

## Crystal Structure of the 1:1 Addition Compound Mercuric Chloride — Cyclohexane-1,4-dione

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The 1:1 molecular compound containing mercuric chloride and cyclohexane-1,4-dione crystallizes in the space group  $C2/c$ . The unit cell contains four molecules of either kind and has the parameters:

$$a = 7.57 \text{ \AA}; b = 17.11 \text{ \AA}; c = 7.56 \text{ \AA}; \beta = 108.5^\circ$$

Both kinds of molecules are situated on two-fold symmetry axes. The dione molecule has a "twisted boat" conformation with an angle between the two C—O bonds of  $176^\circ$ . A certain increase in the observed C—O bond length and a corresponding decrease in the C(O)—C(H<sub>2</sub>) bond length — both amounting to about  $0.04 \text{ \AA}$  — when compared to the values observed for the crystalline dione itself, is believed to be significant.

In order to decide if the cyclohexane-1,4-dione molecule in its addition compounds retains the "twisted boat" conformation<sup>1,2</sup> observed in the crystal of the dione itself, two new solid compounds<sup>3</sup> have been prepared using mercuric chloride and diiodoacetylene as acceptors. The crystal structure of the former compound has been determined by two-dimensional X-ray methods and the results are being given here in some detail (*cf. Ref.*<sup>3</sup>) For the latter compound it was found desirable to carry out a three-dimensional analysis.

Crystals of the mercuric chloride compound were obtained by evaporating the solvent (ethyl alcohol) from a solution containing equimolar amounts of the two components. The crystals belong to the monoclinic system, space group  $C2/c$ , and are elongated along the [101]-direction. The unit cell containing four molecules of either kind has the parameters:

$$a = 7.57 \text{ \AA}; b = 17.11 \text{ \AA}; c = 7.56 \text{ \AA}; \beta = 108.5^\circ.$$

The space group requirement regarding the molecular symmetry is either a centre of symmetry ( $C_i$ ) or a two-fold symmetry axis. It was soon found that the last alternative is the correct one for the mercuric chloride molecules and more elaborate work led to the result that the same holds true for the

dione molecules. This conclusion indicates that the conformation of the dione molecule may still be that of a "twisted boat".

Two-dimensional work based on integrated Weissenberg diagrams with rotation around the principal axes has confirmed this suggestion, the final

$R$  values being:  $R_{100} = 4.2\%$ ,  $R_{010} = 10.3\%$ , and  $R_{001} = 8.2\%$ .

From the atomic parameters listed in Table 1 the interatomic distances and valence angles listed in Table 2 were computed.

Table 1. Final atomic parameters.

	$x$	$y$	$z$
Hg	0.0000	0.0457	0.2500
Cl	0.2471	0.0377	0.1351
O	0.1504	0.1650	0.5060
C <sub>1</sub>	0.3130	0.1630	0.6220
C <sub>2</sub>	0.3532	0.1892	0.8156
C <sub>3</sub>	0.4708	0.1499	0.5560

Table 2. Interatomic distances and angles.

Hg—Cl	2.30 Å
C <sub>1</sub> —O <sub>1</sub>	1.26 Å
C <sub>1</sub> —C <sub>2</sub>	1.45 Å
C <sub>1</sub> —C <sub>3</sub>	1.47 Å
C <sub>2</sub> —C <sub>4</sub>	1.53 Å
Hg.....O	2.79 Å
Cl <sub>1</sub> —Hg—O <sub>1</sub>	96°
Cl <sub>2</sub> —Hg—O <sub>1</sub>	89°
O <sub>2</sub> —Hg—O <sub>1</sub>	86°
Cl <sub>1</sub> —Hg—Cl <sub>2</sub>	173°
C <sub>4</sub> —C <sub>2</sub> —C <sub>1</sub>	111°
C <sub>2</sub> —C <sub>1</sub> —C <sub>3</sub>	117°
C <sub>1</sub> —C <sub>3</sub> —C <sub>5</sub>	111°
C <sub>2</sub> —C <sub>1</sub> —O <sub>1</sub>	119°
C <sub>3</sub> —C <sub>1</sub> —O <sub>1</sub>	122°

Angle between the two C—O directions 176°

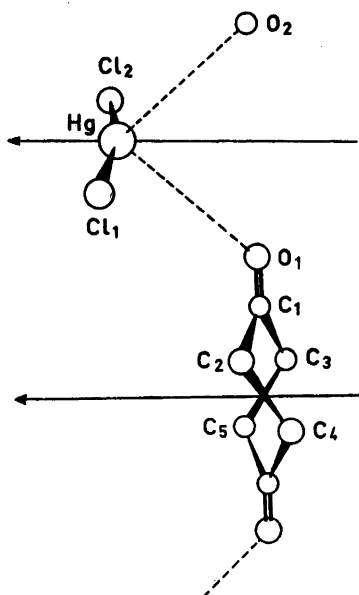


Fig. 1. Schematic drawing of the structure.

A schematic drawing of the structure is reproduced in Fig. 1. It is seen that chains of alternating mercuric chloride and dione molecules are present. The direction of these chains coincide with the [101]-direction.

Table 3. a). Observed and calculated structure factors for  $0kl$  reflexions.  $R = 4.2\%$ .

$k$	$l$	$F_o$	$F_c$	$k$	$l$	$F_o$	$F_c$
1	0	133	130	4	4	- 45	- 44
2	0	49	51	5	4	- 56	- 56
3	0	47	45	6	4	- 42	- 42
4	0	- 96	-103	7	4	- 21	- 19
5	0	-115	-117	9	4	16	16
6	0	- 75	- 73	10	4	20	22
7	0	- 62	- 59	11	4	16	17
8	0	- 25	- 18	1	5	- 37	- 36
9	0	22	16	2	5	- 56	- 56
10	0	25	27	3	5	- 60	- 63
11	0	22	24	4	5	- 34	- 35
12	0	16	16	6	5	15	12
1	1	- 64	- 66	7	5	33	33
2	1	-186	-186	8	5	32	33
3	1	-137	-143	9	5	17	19
4	1	- 87	- 91	0	6	- 59	- 57
5	1	- 49	- 46	1	6	- 56	- 57
6	1	26	21	2	6	- 24	- 24
7	1	50	49	3	6	18	14
8	1	50	52	4	6	34	31
9	1	40	41	5	6	46	46
10	1	19	19	6	6	38	40
0	2	-114	-117	7	6	18	18
1	2	-121	-124	9	6	- 12	- 11
2	2	- 79	- 77	1	7	36	35
3	2	38	35	2	7	49	48
4	2	67	68	3	7	51	53
5	2	68	68	4	7	36	37
6	2	77	77	5	7	13	12
7	2	42	41	6	7	- 12	- 9
9	2	- 12	- 12	7	7	- 25	- 25
10	2	- 23	- 24	8	7	- 22	- 24
11	2	- 21	- 24	0	8	50	51
1	3	70	71	1	8	43	43
2	3	73	78	2	8	23	20
3	3	74	77	4	8	- 29	- 27
4	3	65	64	5	8	- 35	- 36
5	3	15	9	6	8	- 27	- 28
6	3	- 28	- 27	7	8	- 21	- 20
7	3	- 33	- 34	1	9	- 22	- 21
8	3	- 40	- 40	2	9	- 33	- 34
9	3	- 29	- 30	3	9	- 36	- 36
10	3	- 11	- 9	4	9	- 23	- 24
0	4	77	79	0	10	- 34	- 29
1	4	60	61	1	10	- 24	- 25
2	4	25	21	2	10	- 7	- 11
3	4	- 15	- 14				

Table 3. b) Observed and calculated structure factors for  $h0l$  reflexions.  $R = 10.3\%$ .

$h$	$l$	$F_o$	$F_c$	$h$	$l$	$F_o$	$F_c$
1	0	36	42	4	0	30	27
2	0	55	58	5	0	12	11
3	0	34	34	-5	1	15	16

$h l$	$F_o$	$F_c$	$h l$	$F_o$	$F_c$
-4 1	30	24	-4 3	19	22
-3 1	37	40	-3 3	36	26
-2 1	51	49	-2 3	38	46
-1 1	53	65	-1 3	43	33
0 1	58	52	0 3	30	34
1 1	53	55	1 3	34	31
2 1	41	42	2 3	19	22
3 1	26	25	3 3	12	13
4 1	19	19	-4 4	20	18
-5 2	21	17	-3 4	17	18
-4 2	22	19	-2 4	27	26
-3 2	46	42	-1 4	19	19
-2 2	32	31	0 4	25	26
1 2	65	63	1 4	12	14
0 2	40	39	2 4	15	15
1 2	56	57	-3 5	11	15
2 2	21	24	-2 5	16	15
3 2	28	26	-1 5	13	19
4 2	14	14	0 5	13	13
-5 3	21	16			

Table 3. c) Observed and calculated structure factors for  $hk0$  reflexions.  $R = 8.2\%$ 

$h k$	$F_o$	$F_c$	$h k$	$F_o$	$F_c$
0 2	138	132	2 22	16	15
0 4	50	49	3 1	103	104
0 6	43	47	3 3	81	79
0 8	- 91	- 92	3 5	30	24
0 10	- 98	-107	3 7	- 47	- 49
0 12	- 58	- 67	3 9	- 53	- 56
0 14	- 48	- 49	3 11	- 50	- 56
0 16	- 18	- 20	3 13	- 46	- 51
0 18	16	11	3 15	- 14	- 15
0 20	20	19	3 19	10	11
0 22	17	15	3 21	19	16
0 24	9	12	4 0	122	114
1 1	141	128	4 2	119	113
1 3	113	121	4 4	54	53
1 5	19	17	4 6	- 21	- 15
1 7	- 44	- 46	4 8	- 48	- 43
1 9	- 62	- 75	4 10	- 66	- 68
1 11	- 65	- 71	4 12	- 58	- 61
1 13	- 45	- 50	4 14	- 33	- 32
1 15	- 22	- 25	4 20	18	15
1 19	19	16	4 22	10	14
1 21	19	15	5 1	74	75
1 23	17	14	5 3	62	59
2 0	73	85	5 7	- 35	- 28
2 2	83	81	5 9	- 43	- 42
2 4	26	24	5 11	- 47	- 48
2 6	- 32	- 24	5 13	- 34	- 35
2 8	- 42	- 40	5 19	16	10
2 10	- 54	- 61	5 21	5	12
2 12	- 45	- 49	6 0	59	62
2 14	- 20	- 19	6 2	34	35
2 20	23	18			

<i>h</i>	<i>k</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>
6	4	15	13	7	13	— 20	— 21
6	8	— 34	— 31	8	0	46	48
6	10	— 35	— 37	8	2	38	40
6	12	— 25	— 24	8	4	24	21
6	14	— 19	— 16	8	8	— 25	— 22
6	18	12	8	8	10	— 28	— 28
7	1	45	49	8	12	— 27	— 26
7	3	32	31	8	14	— 14	— 15
7	7	— 20	— 14	9	1	32	31
7	9	— 32	— 32	9	3	21	20
7	11	— 28	— 31	9	9	— 18	— 19

The dione molecule is actually in a "twisted boat" configuration not very different from that found by three-dimensional analyses of the crystals of the dione itself.<sup>4,5</sup> Here, however, it approaches the conformation in which the two C=O bonds point in opposite directions — the angle between them being 176°. The bond distances and bond angles in the crystalline dione and in the present compound are very similar. The carbonyl C=O distance, however, is found to be 0.04 Å larger in the addition compound, the bond between the carbonyl carbon atom and the nearest (methylene) carbon atom about 0.04 Å shorter in the addition compound. We believe these figures to be significant although they may be slightly modified by a three-dimensional investigation of the addition compound.

It appears of some interest that the formation of bonds between oxygen and mercury atoms has, to some degree, changed the shape of the dione molecule. The investigation of another 1:1 addition compound of the dione in which diiodoacetylene is the acceptor molecule has also been performed using two-dimensional methods. In this case the symmetry required of both the participating molecular species is *C<sub>i</sub>*, and it appears very probable that the dione molecule has a conformation corresponding to a "chair" form of the six-membered ring. In order to prove if the apparent high symmetry of the

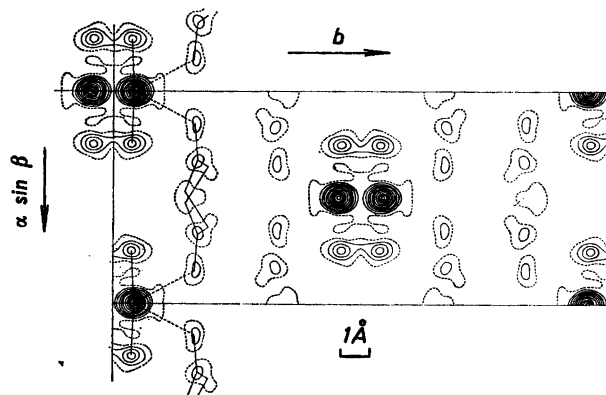


Fig. 2. Electron density map with projection along the *c*-axis.

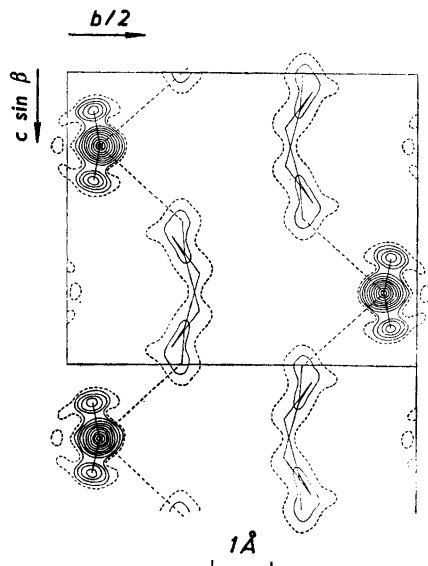


Fig. 3. Electron density map with projection along the  $a$ -axis.

dione molecule in the crystal may depend on a statistical disorder, a three-dimensional structure analysis was started some time ago and is expected to be finished in the near future.

The distance between oxygen and mercury atoms (2.79 Å) is strikingly different from that reported for the mercuric chloride-cumarin compound (2.38 Å)<sup>6</sup> whereas the corresponding distance in the apparently isomorphous mercuric bromide-cumarin compound is reported to be 2.73 Å. A reinvestigation of the mercuric chloride-cumarin structure thus appears desirable.

Table 3 contains observed and calculated structure factors for the mercuric chloride compound.

Final electron density maps for the  $hk0$ - and  $0kl$ -projection are reproduced in Figs. 2 and 3.

#### REFERENCES

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Received March 21, 1964.