ACTA CHEMICA SCANDINAVICA 15 (1961) 1429–1436

Crystal Structure of the 1:1 Addition Compound Dithiane-Iodoform

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The crystal structure of a new (1:1) addition compound formed by 1,4-dithiane and iodoform has been determined. The crystals have a melting point of 72°C and an observed density of 2.8 g·cm^{-3}.

The monoclinic unit cell (space group $P2_1/m$) containing *two* formula units has the parameters

$a = 6.56$ Å $\quad b = 21.06$ Å $\quad c = 4.47$ Å $\quad \beta = 104.4°$

The dithiane molecules are situated in centers of symmetry, the iodoform molecules in symmetry planes. Two iodine atoms belonging to a particular iodoform molecule form charge transfer bonds with sulphur atoms belonging to neighbouring dithiane molecules and the I—S distance (3.32 Å) is about 0.7 Å shorter than anticipated for a van der Waals contact. Each iodoform molecule is therefore linked to two neighbouring dithiane molecules and *vice versa* and chains of alternating donor and acceptor molecules are present in the crystal.

It has become increasingly clear that the elucidation of the structures of molecular compounds in which halides play the rôle of electron acceptors is essential for a thorough understanding of the nature of the charge transfer bond. So far, however, the crystal structure of the 3:1 compound formed by quinoline and iodoform is the only one which has been described in some detail [1]. But a number of additional structures are at present being investigated in our laboratory and detailed reports of the results obtained will be published in the near future.

We start by giving a report dealing with the crystal structure of a compound not previously described in the literature which contains dithiane and iodoform molecules in the ratio 1:1.

Crystals of this new compound may be obtained simply by slow evaporation of the solvent (*e.g.* carbon disulphide) from a saturated solution containing an equimolecular mixture of the two components.

The crystals, colourless flat needles, are monoclinic with the lattice constants

$$a = 6.56 \text{ Å}; \qquad b = 21.06 \text{ Å}; \qquad c = 4.47 \text{ Å}; \qquad b = 104.4°$$

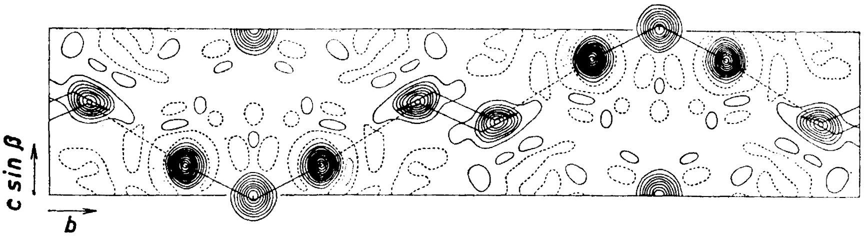

Fig. 1a. Electron density projection along the *a*-axis. Contour intervals: 4 e·Å^{-2} for for sulphur and carbon atoms. 10 e·Å^{-2} for iodine atoms.

The estimated error in the lattice constants is ± 0.5 %. The density was found equal to 2.80 giving the value $Z = 2$ for the number of molecules in the unit cell (density calculated from the lattice parameters 2.85). The space group derived from the X-ray extinctions is either $P2_1/m$ or $P2_1$. The determination of the structure was carried out assuming the former, more symmetrical space group to be the correct one.

The X-ray material on which the structure determination was based consisted of Weissenberg diagrams obtained with Cu$K\alpha$-radiation using an integrating camera of the Wiebenga type. The sections of the crystals selected for this work were approximately 0.08 × 0.08 mm^2.

Zero layer line diagrams were taken with rotation about the three principal axes using the multiple film method and the intensities (*cf.* Table 3) were measured photometrically. Corrections for absorption or extinction effects were not introduced. The number of observed reflexions in the ($h00$), ($0k0$) and [$00l$] zones are 93, 52, and 136, respectively. The number of reflexions compatible with the actual experimental conditions are 119, 71, and 174.

Approximate coordinates of the iodine atoms could easily be found from Patterson syntheses with projection along the *c* and *a*-axes. Choosing the structure factor signs based on these coordinates a Fourier synthesis was first

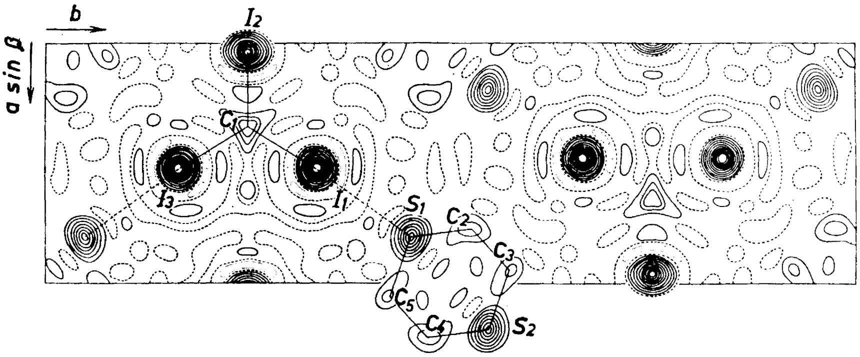

Fig. 1b. Electron density projection along the *c*-axis. Contour intervals: 4 e·Å^{-2} for sulphur and carbon atoms. 10 e·Å^{-2} for iodine atoms.

performed with projection along the *c*-axis. In the resulting map peaks giving the positions of the sulphur atoms were found besides the heavier peaks due to the iodine atoms. In the next Fourier refinement peaks belonging to the lighter atoms were also present. The data obtained from diagrams with rotation about the *a*-axis were treated correspondingly and both Fourier projections refined until no further changes of structure factor signs occurred. The final atomic coordinates based on the material obtained from Weissenberg diagrams about [001] and [100] were computed using a least squares program worked out for the Ferranti Mercury computer used throughout this investigation. As it appeared probable, however, that anisotropy in the atomic vibrations might have to be taken into account, two total difference Fourier syntheses with projection along the *c* and *a* axes were first performed, the results of which clearly showed that such anisotropic vibrations actually occur in the case of the iodine atoms which are not situated in the symmetry planes.

The correctness of this suggestion regarding the ansiotropic vibrations associated with the iodine atoms just mentioned is fully confirmed by the least squares computation, the *R* factor including only observed reflections of the projection along [100] actually dropped from 0.148 to 0.094 when this anisotropy was taken into account. In the case of the [001] projection, on the other side, the *R* factor 0.123 was not improved by such a procedure.

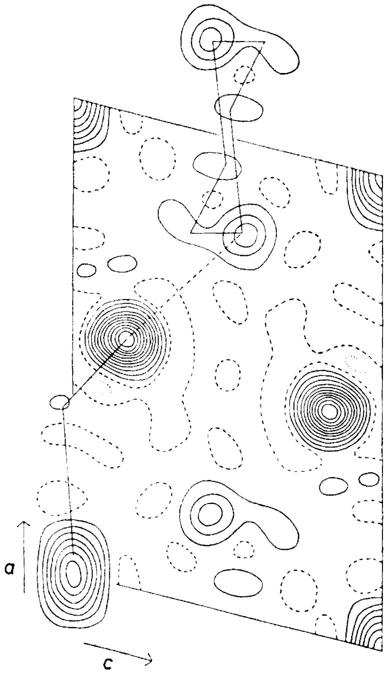

Fig. 2. Electron density projection along the *b*-axis. Contour intervals: 20 e·Å^{-2}.

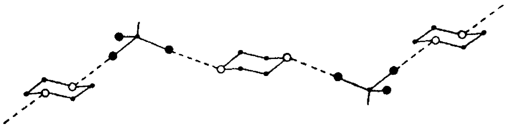

Fig. 3. Structure of the iodoform-dithiane chains. Open circles indicates sulphur, closed circles iodine (large) and carbon (small) atoms.

Table 1. Atomic coordinates as fractions of cell edges.

Atom	x	y	z
I_1	0.5214	0.3339	0.1763
I_2	0.0406	0.2500	−0.0039
S_1	0.805	0.4529	0.551
C_1	0.344	0.2500	−0.037
C_2	0.775	0.5287	0.384
C_3	0.943	0.5733	0.492

Turning now to the ($0k0$) zone, least squares refinements were performed directly, starting with the coordinates obtained from the two other projections. The R factor for this zone dropped to 0.124 assuming all over isotropic vibrations and to 0.108 assuming anisotropic vibrations of the iodine atoms not situated in the symmetry planes.

The final Fourier maps are reproduced in Figs. 1 a, 1 b, and 2. The dithiane molecules are situated in centers of symmetry, the iodoform molecules in symmetry planes. Two iodine atoms belonging to a particular iodoform molecule are linked to sulphur atoms of neighbouring dithiane molecules thus producing endless chains of alternating dithiane and iodoform molecules (Fig. 3). The arrangement C—I—S appears to be nearly linear but the observed small deviation of the CIS angle from 180° is probably significant. Observed and calculated structure factors are listed in Table 3. In the calculations the analytical approximation to the atomic scattering factors computed by Forsyth and Wells [2] was employed.

The atomic coordinates finally arrived at are listed in Table 1. In this table the mean value of each coordinate obtained from the two relevant projections are given (in the case of the iodoform carbon atom the z-coordinate could only be determined from the [010] projection). The agreement between the coordinates as determined from different projections is indeed very good leading to values not differing by more than 0.05 Å for carbon, 0.03 Å for sulphur and 0.012 Å in the case of iodine.

In Table 4 the resulting interatomic distances have been listed. The observed difference in the C—I distance referring to the two types of iodine atoms is not necessarily significant, however. The S—I bond distance (3.32 Å) is about 0.7 Å shorter than the van der Waals radius sum (4.0 Å), a fact clearly indicating the presence of a charge transfer bond between these atoms. The value reported [3] for the corresponding bond in the compound formed by iodoform and three molecules of S_8 is somewhat larger (3.45 Å). It follows from the anisotropic vibration amplitudes of the iodine atoms directly linked to sulphur that these atoms are vibrating more freely in directions perpendicular to the S—I bond than along the direction of the bond. The B values actually has a maximum for a direction nearly perpendicular both to the S—I direction and

Table 2. Standard deviations for the positions of atoms.

Iodine: $\sigma(x) = 0.0037$ Å ; $\sigma(y) = 0.0031$ Å ; $\sigma(z) = 0.0035$ Å
Sulphur: $\sigma(x) = 0.013$ Å ; $\sigma(y) = 0.011$ Å ; $\sigma(z) = 0.012$ Å
Carbon: $\sigma(x) = 0.039$ Å ; $\sigma(y) = 0.043$ Å ; $\sigma(z) = 0.060$ Å

Table 3. Observed and calculated structure factors.

(00l) zone

$h\ k\ l$	F_o	F_c	$h\ k\ l$	F_o	F_c
0 2 0	88	−130	2 15 0	< 17	−2
0 4 0	52	37	2 16 0	18	−15
0 6 0	76	65	2 17 0	< 18	−10
0 8 0	47	−31	2 18 0	63	48
0 10 0	193	−190	2 19 0	< 18	−14
0 12 0	183	168	2 20 0	33	−23
0 14 0	131	−121	2 21 0	< 17	−11
0 16 0	22	−9	2 22 0	64	−69
0 18 0	88	61	2 23 0	36	33
0 20 0	< 18	12	2 24 0	72	69
0 22 0	60	−58	2 25 0	< 13	−10
0 24 0	104	98	3 0 0	97	−109
0 26 0	32	−42	3 1 0	17	−3
1 0 0	63	−64	3 2 0	19	−15
1 1 0	< 6	−2	3 3 0	35	29
1 2 0	55	37	3 4 0	98	103
1 3 0	60	56	3 5 0	104	−108
1 4 0	158	183	3 6 0	159	−169
1 5 0	21	−26	3 7 0	79	79
1 6 0	224	−265	3 8 0	108	114
1 7 0	61	68	3 9 0	35	−30
1 8 0	106	124	3 10 0	38	40
1 9 0	18	−16	3 11 0	< 16	5
1 10 0	< 12	0	3 12 0	40	−37
1 11 0	< 7	−6	3 13 0	< 17	20
1 12 0	89	−77	3 14 0	23	23
1 13 0	31	−27	3 15 0	39	39
1 14 0	22	6	3 16 0	69	73
1 15 0	17	−12	3 17 0	44	−46
1 16 0	105	97	3 18 0	106	−108
1 17 0	57	−49	3 19 0	50	48
1 18 0	126	−121	3 20 0	29	34
1 19 0	< 18	10	3 21 0	< 17	−15
1 20 0	67	67	3 22 0	< 16	2
1 21 0	< 17	−7	3 23 0	< 14	−13
1 22 0	30	20	3 24 0	46	−44
1 23 0	16	12	4 0 0	148	141
1 24 0	60	−40	4 1 0	126	−117
1 25 0	20	15	4 2 0	70	−66
1 26 0	16	9	4 3 0	31	21
2 0 0	160	200	4 4 0	16	−20
1 1 0	62	−74	4 5 0	30	−24
2 2 0	157	−184	4 6 0	73	72
2 3 0	43	44	4 7 0	< 16	−25
2 4 0	42	−42	4 8 0	21	−24
2 5 0	25	23	4 9 0	42	−47
2 6 0	72	82	4 10 0	67	−70
2 7 0	< 12	12	4 11 0	84	94
2 8 0	< 12	0	4 12 0	83	92
2 9 0	16	−17	4 13 0	52	−56
2 10 0	81	−90	4 14 0	50	−53
2 11 0	47	54	4 15 0	43	47
2 12 0	173	183	4 16 0	30	−24
2 13 0	60	−60	4 17 0	19	24
2 14 0	65	−66	4 18 0	47	48

h k l	F_o	F_c
4 19 0	< 18	0
4 20 0	21	−13
4 21 0	20	−23
4 22 0	33	−36
4 23 0	26	37
5 0 0	36	−41
5 1 0	< 17	14
5 2 0	47	52
5 3 0	41	28
5 4 0	69	58
5 5 0	111	−101
5 6 0	90	−83
5 7 0	77	78
6 8 0	32	25
5 9 0	35	−31
5 10 0	< 18	7
5 11 0	< 18	−17
5 12 0	63	−75
5 13 0	< 18	18
5 14 0	< 17	10
5 15 0	21	26
5 16 0	31	33
5 17 0	54	−58
5 18 0	52	−43
5 19 0	45	50
5 20 0	31	35
6 0 0	62	65
6 1 0	97	−81
6 2 0	24	−25
6 3 0	54	39
6 4 0	21	−22
6 5 0	< 18	37
6 6 0	42	48
6 7 0	< 18	−9
6 8 0	24	−27
6 9 0	27	−21
6 10 0	31	−37
6 11 0	67	68
6 12 0	36	40
6 13 0	67	−73
6 14 0	< 16	−26
6 15 0	< 16	2
6 16 0	17	−18
6 17 0	< 13	8
6 18 0	36	39
7 0 0	56	−59
7 1 0	< 16	27
7 2 0	< 16	12
7 3 0	39	35
7 4 0	< 15	9
7 5 0	60	−60
7 6 0	23	−28
7 7 0	86	81
7 8 0	< 17	20
7 9 0	23	−13
7 10 0	32	32
7 11 0	< 14	−22
7 12 0	26	−28
7 13 0	< 11	13
8 0 0	< 11	0
8 1 0	52	−58
8 2 0	< 11	−12
8 3 0	14	10
8 4 0	14	−26

(*h*00) zone

h k l	F_o	F_c
0 2 0	117	−129
0 4 0	41	36
0 6 0	83	71
0 8 0	45	−36
0 10 0	181	−185
0 12 0	165	163
0 14 0	141	−116
0 16 0	30	−28
0 18 0	78	73
0 20 0	< 19	−5
0 22 0	52	−54
0 24 0	95	98
0 26 0	32	−32
0 0 1	80	100
0 1 1	92	−133
0 2 1	176	−202
0 3 1	23	13
0 4 1	37	31
0 5 1	150	159
0 6 1	19	6
0 7 1	93	−104
0 8 1	72	73
0 9 1	24	9
0 10 1	58	−59
0 11 1	102	107
0 12 1	128	130
0 13 1	93	−90
0 14 1	64	−54
0 15 1	23	−13
0 16 1	< 18	13
0 17 1	76	74
0 18 1	< 19	9
0 19 1	72	−72
0 20 1	< 19	−4
0 21 1	< 18	−9
0 22 1	48	−47
0 23 1	58	59
0 24 1	40	35
0 25 1	42	−46
0 26 1	23	−29
0 0 2	25	26
0 1 2	98	−98
0 2 2	< 13	4
0 3 2	33	−27
0 4 2	105	115
0 5 2	67	66
0 6 2	139	−149
0 7 2	111	−111
0 8 2	65	62
0 9 2	20	−14

h k l	F_o	F_c
0 10 2	30	− 32
0 11 2	68	67
0 12 2	39	− 38
0 13 2	54	− 59
0 14 2	21	− 15
0 15 2	< 19	5
0 16 2	57	60
0 17 2	71	71
0 18 2	64	− 66
0 19 2	45	− 44
0 20 2	40	44
0 21 2	< 18	2
0 22 2	19	20
0 23 2	38	44
0 24 2	18	− 17
0 0 3	67	− 69
0 1 3	34	28
0 2 3	< 17	− 10
0 3 3	22	17
0 4 3	95	85
0 5 3	22	12
0 6 3	124	−115
0 7 3	34	32
0 8 3	88	90
0 9 3	20	19
0 10 3	27	25
0 11 3	22	− 16
0 12 3	48	− 42
0 13 3	< 19	6
0 14 3	< 19	10
0 15 3	< 18	− 11
0 16 3	48	52
0 17 3	21	− 23
0 18 3	76	− 82
0 19 3	< 18	− 2
0 20 3	32	31
0 21 3	< 15	2
0 22 3	< 13	12
0 0 4	< 19	29
0 1 4	56	50
0 2 4	21	− 12
0 3 4	19	− 18
0 4 4	23	29
0 5 4	68	− 68
0 6 4	46	− 45
0 7 4	23	29
0 8 4	< 18	21
0 9 4	< 18	− 3
0 10 4	< 18	− 18
0 11 4	46	− 49
0 12 4	< 19	2
0 13 4	51	53
0 14 4	< 19	− 3
0 15 4	17	13
0 16 4	22	21
0 17 4	24	− 27
0 18 4	15	− 18
0 0 5	45	42
0 1 5	28	30
0 2 5	28	− 28
0 3 5	< 18	8
0 4 5	< 17	0
0 5 5	< 17	− 6
0 6 5	22	21
0 7 5	24	29
0 8 5	< 15	2
0 9 5	< 14	6
0 10 5	21	− 25
0 11 5	16	− 25
	(0*k*0) zone	
1 0 0	44	− 65
2 0 0	174	206
3 0 0	108	−112
4 0 0	177	149
5 0 0	47	− 45
6 0 0	75	76
7 0 0	73	− 71
8 0 0	< 23	12
$\bar{8}$ 0 1	55	67
$\bar{7}$ 0 1	75	− 63
$\bar{6}$ 0 1	99	86
$\bar{5}$ 0 1	120	−110
$\bar{4}$ 0 1	122	111
$\bar{3}$ 0 1	27	− 28
$\bar{2}$ 0 1	224	219
$\bar{1}$ 0 1	66	− 56
0 0 1	90	107
1 0 1	< 18	− 13
2 0 1	117	117
3 0 1	72	64
4 0 1	< 33	17
5 0 1	< 37	10
6 0 1	< 34	− 30
7 0 1	< 33	35
$\bar{8}$ 0 2	< 27	3
$\bar{7}$ 0 2	59	− 48
$\bar{6}$ 0 2	< 37	11
$\bar{5}$ 0 2	36	35
$\bar{4}$ 0 2	34	28
$\bar{3}$ 0 2	75	62
$\bar{2}$ 0 2	< 25	− 17
$\bar{1}$ 0 2	140	146
0 0 2	24	28
1 0 2	193	189
2 0 2	50	− 58
3 0 2	122	121
4 0 2	65	− 80
5 0 2	94	108
6 0 2	53	− 63
$\bar{7}$ 0 3	53	51
$\bar{6}$ 0 3	37	− 50
$\bar{5}$ 0 3	70	67
$\bar{4}$ 0 3	83	− 89
$\bar{3}$ 0 3	116	133
$\bar{2}$ 0 3	51	− 49

$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c
$\bar{1}$ 0 3	200	166	$\bar{1}$ 0 4	47	54
0 0 3	94	-77	0 0 4	< 37	16
1 0 3	148	128	1 0 4	66	70
2 0 3	78	-68	2 0 4	34	32
3 0 3	123	126	3 0 4	< 36	7
4 0 3	< 42	-39	4 0 4	< 25	15
5 0 3	57	59	$\bar{5}$ 0 5	< 27	-1
$\bar{7}$ 0 4	23	26	$\bar{4}$ 0 5	< 34	8
$\bar{6}$ 0 4	62	-62	$\bar{3}$ 0 5	< 36	-21
$\bar{5}$ 0 4	53	65	$\bar{2}$ 0 5	53	60
$\bar{4}$ 0 4	< 36	-25	$\bar{1}$ 0 5	< 34	-6
$\bar{3}$ 0 4	85	84	0 0 5	70	74
$\bar{2}$ 0 4	< 37	-23	1 0 5	37	-45

Table 4. Interatomic distances and angles.

	Distance (Å)		Angle (°)
C_1-I_1	2.20	$I_1-C_1-I_2$	113
C_1-I_2	2.03	$I_1-C_1-I_3$	107
I_1-I_2	3.529	$C_5-S_1-C_2$	104
I_1-I_3	3.534	$S_1-C_2-C_3$	117
S_1-C_2	1.75	$C_2-C_3-S_2$	114
C_2-C_3	1.44	$C_1-I_1-S_1$	175
S_1-C_5	1.79	$I_1-S_1-S_2$	137
S_1-S_2	3.35		
I_1-S_1	3.32		

the *b*-axis. It may be added that the direction of the S—I bond corresponds to the equatorial bond direction in *cyclo*hexane.

When the present investigation was started, some crystallographic work dealing with the 1:1 compound formed by iodoform and 1,4-dioxan [4] had already been carried out in this laboratory. It was found, however, that the preparation of sufficiently good single crystals of this compound was more problematic than in the case of the dithiane analogue and the work was therefore first concentrated on the latter. The dioxan compound is orthorhombic and not isostructural with the dithiane compound. It may, however, be stated with confidence that the general characteristics of the two structures are very similar. Thus, even in the dioxan compound chains similar to those found in the dithiane compound and consisting of alternating acceptor and donor molecules are present. Two iodine atoms of each iodoform molecule therefore form charge transfer bonds with ether oxygen atoms of adjacent dioxan molecules.

This investigation has in part been sponsored by the *United States Air Force Development Command* under contract AF 61 (052)-71.

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Received March 23, 1961.