2	-5	115	-81 U	14	3	-6	216	-240	16	2	-3	643	-528	
12	2	-10	295	-299	13	2	-4	114	-58 U	14	3	-5	397	-434	16	2	-2	129	161 U	
12	2	-9	123	168 U	13	2	-3	391	-431	14	3	-4	321	385	16	2	-1	879	1047	
12	2	-8	119	-76 U	13	2	-2	453	488	14	3	-3	329	-247	16	2	0	131	-185 U	
12	2	-7	536	-496	13	2	-1	116	174 U	14	3	-2	227	-260	16	2	1	495	868	
12	2	-6	491	529	13	2	0	232	-365	14	3	-1	811	860	16	3	-5	123	-18 U	
12	2	-5	362	336	13	2	1	531	545	14	3	0	285	370	16	3	-4	590	-624	
12	2	-4	400	-461	13	2	2	122	-229 U	14	3	1	509	-723	16	3	-3	345	-385	
12	2	-3	505	513	13	2	3	669	-950	14	3	2	362	-446	16	3	-2	243	361	
12	2	-2	216	-206	13	2	4	229	258	14	3	3	124	-138 U	16	3	-1	124	144 U	
12	2	-1	1376	-1350	13	3	-10	124	-150 U	15	0	-8	149	-1 U	16	3	0	125	-26 U	
12	2	0	399	400	13	3	-9	410	-369											
12	2	1	1301	1300	13	3	-8	235	282											

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Important interatomic distances and angles calculated from the unit cell dimensions and the positional parameters in Table 1 are given in Table 3. Fig. 1 shows the structural arrangement projected along [010].

The crystal structure of I_2O_5 may to a reasonable approximation be described as a molecular structure, the molecular units being easily recognized in Fig. 1. The I_2O_5 units may be regarded as composed of two IO_3 pyramids which have one oxygen atom in common, which gives a molecular geometry of the type $O_2I-O-IO_2$ with two different kinds of oxygen atoms, *i.e.* the bridge oxygen O(5) and the end oxygens O(1), O(2), O(3), and O(4). The intramolecular distances iodine-oxygen (see Table 3) follow the same distinction, since those which involve the bridge oxygen (1.92–1.95 Å) differ highly significantly from the others (1.77–1.83 Å) according to the significance test of Cruickshank.^{22,23} (The mutual differences within both of the two categories are on the other hand insignificant.) The molecular unit is found

Table 3. Important interatomic distances and angles in the crystal structure of I_2O_5 .
(The standard deviations correspond to those in the positional parameters.)

Interatomic distances (Å)		
Intra- molecular	I(1)—O(1)	1.78(3)
	I(1)—O(2)	1.77(3)
	I(1)—O(5)	1.92(2)
	I(2)—O(3)	1.83(3)
	I(2)—O(4)	1.79(3)
	I(2)—O(5)	1.95(3)
Inter- molecular	I(1)—O(1)	2.45(3)
	I(1)—O(1)	2.94(3)
	I(1)—O(2)	3.12(3)
	I(1)—O(4)	2.72(3)
	I(2)—O(2)	2.54(3)
	I(2)—O(3)	2.23(3)
	I(2)—O(3)	3.26(2)
	I(2)—O(4)	3.25(3)
Interatomic angles (°)		
Intra- molecular	O(1)—I(1)—O(2)	99.5 (1.3)
	O(1)—I(1)—O(5)	96.5 (1.2)
	O(2)—I(1)—O(5)	101.9 (1.0)
	O(3)—I(2)—O(4)	94.8 (1.1)
	O(3)—I(2)—O(5)	93.1 (1.1)
	O(4)—I(2)—O(5)	97.5 (1.0)
	I(1)—O(5)—I(2)	139.2 (1.4)
Inter- molecular	O(1)—I(1)—O(1)	90.6 (1.2)
	O(1)—I(1)—O(2)	77.5 (1.0)
	O(1)—I(1)—O(4)	93.7 (.9)
	O(2)—I(1)—O(4)	80.2 (1.1)
	O(4)—I(1)—O(5)	79.2 (1.0)
	O(1)—I(1)—O(4)	175.5 (1.1)
	O(1)—I(1)—O(5)	172.9 (1.1)
	O(2)—I(2)—O(3)	94.9 (.9)
	O(2)—I(2)—O(4)	81.3 (1.0)
	O(2)—I(2)—O(5)	81.0 (1.0)
	O(3)—I(2)—O(3)	91.7 (1.0)
	O(3)—I(2)—O(4)	89.6 (1.0)
	O(2)—I(2)—O(3)	172.3 (.8)
	O(3)—I(2)—O(5)	171.1 (.9)
	I(1)—O(1)—I(1)	136.2 (1.3)
	I(1)—O(2)—I(2)	146.0 (1.2)
	I(2)—O(3)—I(2)	133.8 (1.3)
I(1)—O(4)—I(2)	128.0 (1.2)	

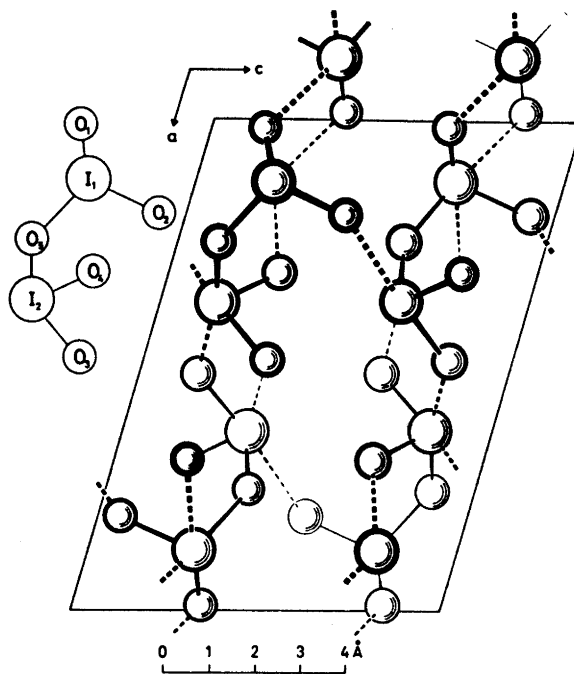


Fig. 1. The crystal structure of I_2O_5 , projected along [010]. The numbering of the crystallographically non-equivalent atoms is shown on the left hand side of the diagram. Intra- and intermolecular bonds are indicated as full and broken lines, respectively.

to possess no mirror plane of symmetry, which is in marked contrast with the configuration C_{2v} proposed by Duval and Lecomte.¹⁶

It is of considerable interest to compare intramolecular distances and angles in the structure of I_2O_5 with the corresponding quantities in the structure of HI_3O_8 . (The numbering of the non-equivalent atoms is chosen in order to facilitate direct comparison with the paper of Feikema and Vos.¹⁵) The two categories of iodine-oxygen distances (*vide supra*) have virtually identical average values (1.96 and 1.79 Å, respectively, in HI_3O_8) in the two structures, the individual values being slightly more scattered in I_2O_5 than in HI_3O_8 . The intramolecular angle $I(1)-O(5)-I(2)$ is considerably larger in I_2O_5 than in HI_3O_8 (139.2 *versus* 125.8°; the difference must clearly be classified as highly significant). The intramolecular angles $O-I-O$ show some scatter in both structures (93.1–101.9° with average 97.2° in I_2O_5 and 88.1–98.1° with average 94.4° in HI_3O_8). In a somewhat superficial consideration of the structures there appears to be no particular justification for separate discussions of the $O-I-O$ angles around $I(1)$ and $I(2)$ or for making a distinction between those which involve $O(5)$ and the others. The most notable difference between the I_2O_5 unit in the two structures concerns the relative orientation of the IO_3 pyramids (in other words the end oxygens). In the

HI_3O_8 structure O(1), O(2), O(3), and O(4) all lie on the same side of a plane through I(1), O(5), and I(2), whereas in the structure of I_2O_5 O(1) and O(4) are located on one side of the corresponding plane and O(2) and O(3) on the other.

Each molecular unit in the I_2O_5 structure is linked to adjacent molecular units *via* short intermolecular I–O distances (*cf.* Table 3). These close contacts, which occur only at the end oxygens, give the structure a character of a firm three-dimensional network. Each end oxygen forms two such contacts, one being always markedly shorter than the other (*cf.* Table 3, where their mutual differences are seen to be ≥ 0.49 Å). Although both these categories of intermolecular I–O distances (2.23–2.72 *versus* 2.94–3.26 Å) are shorter than the van der Waals distance (~ 3.5 Å), there appears to be a fundamental distinction between them since the former category (*i.e.* distances indicated by broken lines in Fig. 1) almost certainly represents bonding interaction whereas the latter includes distances which essentially may be caused by the geometry of the crystal structure. Hence, counting only I–O distances ≤ 2.72 Å, the immediate coordination of (five) oxygen atoms around each iodine atom is that of a distorted octahedron with one corner vacant. (If the second category of intermolecular I–O distances (*vide supra*) also were included, the coordination numbers of I(1) and I(2) would increase to 7 and their coordination polyhedra would become distorted variants of the type named capped (or face-centred) octahedron.) Pseudo octahedral coordinations for iodine are also found in the crystal structures of the oxo-acids $\alpha\text{-HIO}_3$,^{20,24} HI_3O_8 ,¹⁵ and H_5IO_6 ,^{25,26} and in several iodates, *e.g.* LiIO_3 ,²⁷ NaIO_3 ,²⁸ $\text{Ce}(\text{IO}_3)_4$,²⁹ and $\text{Ce}(\text{IO}_3)_4 \cdot \text{H}_2\text{O}$.^{30,31} The most likely coordination number for all oxygen atoms in the I_2O_5 structure is two, the angles of these I–O–I configurations being found in the range 128.0–146.0° (*cf.* Fig. 1 and Table 3).

The intra- and intermolecular I–I (3.62 and ≥ 3.74 Å) and O–O (≥ 2.67 and ≥ 2.69 Å) distances in I_2O_5 appear to be consequences of the crystal structure and are accordingly regarded as essentially non-bonding, even when they are shorter than the corresponding van der Waals distances of 4.3 and 2.8 Å, respectively.

The fact that iodine is a large and easily polarizable atom, which, judging from the free atom, has a number of empty orbitals accessible within reasonable energy, renders a discussion of its bonding properties difficult and possible conclusions are likely to be of a speculative character. The oxygen atom is, on the other hand, considerably smaller in size and it has only a few orbitals available for bonding.

The most fruitful starting-point for some elementary bonding considerations of the I_2O_5 structure appears to be O(5). If two pure *p*-orbitals on O(5) were involved in its bondings to I(1) and I(2), the bond angle I(1)–O(5)–I(2) should have been 90° which consequently would have led to an intramolecular I(1)–I(2) separation of about 2.73 Å retaining the observed I–O(5) distances. However, such an I(1)–I(2) separation would have been far too short in view of the large atomic size of iodine (*vide infra*). This steric factor would indeed enforce an appreciable opening out of the I(1)–O(5)–I(2) angle and the repulsion between the charges which are likely to be found on the iodine atoms may contribute to further enlargement of the angle. Hence, the observed

bond angle of 139.2° may represent a reasonable compromise. If, on the other hand, O(5) had been subject to pure sp hybridization the bond angle should ideally have been 180° . The assumption of incomplete or non-equivalent hybridization may be sufficient to account for the observed deviation from the latter ideal value.

In order to decide between the extreme, idealized versions outlined above, attention may now be turned to the I–O(5) bond distances. The observed values (Table 3) have a weighted average of $1.93(2)$ Å which is significantly shorter than the I–O single-bond length derived from the Schomaker-Steven-son^{32,33} equation:

$$r_I + r_O - c|x_I - x_O| = 1.33 + 0.74 - 0.08|2.5 - 3.5| = 1.99 \text{ \AA}$$

A reasonable interpretation of this shortening is that it reflects a degree of double-bond character in I–O(5).

In terms of the valence-bond language, the degree of double-bonding may, for example, be judged by Paulings³³ bond order equation: $D(n) = D(1) - 0.71 \log n$. Substitution of the values $1.93(2)$ and 1.99 Å for $D(n)$ and $D(1)$, respectively, gives a bond order $n = 1.21(7)$. Assuming that $n = n_\sigma + n_\pi$ with $n_\sigma = 1$, *i.e.* specifying the bonding system as a normal single σ -bond with an additional degree of π -bonding, a π -bond order $n_\pi = 0.21(7)$ is obtained. Virtually the same value for the π -bond order (still valence-bond language) may be derived somewhat differently according to the procedure described by Cruickshank.³⁴ Following Cruickshank a linear bond length *versus* π -bond order relationship is assumed, the line being defined by 1.99 Å for a bond of π -order zero and 1.82 Å (average I–O in IO_3^- according to Wells⁶) for order $\frac{2}{3}$. On this basis the observed I–O(5) distance ($1.93(2)$ Å) corresponds to a π -bond order of $0.23(7)$.

The existence of π -character in the I–O(5) bonds implies a preference for that of the above alternatives which describes the σ -bonds from O(5) in terms of (incomplete) sp -hybridization. The π -system must accordingly be of the type $p_\pi-d_\pi$ with back-bonding from two filled p -orbitals on O(5) to an empty d -orbital on each of I(1) and I(2). The most suitable geometrical arrangement for this type of π -bonding would have been obtained at a I(1)–O(5)–I(2) bond angle of 180° (*i.e.* pure sp -hybridization) where the two p -orbitals on O(5) would be properly oriented for maximum overlap of the d -orbitals on I(1) and I(2). Hence, the large deviation from 180° in the I(1)–O(5)–I(2) bond angle leads to a consequent reduction in the overlap and the π -bond order become therefore appreciably smaller than one in this case. The fact that the I_2O_5 group in the HI_3O_8 structure (*vide supra* and Ref. 15) is found to have a smaller I(1)–O(5)–I(2) bond angle and a slightly longer average I–O(5) bond distance than in the I_2O_5 structure is consistent with this interpretation.

The bond distances from iodine to the end oxygens have an average of $1.79(2)$ Å, which is considerably shorter than the I–O single bond length (1.99 Å). The corresponding values for the π -bond order according to the procedures of Pauling and Cruickshank (*vide supra*) are, respectively, $0.91(12)$ and $0.77(7)$. The difference between these figures is unimportant in this connection, whereas it is of considerable interest to note that the π -bond order

is substantially larger for the I—O bonds which involve the end oxygens than for those involving the bridge oxygen. This is almost certainly associated with the fact that within the molecular I_2O_5 unit the end oxygens have a larger degree of freedom than the bridge oxygen to obtain a favourable orientation relative to the iodine atoms with respect to $p_\pi-d_\pi$ back-bonding (*vide supra*). The same considerations apply equally well to the I_2O_5 group in the HI_3O_8 structure.

The fact that the intramolecular bond angles O—I—O are approximately 90° (*cf.* Table 3) suggests that three pure p -orbitals on each iodine atom could be engaged in its three regular σ -bonds to oxygen (*e.g.* specified as one normal σ -bond to the bridge oxygen and two dative σ -bonds to the end oxygens per iodine atom). On each iodine there are furthermore three empty $5d$ -orbitals (d_{xy} , d_{yz} , and d_{zx}) available with suitable symmetry for π -bonding, *i.e.* consistent with the requirements imposed by the above considerations for the oxygen atoms. The two remaining d -orbitals ($d_{x^2-y^2}$ and d_{z^2}) on each iodine are of appropriate symmetry for further σ -bonding in two mutually perpendicular directions which are also approximately perpendicular to two of the other σ -bonds. This offer matches the findings in the I_2O_5 structure in that two short intermolecular I—O distances per iodine atom have to be accounted for (*cf.* Fig. 1 and *vide supra*.) The geometrical arrangement of these additional intermolecular I—O bonds relative to the intramolecular bonds leads to confidence in the suggestion that each end oxygen extends a dative σ -bond to an iodine in an adjacent I_2O_5 molecule. On this basis it is also likely that the end oxygens are subject to a degree of sp -hybridization, which is furthermore supported by the fact that the intra- and intermolecular I—O—I bond angles (see Table 3) are of approximately the same size. The fact that the intermolecular I—O bond distances exceed the regular single bond length (*vide supra*) is easily accounted for since *inter alia* different orbitals on iodine are assumed to be involved in the intra- and intermolecular bonding.

The large mutual variation between the intermolecular I—O bond lengths is inherently more difficult to explain, although this observation tentatively may be attributed to differences in the geometrical arrangement of the various bonds and/or to the polarization which is likely to occur within the electronic charge cloud on the iodine atoms.

It must be emphasized that the above bonding considerations have a distinct character of oversimplification. In particular, it is worth mentioning that hybridization of the orbitals on iodine has been totally neglected as well as the possible participation of f -orbitals in the bonding. Another and probably more important factor which has been neglected is the uneven charge distribution on iodine and oxygen due to their difference in electronegativity. The latter factor is likely to cause excess positive charge on iodine and negative on oxygen and this ionic character (partial charge separation within the molecule) may in principle provide an alternative explanation of the intermolecular bonds.

The crystal structure of I_2O_5 is clearly not of the simple molecular type. The presence of fairly strong intermolecular forces in the lattice is for example reflected in the relatively high sublimation temperature of the compound.

Due to this fact, the I_2O_5 structure may furthermore be regarded as a hitherto missing link between, say, the distinctly macromolecular structure(s) of TeO_2 and the isolated molecular type of lattice of XeO_3 .

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