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Crystal Structure of the 1 : 3 Addition Compound Iodoform-Sulphur ($CHI_3 \cdot 3S_8$)

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The crystal structure of the 1:3 compound iodoform-sulphur, $CHI_3 \cdot 3S_8$, has been determined by X-ray methods. The structure is trigonal rhombohedral with the (hexagonal) lattice parameters: $a = 24.32$ Å; $c = 4.44$ Å. The space group is $R3m$. Charge transfer bonds connect every iodine atom with a sulphur atom belonging to a S_8-ring. The I-S bond distance (3.50 Å) is about 0.50 Å shorter than the van der Waals radius sum of iodine and sulphur and the C-I-S angle is found equal to 177.7°.

Results obtained in this laboratory regarding the structure of iodoform-dithiane [1] clearly prove the existence of charge transfer bonds between iodoform iodine atoms and dithiane sulphur atoms. The apparently isomorphous iodine-sulphur crystals $RI_3 \cdot 3S_8$ (R being CH, P, As or Sb) [2] might be expected to exhibit analogous I—S bonds. In order to check the correctness of this assumption the crystal structures of $CHI_3 \cdot 3S_8$ resp. $SbI_3 \cdot 3S_8$ have been or are being studied in this laboratory.

The present report is dealing with the investigation of the iodoform-sulphur compound. Preliminary results of the structure determination have been given in a survey article by Hassel [3].

EXPERIMENTAL

Needle-shaped crystals of the iodoform-sulphur compound were obtained by evaporation of a solution of sulphur and iodoform in carbon disulphide. The melting point of the compound was found equal to 95°C. The cross section of the crystals used in the X-ray work was about 0.005 mm².

Integrated Weissenberg photographs were taken with rotation about the trigonal axis which is the needle axis. Cu$K\alpha$-radiation was employed and of the 82 $hk0$ reflections attainable, 65 were observed.

Precession diagrams were taken of the rhombohedral $0kl$ zone. Mo$K\alpha$-radiation was employed and of the 95 reflections attainable, 87 were observed. The intensities of the reflections were measured photometrically. No corrections for absorption or secondary extinction were applied. The computation were carried out using a Ferranti Mercury computer. In the calculations the analytical approximations to the atomic scattering factors computed by Forsyth and Wells [4] were employed.

CRYSTAL DATA

The crystals are trigonal rhombohedral with the hexagonal parameters:

$$a = 24.32 \text{ Å}; \qquad c = 4.44 \text{ Å}$$

Both figures are believed to be accurate to within 0.5 % and are in good agreement with those published by West.[5] The density measured using the flotation method was 2.45 g/cm³ leading to the value $Z = 1$ for the number of molecules in the rhombohedral unit cell. The density calculated from the lattice parameters is 2.55 g/cm³. The space group is $R3m$.

STRUCTURE DETERMINATION

The number of formula units in the primitive rhombohedral unit cell is *one* and the sulphur (S_8) molecules are therefore situated in mirror planes, the iodoform molecules on trigonal axes with the iodine atom in a mirror plane. These requirements and the detailed information already available regarding the structure of the iodoform and the sulphur molecules simplified the determination of the approximate hexagonal x and y coordinates by trial and error methods. Using the values of the phase angles obtained from these calculations combined with the observed data, a Fourier map was computed for the projection along the trigonal axis. The coordinates obtained from this Fourier synthesis served as starting values for least squares refinements. The parameters finally arrived at are listed in Table 1. The phase angles of the reflec-

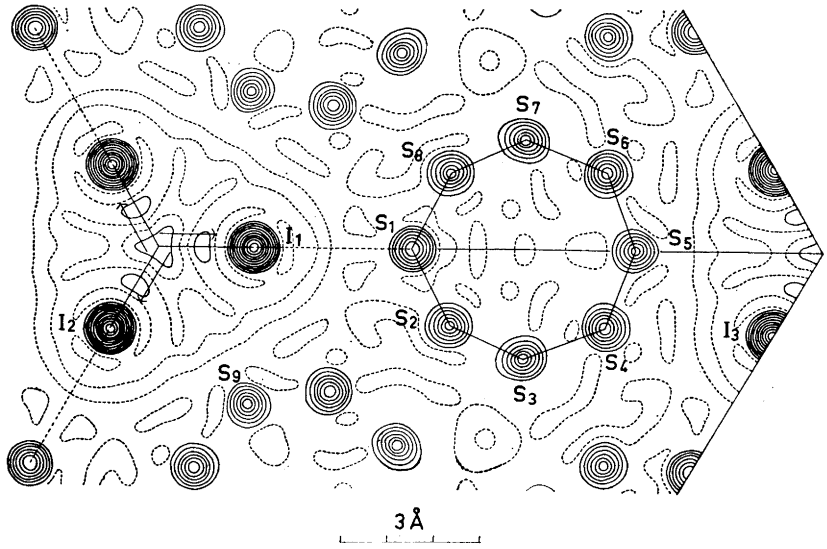

Fig. 1. Electron density projection along the trigonal axis. Contour intervals: 5 e · Å^{-2} for sulphur and carbon atoms, 10 e · Å^{-2} for iodine atoms. The axes indicated are the projections of the rhombohedral axes.

Table 1. Positional and temperature parameters. B_1 and B_2 are temperature factors in the [001] and [211] projection, respectively.

Atom	x	y	z	B_1	B_2
I_1	−0.0487	0.0487	0.0000	2.0	3.3
C	0.0000	0.0000	0.0963	2.0	2.3
S_1	−0.1291	0.1291	−0.1973	1.2	2.3
S_2	−0.0810	0.2158	0.0394	1.5	2.3
S_3	−0.0889	0.2810	−0.2191	1.3	2.3
S_4	−0.1587	0.2928	−0.0410	1.5	2.3
S_5	−0.2407	0.2407	−0.2572	2.4	2.3

Table 2. Interatomic distance and valence angles.

	Distance	Standard deviation		Angle
I_1-I_2	3.56 Å	0.007 Å	I_1-C-I_2	115.9°
I_1-S_1	3.50	0.014	$C-I_1-S_1$	177.7
S_1-S_2	2.11	0.023	$I_1-S_1-S_2$	104.4
S_2-S_3	2.04	0.026	$S_1-S_2-S_3$	106.0
S_3-S_4	2.02	0.022	$S_2-S_3-S_4$	107.6
S_4-S_5	2.00	0.022	$S_3-S_4-S_5$	111.4
$C-I_1$	2.10		$S_4-S_5-S_6$	109.8
I_1-S_9	3.84		$S_8-S_1-S_2$	102.0
I_3-S_4	3.88			

tions and the observed and calculated structure factors have been listed in Table 3. The R factor including only observed reflections is 0.050. A Fourier map based on the final phase angles is reproduced in Fig. 1. In this projection the $C-I-S_1$ arrangement is of course linear as required by the symmetry of the space group.

In order to determine the $C-I-S_1$ angle and the atomic distances, a projection along another direction had to be determined. The hexagonal [211] direction (rhombohedral [100] direction) was chosen for this purpose.

The z coordinates of the iodine atoms could arbitrarily be chosen equal to zero. The $I-C-I$ and $C-I-S_1$ angles were first assumed to be 113° and 180°, respectively. With these assumptions four alternative models could be postulated for the position of the sulphur and iodoform molecules relative to the crystallographic axes. Subsequent trial and error computations led to

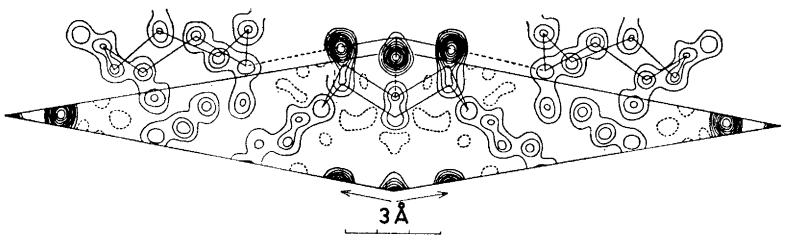

Fig. 2. Electron density projection along a rhombohedral axis. Contour intervals: 10 e · Å^{-2}. The axes indicated are the projections of the rhombohedral axes.

Table 3. Observed and calculated structure factors and phase angles.

[001] projection

h	k	l	F_o	F_c	α	h	k	l	F_o	F_c	α
0	3	0	101	108	5.0	7	10	0	114	114	137.1
0	6	0	408	435	139.4	7	13	0	184	180	110.8
0	9	0	174	168	169.3	7	16	0	<65	57	195.8
0	12	0	319	327	228.8	7	19	0	89	81	244.3
0	15	0	196	195	168.7	7	22	0	115	123	256.7
0	18	0	<65	49	23.6	8	8	0	418	426	0·0
0	21	0	161	162	337.2	8	11	0	79	78	118.4
0	24	0	169	168	12.1	8	14	0	196	201	112.2
1	1	0	141	165	0.0	8	17	0	<68	17	110.7
1	4	0	106	81	90.0	8	20	0	217	228	241.3
1	7	0	307	315	123.1	9	9	0	66	66	180.0
1	10	0	128	102	83.4	9	12	0	83	78	135.0
1	13	0	333	330	257.7	9	15	0	82	81	234.0
1	16	0	<62	71	292.1	9	18	0	<60	20	251.4
1	19	0	159	165	20.8	10	10	0	<63	44	180.0
1	22	0	123	120	1.4	10	13	0	163	156	95.3
1	25	0	116	129	157.4	10	16	0	<65	31	46.6
2	2	0	96	99	0.0	10	19	0	<53	25	96.0
2	5	0	420	438	89.2	11	11	0	<65	34	0.0
2	8	0	193	180	100.6	11	14	0	100	108	13.6
2	11	0	140	144	253.9	11	17	0	79	78	296.6
2	14	0	212	243	245.2	12	12	0	<85	19	180.0
2	17	0	74	66	326.3	12	15	0	125	123	325.6
2	20	0	88	78	23.9	12	18	0	<46	43	61.6
2	23	0	65	48	174.8	13	13	0	136	150	0.0
3	3	0	103	90	180.0	13	16	0	63	66	79.2
3	6	0	181	168	107.3	14	14	0	116	111	0.0
3	9	0	189	180	320.1	15	15	0	156	171	0.0
3	12	0	84	66	123.7						
3	15	0	<62	44	218.3						
3	18	0	128	123	334.0						
3	21	0	<65	11	165.2						
3	24	0	<52	39	131.1						
4	4	0	175	159	180.0						
4	7	0	122	123	-324.8						
4	10	0	80	81	21.8						
4	13	0	103	93	45.0						
4	16	0	141	138	101.0						
4	19	0	123	120	279.7						
4	22	0	83	78	239.7						
5	5	0	188	192	0.0						
5	8	0	67	81	10.3						
5	11	0	105	105	208.7						
5	14	0	172	168	130.1						
5	17	0	132	135	110.8						
5	20	0	<65	37	266.6						
5	23	0	<48	31	286.1						
6	6	0	331	339	0.0						
6	9	0	286	282	358.2						
6	12	0	70	72	102.2						
6	15	0	193	195	119.3						
6	18	0	<62	33	225.6						
6	21	0	108	98	223.9						
7	7	0	323	324	0.0						

[211] projection

h	k	l	F_o	F_c	α
−1	2	0	154	148	0.0
−2	4	0	105	96	0.0
−3	6	0	112	116	180.0
−4	8	0	188	174	180.0
−5	10	0	191	191	0.0
−6	12	0	313	297	0.0
−7	14	0	321	306	0.0
−8	16	0	386	396	0.0
−9	18	0	55	59	180.0
−10	20	0	45	38	180.0
−11	22	0	<20	19	0.0
−12	24	0	<21	22	180.0
−13	26	0	126	122	0.0
−14	28	0	95	83	0.0
−15	30	0	128	119	0.0
−16	32	0	42	45	0.0
−17	34	0	38	30	180.0
−1	1	1	259	302	336.6
−2	3	1	264	273	327.4
−3	5	1	68	62	324.9
−4	7	1	333	330	156.2
−5	9	1	173	159	219.6
−6	11	1	131	123	333.4

h	k	l	F_o	F_c	a	h	k	l	F_o	F_c	a
−7	13	1	266	260	343.5	−10	17	3	45	42	306.9
−8	15	1	227	209	345.3	−11	19	3	27	26	250.6
−9	17	1	104	87	339.4	−12	21	3	98	105	260.3
−10	19	1	62	54	235.2	−13	23	3	27	26	333.4
−11	21	1	107	99	195.6	−14	25	3	22	21	230.7
−12	23	1	105	98	144.9	−15	27	3	66	47	28.9
−13	25	1	70	62	291.6	−16	29	3	62	65	0.0
−14	27	1	145	137	357.0	−2	0	4	65	68	88.7
−15	29	1	39	29	348.7	−3	2	4	133	143	351.5
−16	31	1	73	65	307.3	−4	4	4	119	89	257.5
−17	33	1	49	47	190.6	−5	6	4	94	99	221.7
−1	0	2	304	338	1.1	−6	8	4	60	71	298.5
−2	2	2	147	176	357.6	−7	10	4	69	75	316.8
−3	4	2	94	86	14.9	−8	12	4	55	62	35.0
−4	6	2	191	185	212.4	−9	14	4	85	98	343.5
−5	8	2	81	71	331.0	−10	16	4	21	23	17.1
−6	10	2	101	90	53.5	−11	18	4	95	90	315.0
−7	12	2	131	132	16.8	−12	20	4	73	83	192.0
−8	14	2	162	168	337.5	−13	22	4	42	42	214.8
−9	16	2	119	108	0.0	−14	24	4	44	39	0.0
−10	18	2	98	75	295.8	−15	26	4	35	41	282.3
−11	20	2	42	84	110.7	−3	1	5	21	26	287.1
−12	22	2	35	41	242.3	−4	3	5	27	36	3.2
−13	24	2	55	50	30.1	−5	5	5	56	60	222.8
−14	26	2	79	69	9.8	−6	7	5	62	75	216.0
−15	28	2	32	30	305.2	−7	9	5	35	41	254.1
−16	30	2	42	36	342.8	−8	11	5	<21	27	19.8
−17	32	2	38	38	43.4	−9	13	5	<21	47	315.9
−2	1	3	149	159	342.3	−10	15	5	<20	18	110.0
−3	3	3	71	60	22.2	−11	17	5	42	42	225.0
−4	5	3	116	128	264.7	−12	19	5	<15	6	315.0
−5	7	3	37	41	215.0	−3	0	6	<18	18	312.7
−6	9	3	137	135	252.0	−4	2	6	<18	21	63.4
−7	11	3	53	69	318.0	−5	4	6	22	33	204.8
−8	13	3	144	167	354.6	−6	6	6	45	60	322.0
−9	15	3	67	69	41.3	−7	8	6	19	18	270.0

preliminary values of all the z-coordinates. These coordinates and the coordinates obtained from the [001] projection served as starting values in the least squares computations. In the two final least squares refinements of the parameters a mean value of the temperature factor was employed for the sulphur and carbon atoms.

Observed and calculated structure factors and phase angles finally arrived at in the [211] projection are listed in Table 3. The corresponding R factor is 0.089 including observed reflections only. A Fourier projection along [211] based on the final phase angles is reproduced in Fig. 2. The z coordinates and B values are listed in Table 1. The x and y coordinates determined from the projection along [211] are in good agreement with those obtained from the projection along the trigonal axis. The latter are considered to be more accurate and these values are therefore listed in Table 1.

DISCUSSION OF THE STRUCTURE

Interatomic distances and valence angles are listed in Table 2. The observed $I-S_1$ distance (3.50 Å) is 0.50 Å shorter than the van der Waals radius sum and the $C-I-S_1$ arrangement is nearly linear (angel $C-I-S_1 = 177.7°$). This clearly indicates the presence of a charge transfer bond between iodine and sulphur. The corresponding I—S bond in the iodoform-dithiane compound is somewhat shorter (3.32 Å) [1]. The iodine atom is attached to the ring system in the "equatorial" position.

The distances within the iodoform molecule agree closely with those obtained from crystalline [6] and gaseous [7] iodoform. The mean values for the S—S distances and S—S—S valence angles in the sulphur molecule is 2.043 Å and 107.7°, respectively. This is in very good agreement with the corresponding values reported for orthorhombic sulphur (2.048 Å and 107.9°, respectively) [8]. Differences in valence angles within the sulphur molecule indicate, however, that the ring system is slightly distorted. The mean value for the standard deviation of the S—S—S valence angles is 1.2°. The observed S_1-S_2 distance is 0.06 Å longer and the S_4-S_5 distance is 0.05 Å shorter than the mean S—S distance in orthorhombic sulphur. These differences in S—S distances are probably significant and are believed to be caused by the charge transfer interaction between the sulphur molecule and the relevant iodine atom of the iodoform molecule.

Each iodine atom is closely surrounded by five sulphur atoms belonging to different S_8 molecules. The shortest I—S separation is the one mentioned above. The four additional sulphur atoms which are not situated in the symmetry plane give rise to two further I—S distances which are, respectively, 3.84 Å and 3.88 Å. These four I—S separations are believed to depend on van der Waals type interactions.

Four intermolecular S· · ·S distances are found which are 0.02, 0.12, 0.21 and 0.34 Å shorter than the van der Waals radius sum given by Pauling. Apart from these short distances all intermolecular distances are found to be larger than the sum of the van der Waals radii.

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