Crystal Structure of the (1:1) Addition Compound Cyclohexane-1,4-dione—Diiodoacetylene

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A (1:1) addition compound formed by cyclohexane-1,4-dione and diiodoacetylene has been prepared and its crystal structure investigated from three-dimensional X-ray data. The *monoclinic* unit cell containing two formula units has the parameters:

$$a = 9.61 \text{ Å}; \ b = 7.59 \text{ Å}; \ c = 8.72 \text{ Å}; \ \beta = 117.3°$$

The space group ($P2_1/c$) requires both molecular species to be centrosymmetric, but the analysis shows this to be true only for the diiodo-acetylene molecules. The dione molecules are in the "twisted boat" conformation as they are also in the crystals of the dione itself and in the addition compound in which mercuric chloride is the acceptor molecule. In the present case the angle between the two C—O bonds is approximately that found in the crystalline dione, whereas in the mercuric chloride adduct this angle is not far from 180°. This indicates that the bonds linking the oxygen atoms to iodine atoms are weaker than the bonds between oxygen and mercury.

The apparent high symmetry of the dione molecules is due to a statistical disorder, a conclusion which is confirmed by proton magnetic resonance measurements.

The carbon skeleton of the cyclohexane-1,4-dione molecule in the crystal has been determined with considerable care both at room temperature[1] and at low temperature[2] using three-dimensional X-ray methods. It corresponds to that of a "twisted boat" form. These findings are in full agreement with the fact that the dione shows an electric dipole moment in solution.[3] We found it interesting to try to prepare some addition compounds with suitable acceptor molecules and to investigate their crystal structures. Our chief aim was to establish whether or not the dione molecule may change its conformation when it acts as a donor, and perhaps appear in the "chair" form in addition compounds.

Structure investigations related to one of the new compounds prepared, the 1:1 adduct with mercuric chloride, have already been reported.[4] A second addition compound containing the dione and diiodoacetylene in equimolecular
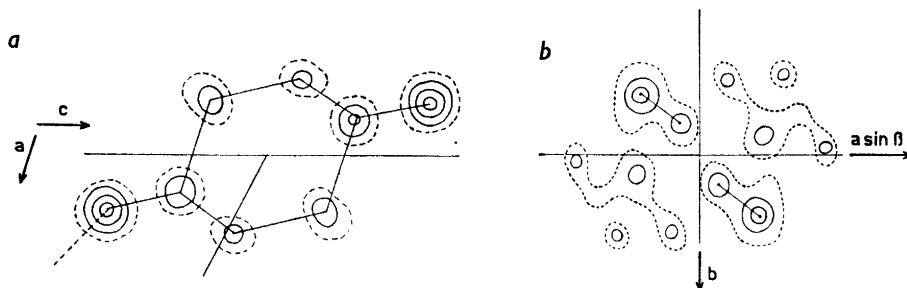
Fig. 1. a. Fourier projection along b-axis. b. Fourier projection along c-axis.

amounts has also been prepared simply by evaporating the solvent (ethyl alcohol) from a solution containing the two molecular species in this proportion.

Contrary to the findings in the case of the mercuric chloride compound, the space group ($P2_1/c$) and the number ($Z = 2$) of molecular units in the unit cell indicate that both partner molecules are situated in centres of symmetry in the crystal. This is not surprising in the case of the diiodoacetylene molecules, but for the dione molecule it would indicate that it may be present in the "rigid" chair conformation.

The lattice constants of the cyclohexane-1,4-dione diiodoacetylene compound are:

$$a = 9.61 \text{ Å}; \ b = 7.59 \text{ Å}; \ c = 8.72 \text{ Å}; \ \beta = 117.3°$$

From two-dimensional X-ray data ($h0l$ and $hk0$-zones) the following results were obtained: The Fourier projection along the b-axis was clear

Table 1. Final atomic coordinates.

	x	y	z
O_1	0.0952	0.4160	0.3166
O_2	0.1066	0.3672	0.3178
C_1	0.0528	0.4514	0.1845
C_2	0.0553	0.4283	0.1639
C_3	0.4618	0.4852	0.9263
I	0.34235	0.45208	0.67369

Table 2. Interatomic distances (Å) and angles (°).

C_1-O_2	1.21	C_4-C_3-I	175
C_2-O_1	1.21	C_3-I-O_1	165
$(C_1-C_2$	0.26)	C_3-I-O_2	166
$(O_1-O_2$	0.38)		
$I-O_1$	2.94		
$I-O_2$	2.95		
C_3-I	1.98		
C_3-C_4	1.17		
$I-I$	5.13*		

* Unpublished values obtained from E. D. investigations of diiodo-acetylene vapour in our laboratory are: 5.16 Å (1942) and 5.17 Å (1951).

and well resolved and in agreement with the assumption of a dione molecule having a conformation corresponding to the "chair" model and a linear diiodoacetylene molecule of the expected kind. The final R factor of this projection was 5.9 %. The image of the dione molecule is reproduced in Fig. 1 a. In the c-axis Fourier projection, on the other hand, the image of the dione molecule, contrary to that of the acceptor molecule, was blurred, however, in spite of the fact that the R factor was brought down to the value 8.7 % by successive refinements (cf. Fig. 1 b).

This finding strongly suggested that some kind of disorder with respect to the dione molecule prevails, a disorder which does not, however, influence the b-projection to the same degree as the c-projection. It was found necessary to collect threedimensional X-ray data in order to test the hypothesis of a statistical disorder related to the dione molecules. Before doing so, however, a proton magnetic resonance investigation was carried out on the solid at temperatures between $-70°C$ and room temperature. The broad peak observed at lower temperatures is changed into a narrow one at about $-20°C$. This observation favours the view that the dione molecules attain a certain degree of orientational freedom at this temperature. At lower temperatures this reorientation is hampered and a frozen-in statistically disordered structure results.

The three-dimensional intensity data were obtained from photometrical measurements of Weissenberg films taken with $CuK\alpha$ radiation at $-20°C$. In the Fourier synthesis based on these data and with structure factor signs computed from the already well established atomic coordinates of the diiodo-acetylene molecules, the peaks corresponding to oxygen and carbon atoms are actually "smeared out", an indication that these atoms do not occupy well-defined positions in the crystal. When trying to investigate this observation quantitatively we introduced a trial structure correspondig to the model of the dione molecule found in the X-ray investigation of the solid dione.[1] Two "resting positions" were envisaged and were assumed to have equal probabilities so that the carbon and oxygen atoms corresponding to each of them are "half" atoms.

The three-dimensional full-matrix least squares refinement computed led to a final R value of 8.2 %. Anisotropic B factors were introduced for the iodine atoms only. It is clear that the atomic coordinates thus obtained for the methylene "half" carbon atoms can only be regarded as approximate, but we believe that the corresponding coordinates of the carbonyl carbon and oxygen atoms are fairly accurate.

It may be of interest to consider the angle between the two C—O bond directions. In the dione itself this angle is 154°, but in the mercuric chloride compound it is much larger, in fact nearly 180°. It is to be expected that
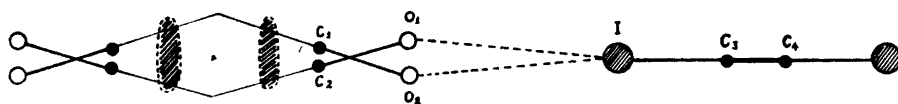

Fig. 2. Schematical drawing showing those atoms the coordinates of which are listed in Table 1.

Table 3. Observed and calculated structure factors ($10 \times F_o$ and $10 \times F_c$ are listed).

$h = 0, l = 0$

2	1817	1886
4	390	340
6	164	−149
8	178	−209

$h = 1, l = 0$

0	534	−569
1	481	−475
2	741	−686
3	945	−890
4	377	−362
5	639	−627
7	254	−257

$h = 2, l = 0$

0	374	−351
1	455	446
2	370	−345
3	854	873
4	147	−132
5	690	709
7	296	318
8	86	63

$h = 3, l = 0$

0	1088	1261
1	141	−163
2	789	932
3	278	−285
4	277	295
5	148	−143
6	128	−112
8	160	−162

$h = 4, l = 0$

0	1009	−1038
1	262	−317
2	556	−629
3	573	−644
4	218	−89
5	448	−468
6	202	108
7	177	−181
8	101	111

$h = 5, l = 0$

0	387	−423
1	244	251
2	219	−232
3	464	476
5	360	367
7	169	173

$h = 6, l = 0$

0	639	687
1	101	−75
2	535	561

$h = 6, l = 0$

3	215	−200
4	214	213
5	171	−175
8	71	−87

$h = 7, l = 0$

0	514	−489
1	103	−81
2	332	−325
3	210	−209
5	187	−205
7	96	−99

$h = 8, l = 0$

1	177	143
3	304	292
5	234	227
6	75	−21

$h = 9, l = 0$

0	290	267
2	205	199
3	113	−88
5	65	−66

$h = 10, l = 0$

0	231	−214
2	176	−163

$h = −11, l = 1$

1	104	−114

$h = −10, l = 1$

2	140	134
4	151	160

$h = −9, l = 1$

1	296	284
2	97	−83
3	125	120
4	114	−103

$h = −8, l = 1$

1	393	−419
2	144	−121
3	242	−261
4	127	−121
7	46	67

$h = −7, l = 1$

1	103	102
2	227	247
4	311	322
6	195	200

$h = −6, l = 1$

1	442	524
2	377	−410
3	183	204

$h = −6, l = 1$

4	407	−407
6	215	−216
7	78	−74
8	59	−73

$h = −5, l = 1$

1	738	−931
2	271	−301
3	467	−472
4	257	−257
6	109	−98
7	145	138

$h = −4, l = 1$

1	239	281
2	578	584
3	200	192
4	655	655
6	408	402
7	83	−49
8	129	131
9	52	−45

$h = −3, l = 1$

1	811	839
2	444	−446
3	573	539
4	628	−621
5	105	92
6	378	−361
7	101	−100
8	116	−107
9	63	−74

$h = −2, l = 1$

1	1940	−2224
2	349	292
3	918	−854
4	82	47
7	176	177
9	119	141

$h = −1, l = 1$

1	723	646
2	1405	1211
3	574	502
4	1055	969
5	118	106
6	476	482
8	137	155

$h = 0, l = 1$

1	541	427
2	763	−607
3	277	252
4	949	−825
6	512	−504
7	86	−82
8	112	−155

$h = 1, l = 1$		
1	1356	−1491
2	204	188
3	801	−745
4	156	143
5	82	−64
7	189	210
9	122	156

$h = 2, l = 1$		
1	981	1113
2	527	566
3	415	402
4	725	683
5	70	−66
6	376	380
7	121	−136
8	101	107
9	63	−85

$h = 3, l = 1$		
1	609	647
2	697	−702
3	268	267
4	650	−651
6	338	−361
8	104	−120

$h = 4, l = 1$		
1	855	−927
2	91	88
3	492	−489
4	211	221
5	66	−59
6	109	128
7	99	103

$h = 5, l = 1$		
1	624	639
2	270	243
3	322	320
4	388	381
6	247	247
7	105	−113
8	63	80

$h = 6, l = 1$		
1	81	100
2	393	−386
4	441	−408
6	243	−240

$h = 7, l = 1$		
1	486	−455
2	139	121
3	245	−242
4	116	133
6	55	66

$h = 7, l = 1$		
7	39	49

$h = 8, l = 1$		
1	366	329
2	97	96
3	177	162
4	95	96
6	44	58

$h = 9, l = 1$		
2	139	−127
4	157	−175

$h = 10, l = 1$		
1	106	−125
2	57	66

$h = -11, l = 2$		
0	212	−181
2	144	−128

$h = -10, l = 2$		
0	275	226
2	198	177
3	101	80
4	69	70
5	58	46

$h = -9, l = 2$		
1	111	−80
3	234	−212
5	220	−198

$h = -8, l = 2$		
0	288	−295
1	131	128
2	215	−210
3	244	215
5	166	145
7	75	77

$h = -7, l = 2$		
0	725	738
1	111	120
2	514	525
3	210	194
4	143	126
5	120	115
6	110	−86

$h = -6, l = 2$		
1	219	−230
2	95	−89
3	513	−481
4	79	−77
5	432	−382
7	176	−165

$h = -5, l = 2$		
0	708	−769
1	151	164

$h = -5, l = 2$		
2	562	−558
3	468	429
4	206	−198
5	446	396
7	213	175
8	103	87

$h = -4, l = 2$		
0	1321	1399
1	122	−129
2	949	1030
3	78	−49
4	329	322
6	103	−84
8	152	−127

$h = -3, l = 2$		
0	946	−887
1	637	−671
2	592	−579
3	1056	−1030
4	178	−171
5	665	−636
7	267	−278
9	50	−60

$h = -2, l = 2$		
0	813	−844
1	222	213
2	523	−496
3	700	640
4	92	−42
5	630	581
6	113	105
7	246	239
8	88	91
9	63	54

$h = -1, l = 2$		
1	186	−94
2	1327	1135
3	102	−101
4	446	380
5	98	−66
6	145	−121
8	176	−197

$h = 0, l = 2$		
0	1149	−1098
1	369	−342
2	765	−722
3	788	−724
4	138	−120
5	643	−604
6	127	122
7	248	−256
8	97	103

$h = 1, l = 2$		
0	721	−783
1	522	524

	h = 1, l = 2			h = 8, l = 2			h = -3, l = 3	
2	616	-600	3	104	-105	7	159	164
3	954	904	5	45	-77	9	99	114
4	199	-181						
5	629	602		h = 9, l = 2			h = -2, l = 3	
6	85	52	0	201	-207	1	813	743
7	231	254	2	122	-137	2	621	530
			3	50	-51	3	354	320
	h = 2, l = 2					4	740	649
0	1330	1416		h = -11, l = 3		6	410	413
2	816	913	2	92	85	7	105	-111
3	109	-111				8	112	122
4	237	236		h = -10, l = 3		9	76	-72
5	133	-139	1	157	160			
6	92	-75	3	106	96		h = -1, l = 3	
8	107	-132				1	848	733
				h = - 9, l = 3		2	930	-749
	h = 3, l = 2		1	336	-385	3	475	412
0	784	-772	2	104	-81	4	903	-777
1	168	-198	3	165	-172	6	412	-403
2	634	-649	4	91	-69	7	116	-96
3	484	-485				8	108	-128
4	226	-231		h = -8, l = 3		9	70	-60
5	421	-424	2	257	278			
6	103	98	4	313	325		h = 0, l = 3	
7	177	-190	6	171	177	1	1337	-1377
8	95	121				2	97	91
				h = -7, l = 3		3	628	-557
	h = 4, l = 2		1	392	465	4	87	67
0	175	-162	2	191	-192	7	128	131
1	298	307	3	201	226	9	86	111
2	195	-190	4	270	-256			
3	577	595	6	182	-183		h = 1, l = 3	
4	114	-120	7	63	-51	1	709	785
5	448	460				2	583	589
7	182	206		h = -6, l = 3		3	548	512
			1	641	-776	4	589	584
	h = 5, l = 2		3	468	-467	6	313	325
0	755	761	4	112	-77	7	134	-133
1	108	-85	7	132	104	8	108	112
2	572	552				9	63	-85
3	198	-181		h = -5, l = 3				
4	175	178	1	511	576		h = 2, l = 3	
5	122	-128	2	584	596	1	296	274
			3	236	203	2	506	-520
	h = 6, l = 2		4	643	606	3	242	251
0	565	-540	6	347	334	4	630	-657
1	105	-89	8	101	110	6	360	-400
2	368	-372				8	90	-117
3	194	-187		h = -4, l = 3				
4	96	-96	1	696	739		h = 3, l = 3	
5	139	-143	2	463	-443	1	931	-956
7	48	-61	3	214	208	2	200	187
			4	528	-529	3	466	-464
	h = 7, l = 2		6	318	-298	4	180	177
1	141	128	7	104	-100	6	98	83
3	284	277	8	107	-90	7	107	107
5	204	238						
	h = 8, l = 2			h = -3, l = 3			h = 4, l = 3	
0	243	229	1	1060	-1101	1	632	612
2	195	193	2	59	-49	2	259	215
			3	699	-626	3	290	286

$h = 4,\ l = 3$

4	283	263
6	134	156

$h = 5,\ l = 3$

2	387	−372
4	381	−404
6	193	−244

$h = 6,\ l = 3$

1	410	−361
3	211	−219
4	107	122
6	75	63

$h = 7,\ l = 3$

1	320	295
3	137	130
4	109	103

$h = 8,\ l = 3$

2	136	−139
4	95	−151

$h = 9,\ l = 3$

1	84	−159

$h = -12,\ l = 4$

0	95	−90

$h = -11,\ l = 4$

0	202	197
2	120	130

$h = -10,\ l = 4$

1	126	−93
3	212	−195
5	145	−152

$h = -9,\ l = 4$

0	282	−306
2	230	−218
3	151	119
5	107	114

$h = -8,\ l = 4$

0	433	461
2	368	374
4	160	151

$h = -7,\ l = 4$

0	326	−349
1	159	−174
2	213	−215
3	385	−398
5	339	−327
7	120	−129

$h = -6,\ l = 4$

0	575	−580
1	203	205
2	346	−352

$h = -6,\ l = 4$

3	422	366
5	304	262
7	148	128

$h = -5,\ l = 4$

0	815	864
1	83	82
2	659	656
3	88	88
4	191	186
6	133	−103
8	118	−110

$h = -4,\ l = 4$

0	422	−447
1	239	−226
2	365	−324
3	561	−516
4	127	−118
5	471	−453
7	200	−206
8	98	71

$h = -3,\ l = 4$

0	544	−624
1	350	333
2	520	−473
3	728	683
4	191	−168
5	534	510
7	188	201
8	90	87

$h = -2,\ l = 4$

2	1044	901
4	270	253
8	102	−119

$h = -1,\ l = 4$

0	801	−859
1	437	−410
2	735	−636
3	732	−654
4	218	−187
5	450	−417
7	177	−190
8	93	107

$h = 0,\ l = 4$

0	509	−513
1	196	226
2	424	−389
3	698	626
4	141	−124
5	620	583
7	233	249

$h = 1,\ l = 4$

0	1076	1106
1	132	−150
2	769	801

$h = 1,\ l = 4$

3	205	−216
4	286	262
5	116	−114
8	124	−129

$h = 2,\ l = 4$

0	685	−714
1	177	−179
2	521	−515
3	388	−370
4	155	−139
5	320	−302
7	156	−145

$h = 3,\ l = 4$

1	295	281
3	573	536
5	429	391
7	193	166

$h = 4,\ l = 4$

0	692	619
2	514	451
3	128	−103
4	164	145
5	124	−114

$h = 5,\ l = 4$

0	446	−388
2	329	−286
3	149	−125
5	174	−136

$h = 6,\ l = 4$

1	174	131
3	316	252
5	212	194

$h = 7,\ l = 4$

0	332	259
2	260	191
3	151	−114
4	80	61

$h = 8,\ l = 4$

0	211	−187
2	110	−137

$h = -8,\ l = 5$

2	197	−199

$h = -7,\ l = 5$

1	399	−496
3	228	−232

$h = -6,\ l = 5$

1	211	216
2	331	325
3	166	150
4	435	410
6	227	236

$h = -5,\ l = 5$

1	390	403
2	376	−349
3	269	228
4	421	−404
6	242	−240

$h = -4,\ l = 5$

1	907	−932
3	501	−486

$h = -3,\ l = 5$

1	573	591
2	523	463
3	271	233
4	471	432
6	188	241

$h = -2,\ l = 5$

1	541	548
3	231	184
4	704	−637
6	344	−383

$h = -1,\ l = 5$

1	701	−876
2	122	124
3	596	−522

$h = 0,\ l = 5$

1	523	685
2	331	353
3	332	321
4	404	398
6	246	252

$h = 1,\ l = 5$

2	424	−459
4	456	−494
6	223	−261

$h = 2,\ l = 5$

1	658	−742
3	314	−335
7	106	107

$h = 3,\ l = 5$

1	300	354
2	158	157
3	214	213
4	201	216
6	135	144

$h = 4,\ l = 5$

2	279	−276
4	310	−315
6	159	−194

$h = 5,\ l = 5$

1	386	−354
3	189	−172
4	143	124

$h = 6,\ l = 5$

1	336	266
2	100	79
3	142	142
4	78	99

$h = 7,\ l = 5$

2	65	−98

the interaction between donor and acceptor molecules is considerably stronger in the mercuric chloride compound than in the present compound and the angle deduced from the present investigation (155.6°) therefore appears reasonable.

In Fig. 2 a schematical drawing of the dione molecule is presented indicating the positions of all atoms the coordinates of which are given in Table 1.

Table 1 contains the coordinates of all atoms the positions of which we actually regard as having been determined. Interatomic distances and angles are listed in Table 2. A comparison between calculated and observed structure factors is presented in Table 3 (on a scale ten times that of an absolute scale).

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