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Refinement of the Crystal Structure of Iodine at 110°K

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The crystal structure of iodine at 110°K has been refined. The I–I bond, 2·715 Å, e.s.d. 0·006 Å, appears to be significantly longer than the bond, 2·662 Å, in gaseous iodine molecules.

Description of the structure

The crystal structure of iodine at room temperature was determined in an early X-ray study by Harris, Mack & Blake (1928) and refined later by Kitaigorodskii, Khotsyanova & Struchkov (1953, 1955). The element crystallizes in the space group *Cmca* with four molecules at special positions with symmetry 2/*m* in the unit cell [Fig. 1(*a*)]. In contradistinction to Kitaigorodskii's work (I–I = 2·68 Å), the present refinement of the structure based on low-temperature data (110°K) shows that the I–I bond in the solid state, 2·715 Å, e.s.d. 0·006 Å, is significantly longer than that in gaseous molecules (2·662 Å; Karle, 1955). In the solid state an elongation of the bond may be expected on theoretical grounds from the short distances occurring between the iodine molecules in the same plane. Fig. 1(*b*) shows that owing to the short distances of 3·50 Å (van der Waals distance 4·30 Å) a two-dimensional network is formed of nearly linear chains I···I–I···I, each iodine atom being involved in two nearly perpendicular chains. The angles of approximately 90° suggest that (in first approximation) the bonds in intersecting chains are formed by orthogonal iodine 5*p* orbitals. For each of the chains a description of the bonding as 4-centre, 6-electron bonding (Hach & Rundle, 1951; Pimentel, 1951) may be assumed, resulting in a bond order smaller than 1 for the I–I bond (Havinga & Wiebenga, 1959) in agreement with the elongation observed during the present work. The remaining short intermolecular distances of 3·97 Å are expected to have relatively little influence on the I–I bond length.

By reducing the temperature to 110°K the Fourier map in the plane of the molecule could be improved considerably. In Kitaigorodskii's map the molecules have a cylindrical shape without marked maxima for the separate atoms (Kitaigorodskii *et al.*, 1955). The present electron density distribution (Fig. 2), however, clearly shows the peaks belonging to the individual atoms.

Experimental

Cell dimensions and intensities were measured at 110°K with a (non-automatic) single-crystal diffractometer (Table 1). The crystals were mounted in a capillary, which also contained some iodine powder. For the intensity measurements a crystal roughly measuring 0·25 × 0·18 × 0·11 mm was used. To make it possible to calculate the absorption corrections ($\mu = 191{\cdot}3$ cm^{-1}) with a program according to the Busing & Levy scheme (Busing & Levy, 1957) the shape and dimensions of the crystal were determined as accurately as possible. Errors were made, however, as the bounding planes were not very well defined. Anisotropic least-squares refinement was done on a TR4 computer using the program written by Palm and Peterse according to Cruickshank's scheme (Cruickshank, 1961). As we were not able to estimate the errors in the absorption corrections, the weighting scheme $w = [\sigma(F)]^{-2}$ was used for the observed reflexions, $\sigma(F)$ being the standard deviation in F as estimated on statistical grounds. The scattering factor represented by an analytical function according to Moore (1963), was corrected for the anomalous components, $\Delta F' = -0{\cdot}5$ and $\Delta f'' = 2{\cdot}4$. The index R decreased to 0·068. The observed and calcu-

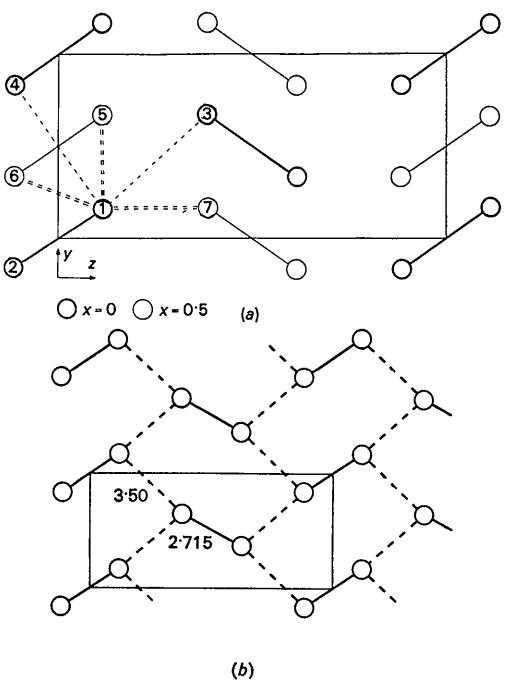

Fig. 1. (*a*) The structure of solid iodine in (100) projection. (*b*) The two-dimensional network of iodine molecules in the (100) plane.

Table 1. *Observed data for solid iodine at* 110°K

Observed data		Details of method used
$a = 7{\cdot}136$ Å	e.s.d. 0·010 Å	13 reflexions with $6° < \theta < 30°$
$b = 4{\cdot}686$	0·007	λ(Mo $K\alpha$) = 0·7107 Å
$c = 9{\cdot}784$	0·015	
208 reflexions *hkl* ($h = 0, 1, 2, 3$)		Mo radiation with balanced Zr and Y filters, $\theta - 2\theta$ scan

Table 2. *Observed and calculated structure factors*

In order to obtain F on the absolute scale the values in the Table must be divided by 10.

H	K	L	FO	FC	AC	BC	H	K	L	FO	FC	AC	BC	H	K	L	FO	FC	AC	BC
0	2	0	974	1133	−1132	−65	1	3	3	1332	1328	1324	96	2	2	9	651	597	595	52
0	4	0	1300	1406	−1401	−110	1	5	3	137	129	−128	−12	2	4	9	356	348	−347	−35
0	6	0	1061	974	970	97	1	7	3	416	391	−389	−45	2	0	10	893	896	893	79
0	10	0	389	239	−236	−38	1	1	4	524	477	476	29	2	2	10	217	264	−263	−24
0	2	1	1837	1950	1947	113	1	3	4	147	118	117	9	2	4	10	484	463	−460	−48
0	4	1	846	859	−856	−68	1	5	4	227	260	−259	−24	2	6	10	322	306	304	38
0	6	1	345	323	−322	−32	1	3	5	1763	1737	1732	134	2	2	11	1514	1479	1472	143
0	0	2	390	373	372	18	1	5	5	174	139	−139	−13	2	4	11	781	775	−771	−84
0	2	2	110	94	−93	−6	1	7	5	583	548	−544	−65	2	6	11	319	333	−330	−43
0	2	3	2341	2154	2150	134	1	1	6	2205	2086	−2061	−164	2	0	12	1367	1422	−1415	−140
0	4	3	928	976	−973	−79	1	3	6	507	432	−430	−35	2	2	12	494	479	476	49
0	6	3	392	389	−387	−39	1	5	6	1197	1217	1211	118	2	4	12	692	686	682	78
0	8	3	497	427	423	52	1	7	6	386	334	−332	−40	2	6	12	568	542	−537	−72
0	0	4	2999	3097	−3091	−186	1	1	7	664	591	589	44	2	2	13	204	206	−205	−22
0	2	4	1158	965	963	63	1	3	7	933	812	−809	−68	2	0	14	861	899	−893	−99
0	4	4	1239	1289	1284	107	1	5	7	159	107	107	11	2	2	14	237	270	268	31
0	6	4	902	914	−909	−94	1	7	7	287	247	245	31	2	4	14	481	479	475	60
0	2	5	1404	1230	−1227	−85	1	1	8	728	689	−687	−54	2	2	15	1117	1133	−1125	−136
0	4	5	624	620	618	53	1	5	8	409	440	437	45	2	4	15	649	615	609	81
0	6	5	199	215	214	23	1	1	9	1156	1127	1123	94	2	0	16	873	892	885	110
0	8	5	329	269	−266	−35	1	3	9	1611	1542	−1536	−141	2	2	16	212	314	−311	−40
0	0	6	828	791	−790	−53	1	7	9	568	523	518	68	3	1	1	1258	1225	1222	73
0	2	6	279	220	220	16	1	1	10	1473	1452	1447	127	3	3	1	1353	1491	−1487	−111
0	4	6	373	368	367	32	1	3	10	356	307	305	29	3	5	1	137	127	126	12
0	6	6	319	234	−233	−25	1	5	10	951	932	−926	−104	3	7	1	491	457	454	53
0	2	7	2062	1885	−1879	−146	1	7	10	389	274	272	37	3	1	2	2356	2334	2329	144
0	4	7	992	944	940	86	1	3	11	410	384	382	39	3	3	2	474	466	465	35
0	6	7	367	394	392	44	1	1	12	729	756	752	74	3	5	2	1221	1263	−1258	−118
0	0	8	2262	2210	2204	169	1	5	12	482	512	−509	−62	3	7	2	166	337	−335	−39
0	2	8	791	713	−711	−58	1	1	13	818	888	−883	−92	3	1	3	964	917	−915	−59
0	4	8	1062	1023	−1019	−96	1	3	13	1227	1246	1238	139	3	3	3	1147	1164	1161	90
0	6	8	759	759	754	86	1	1	14	934	957	−951	−105	3	5	3	131	116	−116	−11
0	2	9	693	630	628	54	1	3	14	160	191	−190	−22	3	7	3	395	356	−354	−42
0	4	9	400	366	−364	−36	1	5	14	632	641	636	85	3	1	4	411	399	398	27
0	6	9	240	160	159	23	1	1	16	657	705	−699	−87	3	5	4	212	235	−234	−23
0	0	10	926	946	942	82	1	1	17	594	650	644	84	3	1	5	1247	1179	−1177	−83
0	2	10	274	278	−277	−25	2	0	0	2948	3626	3621	186	3	3	5	1637	1542	1537	126
0	4	10	550	486	−484	−50	2	2	0	882	1024	−1022	−63	3	5	5	241	126	−125	−12
0	6	10	335	321	318	39	2	4	0	1173	1325	−1320	−107	3	7	5	541	496	−495	−61
0	2	11	1565	1556	1549	128	2	6	0	956	927	922	94	3	1	6	1854	1812	−1807	−135
0	4	11	867	814	−809	−87	2	2	1	1562	1764	1761	109	3	3	6	445	386	−384	−33
0	6	11	380	349	−346	−44	2	4	1	763	810	−807	−65	3	5	6	1088	1101	1095	111
0	0	12	1479	1495	−1488	−144	2	6	1	302	308	−306	−31	3	7	6	359	304	−302	−38
0	2	12	497	503	501	51	2	8	1	434	350	347	45	3	1	7	552	521	519	41
0	4	12	795	720	716	81	2	0	2	311	328	328	18	3	3	7	800	728	−726	−64
0	6	12	564	567	−562	−74	2	2	2	187	85	−85	−5	3	5	7	106	97	97	10
0	2	13	194	216	−215	−23	2	4	2	573	219	−132	−11	3	7	7	219	229	224	29
0	0	14	874	943	−938	−102	2	2	3	2124	1971	1967	129	3	1	8	624	613	−611	−51
0	2	14	227	283	281	32	2	4	3	867	922	−919	−76	3	3	8	170	170	−169	−15
0	4	14	502	501	497	62	2	6	3	370	371	−369	−38	3	5	8	402	399	396	43
0	6	14	348	346	−343	−49	2	8	3	529	408	404	53	3	1	9	1022	1010	1006	108
0	2	15	1193	1188	−1179	−141	2	0	4	2822	2971	−2965	−180	3	3	9	1479	1392	−1385	−132
0	4	15	657	643	638	84	2	2	4	990	890	888	61	3	5	9	179	116	115	13
0	6	15	284	279	276	41	2	4	4	1164	1219	1215	103	3	7	9	527	478	473	64
0	0	16	924	935	928	114	2	6	4	874	870	−865	−81	3	1	10	1285	1307	1302	119
0	2	16	255	328	−326	−41	2	2	5	1276	1144	−1141	−82	3	3	10	301	277	276	28
0	4	16	440	455	−450	−62	2	4	5	568	588	585	51	3	5	10	866	847	−841	−97
0	6	16	417	390	385	60	2	6	5	172	205	204	22	3	1	11	132	229	−228	−22
0	0	18	812	829	821	113	2	8	5	349	257	−255	−34	3	3	11	340	348	346	36
0	4	18	465	455	−449	−68	2	0	6	759	732	−730	−51	3	1	12	656	684	681	69
0	2	19	819	855	846	126	2	2	6	266	206	206	16	3	3	12	163	191	190	21
0	0	20	547	538	−532	−81	2	4	6	338	349	348	31	3	1	13	782	805	−800	−86
1	1	1	1727	1537	1535	78	2	6	6	226	223	−222	−24	3	3	13	1167	1132	1125	130
1	3	1	1561	1717	−1713	−119	2	2	7	1910	1774	−1769	−181	3	1	14	832	869	−864	−98
1	1	1	583	503	500	57	2	4	7	910	896	892	83	3	3	14	178	174	−173	−21
1	1	2	2941	2896	2892	153	2	6	7	371	376	374	42	3	1	16	612	643	−638	−81
1	3	2	541	535	534	38	2	0	8	1729	2079	2073	164	3	3	16	177	179	−178	−24
1	5	2	1310	1401	−1396	−126	2	2	8	686	614	−612	−56	3	1	17	560	594	588	79
1	1	2	379	371	368	52	2	4	8	976	972	−968	−93							
1	1	3	1250	1119	−1118	−63	2	6	8	706	723	718	83							

Table 3. *Final parameters for* I(1) *and atomic distances*

Estimated standard deviations are given in brackets. The distances are not corrected for the effects of thermal motion.

x	0	I(1)–I(2)	2·715 (6) Å
y	0·15434 (36)		
z	0·11741 (13)		
		I(1)···I(3)	3·496 (6)
U_{11}	0·0218 (33) Å²	I(1)···I(4)	3·972 (7)
U_{22}	0·0177 (5)	I(1)···I(5)	4·269 (6)
U_{33}	0·0038 (3)	I(1)···I(6)	4·337 (7)
$2U_{23}$	0·0021 (15)	I(1)···I(7)	4·412 (7)

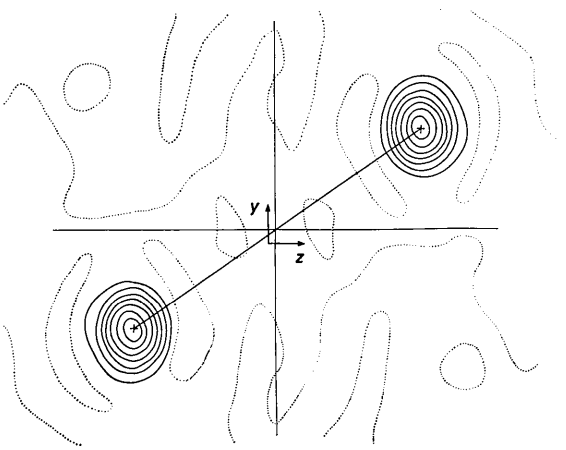

Fig. 2. Electron density map of the iodine molecule in the $x = 0$ plane; contours are drawn at 25 e.Å^{-3}, the zero line being dashed.

lated structure factors are listed in Table 2; strictly speaking the Fourier map of Fig. 2 was calculated with the real parts of the observed structure factors. The final parameters and atomic distances are given in Table 3. In calculating the standard deviations for the atomic distances the positional standard deviations, as calculated from the least-squares residuals and the errors estimated for the cell constants, were taken into account.

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