Crystal Structure of the 1:1 Addition Compound

Iodoform-1,4-Dioxan

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The crystal structure of the 1:1 addition compound formed by iodoform and 1,4-dioxan has been determined by X-ray crystallographic methods at $-25°C$. The space group is *Pnma* and the unit cell containing four formula units has the lattice constants: $a = 6.89(0.006)$ Å, $b = 19.97(0.010)$ Å, $c = 8.08(0.008)$ Å. The dioxan molecules are situated in centres of symmetry, the iodoform molecules in symmetry planes. Two iodine atoms belonging to a particular iodoform molecule form charge transfer bonds with oxygen atoms belonging to neighbouring dioxan molecules, the result being endless chains of alternating donor and acceptor molecules in the crystal. The $O\cdots I$ distance is $3.04(0.04)$ Å, and about 0.50 Å shorter than that anticipated for van der Waals' contact.

PMR spectra of the compound have been recorded between temperatures $-50°C$ and $+10°C$. The line width narrows from 14 gauss at $-50°C$ to 4.2 gauss at $+10°C$, demonstrating that a reorientation takes place in the solid. The X-ray analysis indicates that the movement may be described as a rotation of the dioxan molecule about an axis drawn between the two oxygen atoms.

This study, dealing with the structure of the compound iodoform-1,4-dioxan, is part of an investigation of the structures of charge transfer complexes with a halide molecule as acceptor. The crystal structures of four addition compounds have already been determined in which iodoform molecules act as electron acceptors, *i.e.* complexes with dithiane, quinoline, sulphur (S_8), and diselenane. These complexes exhibit the common feature in that the linkage donor(N, S, or Se)-halogen-carbon is approximately linear, corresponding to the linear or nearly linear donor-halogen-halogen groupings in the complexes with halogen molecules as acceptors.[1] However, iodine bonded to carbon is a poorer acceptor than molecular iodine as shown by the large donor-iodine distance observed; for example with nitrogen as donor atom

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the N$\cdots$I distance in the iodoform complex is about 3.05 Å compared with 2.30 Å in the I_2 complex.

The C—I bond distances in the complexes studied so far are not significantly different from that in the free molecule. A lengthening may, however, be expected, although to a smaller extent than the elongated I—I distances in the complexes with iodine as the acceptor molecule.

Unlike these iodoform adducts, the components of the solid complex of bromodichloromethane with diethyl ether are linked by a hydrogen bond.[2] No structure of an iodoform adduct with an ether has been investigated, however. The compound iodoform-1,4-dioxan, first described by Rheinboldt and Luyken [3] therefore appeared to be of considerable interest.

EXPERIMENTAL

Needle-shaped crystals of the compound were prepared by evaporation of the solvent from a solution of iodoform in dioxan at about 15°C. The crystals sublime and decompose easily in free air. They were therefore sealed in thin-walled glass capillaries and kept at −25°C during X-ray exposure. With excess of dioxan in closed capillaries the crystals were stable up to about 20°C. The crystals used for the experiments had a nearly circular cross section with diameter about 0.12 mm. Oscillation and Weissenberg diagrams showed that the compound formed orthorhombic crystals. The space group derived from the X-ray extinctions can either be $Pn2_1a$ or $Pnma$. The latter was assumed to be the correct one and this was confirmed in the course of the structure determination. The intensity material collected consisted of $hk0$ zone precession diagrams ($\mu=30°$, MoKα-radiation) and equi-inclination integrated Weissenberg diagrams (CuKα-radiation) with rotation about the needle axis which is parallel with [100] ($h=0$ to $h=3$). The intensities were measured photometrically, except for the weakest reflections which were estimated visually. Of the 732 possible independent reflections on these films, 509 were observed. Corrections for absorption and secondary extinction [4] were applied. The b- and c-axes were determined from a zero layer Weissenberg photograph which was calibrated with a superimposed barium fluoride powder pattern (based on $a=6.2001$ Å for BaF_2). The a-axis was determined from $hk0$-zone precession diagrams, calibrated with the b-axis determined from the Weissenberg photograph as a secondary standard.

PMR spectra of the polycrystalline material were recorded between temperatures −50°C and +10°C. A Varian broadline spectrometer operating at 60 MHz was applied. The compound was too unstable for recordings above +10°C.

CRYSTAL DATA

Orthorhombic space group $Pnma$.
Cell constants at −25°C, with estimated standard deviations: $a=6.89(0.006)$ Å, $b=19.97(0.010)$ Å, $c=8.08(0.008)$ Å. Calculated density 2.38 g cm^{-3}. $Z=4$.

STRUCTURE ANALYSIS

The positions of the iodine atoms were found from Patterson maps in the [100] and [001] projections and the parameters were refined, first by Fourier calculations, then by a full matrix least squares program * utilizing all the

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* Program written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood (*IUCr World List* No. 384), modified and adapted for UNIVAC 1107 by Chr. Rømming.

intensity data. The weighting scheme used in the least squares calculations was that of Hughes [5] with $4F_o$ (min)$=20$ and the atomic form factors those given by Hanson, Herman, Lea, and Skillman.[6] The light atom positions could not be found from the two-dimensional analyses and a three-dimensional Fourier map with signs based on the heavy atoms was therefore worked out.* From this map the positions of the oxygen and carbon atoms were found. The electron density of the dioxan carbon atoms appeared, however, as elongated maxima and the molecule from the refinements approached closely a planar model. The distance of the carbon and oxygen atoms from the least squares plane was about 0.006 Å (cf. Table 4). These findings indicate that the dioxan molecule is orientationally disordered. For this reason, PMR spectra of the polycrystalline material were recorded. With only one proton in the iodoform molecule, this corresponds rather closely to the resonance spectra of dioxan. The resulting line width plotted against temperature is shown in Fig. 1. The line width narrows from 14.0 gauss at $-50°C$ to 4.2 gauss at $+10°C$.
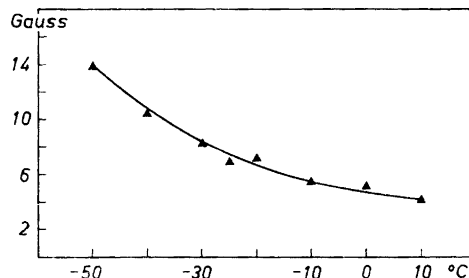
Fig. 1. Line width plotted against temperature for proton magnetic resonance in the polycrystalline material.

This demonstrates that a transition takes place in the solid, from a low temperature "resting model" to a high temperature state representing a rotational motion of the dioxan molecule. The fact that oxygen positions from the Fourier calculations were well defined, indicated that the movement may be described as a rotation of the molecule about an axis drawn between the two oxygen atoms. Two resting models of equal weight were then assumed which would explain the nearly planar model obtained for the dioxan molecule from the Fourier map. The parameters were refined using isotropic temperature factors for the carbon atoms and anisotropic for the oxygen and iodine atoms. The hydrogen atoms were not included in the least squares refinements or the structure factor calculations. The final atomic parameters, with standard deviations estimated from the inverse matrix of the normal equations, are listed in Tables 1 and 2 and the observed and calculated structure factors in Table 3. The final R-factor was 0.120. The distances of the dioxan carbon and oxygen atoms from the least squares plane are given in Table 4. The carbon distances from the plane are 0.41 ± 0.09 Å compared with 0.35 Å calculated for an ideal model of dioxan.

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* Program written by P. K. Gantzel and H. Hope, adapted for UNIVAC 1107 by H. Hope.

Table 1. Atomic coordinates and their standard deviations.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
I_1	0.3679	0.0004	0.3387	0.0001	0.4506	0.0002
I_2	0.7969	0.0007	0.2500	0.0000	0.5485	0.0005
O_1	0.1597	0.0062	0.4662	0.0017	0.5533	0.0035
C_1	0.5315	0.0088	0.2500	0.0000	0.4058	0.0054
C_2	−0.0757	0.0184	0.4399	0.0043	0.5593	0.0102
C_3	−0.0085	0.0158	0.4647	0.0038	0.6276	0.0096
C_4	−0.1693	0.0130	0.4965	0.0036	0.5854	0.0079
C_5	−0.1694	0.0142	0.4644	0.0035	0.5077	0.0084

Table 2. Thermal vibration parameters. The number below each parameter is its standard deviation. Anisotropic values are multiplied by 10^5; isotropic are in $Å^2$. The anisotropic temperature factor is given by $exp - (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

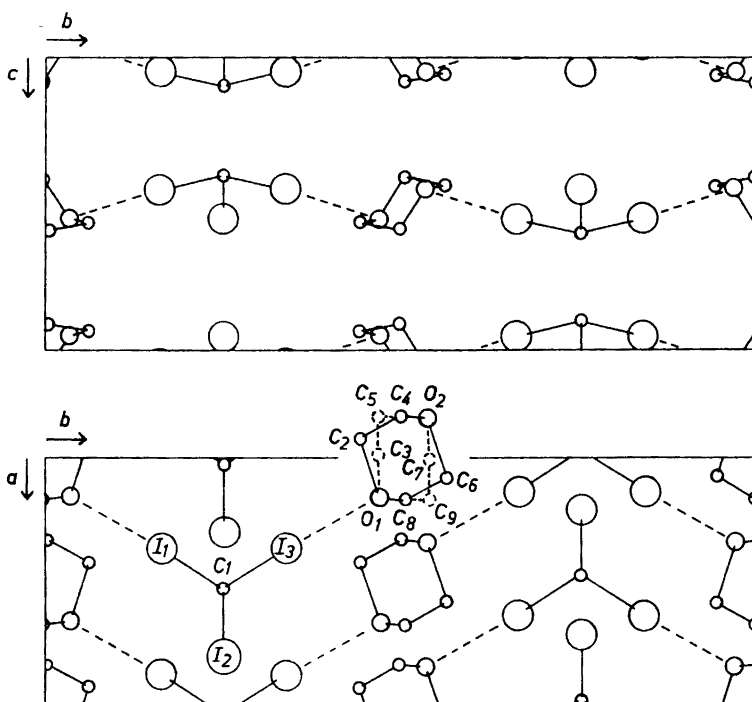| Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Atom	B
I_1	2242	451	2015	432	−9	65	C_1	5.2
	91	9	40	36	75	27		0.9
I_2	1754	650	2942	0	−2196	0	C_2	6.2
	118	16	76	0	149	0		1.6
O_1	4916	668	2876	2085	933	872	C_3	6.3
	1393	123	567	720	1286	401		1.6
							C_4	5.4
								1.3
							C_5	4.9
								1.2

Fig. 2. The structure as seen along the a-axis and the c-axis. For simplicity, only one of the two orientations of dioxan is shown, exept for one molecule.

Table 3. Observed and calculated structure factors. The three columns in each group list values of k, $10F_o$ and $10F_c$. Unobserved reflections are indicated by an asterisk and the values of $10F_o$ given correspond to the minimum observable intensities.

H = 0, L = 0
2	2944	-2697
4	713	519
6	1742	1599
8	527	512
10	3016	-2628
12	2159	1892
14	724	-593
16	539	-473
18	295	279
20	200*	163
22	154*	-273
24	124	149

H = 0, L = 1
1	238*	-460
3	276	-285
5	1737	1594
7	758	-683
9	253*	180
11	431	422
13	234*	-105
15	294	-198
17	277	235
19	224*	-85
21	194*	-50
23	150*	49
25	132*	-10

H = 0, L = 2
0	5197	5079
2	1954	-1973
4	214*	53
6	1199	1192
8	532	281
10	1948	-1947
12	1507	1342
14	419	-385
16	405	-363
18	240	215
20	230*	113
22	152*	-200
24	122*	101

H = 0, L = 3
1	817	-915
3	799	-764
5	2929	2931
7	1502	-1557
9	282	255
11	772	819
13	276	-238
15	515	-430
17	638	514
19	189	-173
21	172*	-97
23	123*	105

H = 0, L = 4
0	939	1046
2	537	-571
4	258	-210
6	358	311
8	234*	-10
10	530	-523
12	305	313
14	245*	-75
16	228*	-147
18	205*	65
20	171*	29
22	123*	-55

H = 0, L = 5
1	538	-756
3	736	-687
5	2129	2129
7	1333	-1324
9	234*	94
11	593	620
13	212	-209
15	419	-375
17	457	434
19	153*	-141
21	118*	-77

H = 0, L = 6
0	627	-589
2	292	266
4	220*	7
6	236	-224
8	214*	-49
10	221*	187
12	253	-264
14	235*	42
16	132*	19
18	146*	-56

| 20 | 103* | -14 |

H = 0, L = 7
1	382	-355
3	360	-298
5	1019	890
7	643	-575
9	307*	6
11	553	274
13	171*	-94
15	188	-189
17	180	194

H = 0, L = 8
0	690	-645
2	378	332
4	192*	148
6	308	-305
8	171*	15
10	285	271
12	259	-277
14	120*	38

H = 0, L = 9
1	157*	-65
3	150*	-56
5	200	172
7	145*	-95
9	123*	-5
11	104*	54

H = 0, L = 10
0	238	-304
2	111	155
4	86*	112

H = 1, L = 1
0	1677	1315
1	702	528
2	1748	-1276
3	1872	1863
4	1458	-1986
5	2030	-3323
6	1796	2029
7	2052	2570
8	369	-421
9	403	-344
10	740	-656
11	566	-477
12	1153	834
13	209	161
14	178	131
15	640	559
16	611	-473
17	697	-620
18	530	281
19	261	237
20	109*	41
21	99*	59
22	99	-148
23	76*	-96
24	61*	51
25	44*	8

H = 1, L = 2
0	2046	2266
1	1455	-1562
2	1662	-1520
3	125*	-60
4	127*	-38
5	420	468
6	453	452
7	551	-655
8	287	243
9	437	-543
10	455	-855
11	610	680
12	416	862
13	364	-340
14	207	-173
15	138	-93
16	140	-96
17	260	202
18	177	151
19	114*	-16
20	105*	60
21	95*	-86
22	83*	-93
23	70*	80
24	56*	59

H = 1, L = 3
0	817	685
1	484	318
2	314	-252
3	634	800

H = 1, L = 4 (continued from k=4)
4	1019	-939
5	1462	-1536
6	868	1125
7	838	1156
8	218	-271
9	160	-146
10	242	-292
11	233	-296
12	271	340
13	134*	75
14	133*	92
15	258	275
16	290	-283
17	305	-305
18	150	151
19	118	115
20	97*	13
21	86*	45
22	74*	-67
23	115*	-46

H = 1, L = 4
0	2203	2328
1	1750	-1534
2	1831	-1592
3	133*	-12
4	182	-135
5	882	762
6	645	555
7	657	-653
8	297	222
9	454	-493
10	773	-975
11	658	810
12	719	965
13	289	-354
14	191	-197
15	154	-137
16	161	-142
17	248	245
18	167	176
19	96*	-40
20	86*	65
21	74*	-109
22	61*	-118

H = 1, L = 5
0	134*	-70
1	134*	15
2	224	171
3	134*	-5
4	175	-107
5	135*	-50
6	193	145
7	135*	-39
8	134*	-49
9	134*	-9
10	133*	63
11	131*	-50
12	129*	-43
13	126*	-27
14	121*	65
15	116*	11
16	109*	-34
17	101*	2
18	92*	18
19	81*	0
20	70*	-4
21	58*	19

H = 1, L = 6
0	1444	1259
1	963	-824
2	949	-841
3	134*	-8
4	204	-151
5	587	530
6	419	375
7	370	-365
8	134	87
9	285	-246
10	549	-569
11	488	481
12	505	539
13	187	-182
14	134	-112
15	121	-104
16	122	-115
17	142	162
18	73*	101
19	62*	-31
20	49*	16

H = 1, L = 7
0	420	-332
1	237	-163

H = 1, L = 7 (continued)
2	212	165
3	246	-194
4	248	190
5	429	403
6	536	-270
7	394	-371
8	119*	61
9	115*	3
10	179	161
11	125	94
12	159	-141
13	94*	-72
14	86*	29
15	79*	-74
16	95	85
17	85	107
18	47*	-42

H = 1, L = 8
0	417	361
1	234	-250
2	250	-233
3	111*	-11
4	109*	-77
5	139	165
6	148	135
7	145	-119
8	97*	15
9	116	-85
10	196	-180
11	151	147
12	149	152
13	58*	-48
14	60*	-32
15	50*	-40

H = 1, L = 9
0	199	-223
1	151	-153
2	93	85
3	129	-113
4	153	166
5	228	282
6	206	-232
7	195	-241
8	69*	54
9	54*	-1
10	79	100
11	56	96

H = 2, L = 0
0	1657	-1695
1	1409	3720
2	1313	1291
3	445	-535
4	1151	-1201
5	2026	-1995
6	526	491
7	1059	1054
8	750	-690
9	997	948
10	544	473
11	2078	-1903
12	576	-579
13	1030	857
14	453	380
15	371	284
16	197*	-132
17	391	-501
18	194*	22
19	178*	123
20	200*	5
21	199*	214
22	197*	27
23	195*	-175
24	190*	-43

H = 2, L = 1
0	567	737
1	437	-417
2	253	-187
3	611	523
4	695	-747
5	359	-415
6	762	934
7	369	447
8	399	-327
9	350	-286
10	398	-312
11	410	143
12	341	256
13	191	-107
14	106*	-6
15	105*	51
16	323	-248
17	115	-90

H = 2, L = 1 (continued)
18	192	128
19	97*	49
20	89*	-10
21	80*	-35
22	70*	-57
23	59*	3
24	46*	23

H = 2, L = 2
0	1156	-1264
1	2863	2669
2	615	837
3	408	-440
4	697	-865
5	1011	-1367
6	340	361
7	567	715
8	371	-447
9	570	745
10	367	393
11	1005	-1395
12	398	-374
13	621	644
14	369	314
15	248	206
16	110*	-74
17	378	-360
18	101*	31
19	116	78
20	86*	7
21	147	161
22	66*	23
23	96	-134
24	39*	-36

H = 2, L = 3
0	1447	1536
1	807	-725
2	417	-358
3	499	839
4	1619	-1469
5	790	-831
6	1540	1904
7	526	751
8	483	-650
9	409	-576
10	409	-656
11	197	230
12	380	557
13	194	-191
14	114*	-2
15	112	95
16	437	-520
17	153	-160
18	298	277
19	121	109
20	79*	-13
21	69*	-57
22	103*	-122
23	46*	8

H = 2, L = 4
0	405	-358
1	901	841
2	222	176
3	296	-217
4	282	-216
5	338	-272
6	148	111
7	166	127
8	117*	-68
9	311	331
10	156	165
11	331	-426
12	114*	-57
13	216	222
14	142	131
15	105*	56
16	100*	3
17	94*	-92
18	86*	27
19	85*	-7
20	69*	1
21	58*	52
22	46*	13

H = 2, L = 5
0	1532	1232
1	502	-421
2	797	-270
3	504	459
4	1343	-1135
5	632	-978
6	1421	1508
7	450	442
8	495	-489

H = 2, L = 5 (continued)
9	398	-400
10	482	-533
11	135	108
12	422	477
13	113	-101
14	101*	21
15	95*	57
16	364	-417
17	86	-94
18	244	237
19	102	89
20	54*	5
21	42*	-25

H = 2, L = 6
0	209	162
1	325	-236
2	139*	-121
3	115*	-46
4	145	125
5	392	320
6	113*	-34
7	204	-192
8	110*	84
9	108*	21
10	105*	-21
11	216	179
12	98*	75
13	94	-60
14	87*	-25
15	81*	-39
16	74*	22
17	89	72
18	56*	5
19	46*	-48

H = 2, L = 7
0	529	538
1	127	-99
2	131	-105
3	168	121
4	514	-504
5	215	-181
6	164	670
7	166	138
8	226	-201
9	134	-119
10	217	-236
11	86*	16
12	197	224
13	76*	-8
14	69*	33
15	61*	12
16	153	-182
17	44*	-25

H = 2, L = 8
0	161	176
1	369	-409
2	127	-139
3	91*	10
4	96	116
5	313	344
6	85*	-48
7	190	-200
8	79*	63
9	117	-76
10	70*	-56
11	216	268
12	59*	71
13	108	-114
14	44*	-55

H = 2, L = 9
0	77	88
1	69*	7
2	68*	0
3	67*	3
4	127	-111
5	63*	-9
6	137	136
7	56*	15
8	53*	-37
9	48*	0
10	42*	-41

H = 2, L = 10
0	36*	64

H = 3, L = 1
0	461	-543
1	234	2006
2	200	157
3	536	-506
4	1906	2233
5	535	-655

Table 3. Continued.

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 6  1855  -2248     21   71*   59      11  603  -761      5  289  -268      6  161  150      20  196*  -31
 7   274    213     22   73   -53      12  215   202      6  989   607      7   77*   53      21  191*  -13
 8  1030   1127     23   45*  -66      13  410   506      7  259   272      8   73*  -12      22  190*  131
 9   819    805                        14  173   201      8  180  -171      9  133   122
10   279    247      H = 3, L = 3      15  105*   50      9  351   339     10   97   -91      H = 6, L = 0
11  1140  -1037      0  233  -212      16  279  -313     10  192  -189     11  156  -182      0  581   521
12   583   -517      1  976   895      17  198  -219     11  436  -493     12   69    67      1  294  -268
13   520    407      2  128    63      18  159   168     12   96*  160     13   90    98      2  287  -217
14   222   -165      3  194  -136      19   75    70     13  497   311                        3  620  -669
15   210    149      4  1210  1125     20   62*   18     14  104    95      H = 3, L = 9      4  191*  121
16   491    499      5  376  -382      21   63    67     15   76*   14      0  149   187      5  1320 1427
17   307   -239      6  923  -1171                       16  167  -178      1  164  -223      6  294   218
18   417   -409      7  164   173      H = 3, L = 5      17  113  -138      2   61*  -62      7  938  -974
19    95*   -41      8  415   512      0  138   101      18   73    86      3   60*   47      8  195*  -86
20   102     68      9  294   369      1  136   -85                        4  154  -172      9  197*   88
21   133    137     10  126*   63      2  125   -87      H = 3, L = 7      5   56*   98     10  198*  -97
22    55    101     11  393  -491      3  130   120      0  245   231      6  184   234     11  301   316
23    57    -90     12  224  -312      4  127   101      1  377  -352      7   48*  -41     12  252   213
                    13  173   173      5  126   -82      2  136  -119      8   73   -91     13  199*  -75
 H = 3, L = 2       14  138  -141      6  128  -124      3  170   123                       14  270  -217
 0   289    312     15  109    94      7  123*   72      4  691  -240      H = 4, L = 0     15  323  -332
 1  1439   1332     16  223   230      8  121*   -4      5  146    64      0  1577 -1699    16  196*  -23
 2   557    269     17  144  -126      9  119*  -36      6  310   290      1  1550 -1387    17  334   305
 3   280   -263     18  199  -220     10  111   -78      7   99*  -19      2  411   311     18  190*   66
 4   975   -995     19   83*  -21     11  114*   24      8  148  -143      3  1133 1147
 5   427   -511     20   77    21     12  104   -26      9  157  -150      4  1666 1541      H = 8, L = 0
 6   936   1094     21   72    74     13  105*  -42     10  133  -107      5  578  -573      0  196   206
 7   347    433     22   50*   58     14   99*  -73     11  178   188      6  1864 -1982     1  196*  -93
 8   375   -430                       15   92*   25     12  123   117      7  535   476      2  196*   28
 9   319    382      H = 3, L = 4      16   85*   -3     13   94   -95      8  710   666      3  273   201
10   134   -127      0  446   454     17   76*   -6     14   53*  -21      9  466  -426      4  421  -496
11   635   -630      1  1792  1587    18   68*  -16     15   54*  -17     10  746   736      5  340  -324
12   190    135      2  117   159     19   57*    0     16   56   -75     11  461   600      6  462   546
13   439    419      3  431  -309     20   45*  -11                       12  701  -637      7  319   333
14   193    193      4  1224 -1050                      H = 3, L = 8     13  597  -527      8  261  -209
15   113*    61      5  566  -506      H = 3, L = 6      0  152   164     14  392*  -03      9  188*  -193
16   309   -277      6  1198  1167    0  463   367      1  346   330     15  414   295
17   189   -175      7  481   507     1  1092  977      2   98*  -60     16  526   533
18   155    154      8  403  -417     2  121*  -24      3  133   -92     17  199*  -38
19   133     79      9  447   510     3  297  -211      4  137  -123     18  402  -344
20    91*     5     10  200  -213     4  530  -532      5  101   -74     19  198*  -21
```

Table 4. Distances from the least squares plane defined by the dioxan molecule.

	Non-planar model	Planar model
Components of normal	(0,0045, 0,0290, 0,1008)	(0,0111, 0,0310, 0,09660)
Distance to origin	-3.292 Å	-3.155 Å
Distances to atoms defining plane:		
O_1	-0.006 Å	-0.005 Å
C_2	-0.322	0.007
C_3	0.430	
C_4	0.485	-0.007
C_5	-0.398	

The principal axes of the thermal vibration ellipsoids for the oxygen and iodine atoms were derived from the final temperature parameters with the results given in Table 5. For the oxygen atoms, the minimum vibrational amplitude is found in a direction approximately parallel with the axis drawn between the two oxygen atoms (angle=6°). The minimum vibrational amplitude of the iodine atom not engaged in donor-acceptor interaction occurs in a direction approximately parallel with the C—I bond (angle=8°). The vibrational motion for the other iodine atom is not markedly anisotropic. The number of thermal parameters for the iodoform molecule was too low to justify a rigid-body analysis of the molecular vibrations.

Table 5. The principal axes of the thermal vibration ellipsoids for the oxygen and iodine atoms.

	Direction cosines of eigenvectors			$(\overline{u^2})^{\frac{1}{2}}$	B
I_1	0.330	−0.940	0.081	0.31 Å	7.6 Å^2
	0.079	−0.058	−0.995	0.26	5.3
	0.941	0.335	0.055	0.22	3.8
I_2	0.000	1.000	0.000	0.36	10.4
	−0.409	0.000	0.913	0.33	8.8
	−0.913	0.000	−0.409	0.17	2.2
O_1	0.616	0.730	0.296	0.45	16.6
	0.449	−0.017	−0.893	0.30	7.0
	0.648	−0.683	0.338	0.22	3.8

DISCUSSION

Interatomic distances and angles, referred to Fig. 2, are listed in Table 6. The dioxan molecules are situated in centres of symmetry, the iodoform molecules in symmetry planes. The shortest intermolecular $I \cdots I$ distance is 4.39 Å and the shortest $O \cdots C$ and $C \cdots C$ distances between neighbouring dioxan molecules are 3.21 Å and 3.35 Å, respectively. Two iodine atoms belonging to a particular iodoform molecule form charge transfer bonds with oxygen atoms of neighbouring dioxan molecules. The $O \cdots I$ distance is 3.04(0.04) Å and about 0.50 Å shorter than the corresponding van der Waals' distance. The angle $O-I-C$ is 173.2(1.4)° and the compound contains chains similar

Table 6. Interatomic distances and angles and their estimated standard deviations.

Distance			Angle		
I_1-I_3	3.542 Å	0.006 Å	$I_1-C_1-I_3$	112.5°	2.7°
I_1-I_2	3.534	0.006	$I_1-C_1-I_2$	110.9	1.4
I_1-C_1	2.130	0.033	$C_1-I_3-O_1$	173.2	1.4
I_2-C_1	2.162	0.057	$I_3-O_1-O_2$	135.3	1.4
I_3-O_1	3.039	0.036	$I_3-O_1-C_2$	101.4	3.3
O_1-O_2	2.72	0.08	$I_3-O_1-C_8$	102.3	3.6
O_1-C_2	1.70	0.13	$I_3-O_1-C_3$	121.6	3.9
O_1-C_8	1.35	0.08	$I_3-O_1-C_9$	132.5	3.8
C_2-C_4	1.32	0.12			
O_1-C_3	1.31	0.11			
O_1-C_9	1.47	0.08			
C_3-C_5	1.47	0.13			

to those found in the 1:1 complex formed between iodoform and dithiane.[7] The dithiane complex is, however, monoclinic and not isomorphous with the present compound. The plane through the dioxan oxygen atoms and the iodine atoms linked to it is not significantly different from a mirror plane for each of the two resting models of the dioxan molecule. The angle $O-O-I$ is 135° whereas the "ideal" axial and equatorial angles are 99° and 152°. For one of the resting positions of dioxan, the $O-I$ bond direction thus deviates about 36° from the axial direction, for the other position 17° from the equatorial

Table 7. Differences (in Å) between donor-acceptor bond distances and the sums of the corresponding covalent radii for N−I, Se−I, S−I and O−I bonds.

Donor	Covalent radii sum (Å)	Acceptor					
		I_2[9,10]	ICl[11−13]	C_2I_4[14]	C_2I_2[15]	CHI_3[7,16] (two-coord.)	CHI_3[17,18] (three-coord.)
Quinoline	2.02						1.03
Pyridine	2.02		0.24				
Trimethyl-amine	2.02	0.25	0.28				
Diselenane (two-coordinated)	2.50	0.33			0.84		
Dithiane	2.37	0.50			0.90	0.95	
Diselenane (four-coordinated)	2.50			{0.90 {0.93		{0.97 {1.01	
Dioxan	1.98		0.59			1.06	
Sulphur(S_8)	2.37						1.13

direction. The intramolecular O···O distance is 2.72(0.08) Å and not significantly different from the value 2.770 Å found for the free molecule.[8]

In Table 7 the lengthening of the charge-transfer bond from that of a covalent single bond is compared for several complexes with iodine as the acceptor atom. If one assumes that the strength of the interaction increases as the donor-acceptor distance approaches the covalent bond length, then it follows from the complexes with I_2 and ICl as acceptors that the strength of the n donors increases with change of centre of coordination in the order O<S<Se<N. Selenium is also a stronger donor than sulphur in the diselenane and dithiane compounds with di-iodoacetylene. In the latter two complexes, molecules are linked together by charge transfer bonds to form endless chains of alternating donor and acceptor molecules. In the I_2- and ICl-complexes each acceptor molecule is only bonded with one donor atom, and each donor atom is linked to one acceptor atom.

For the iodoform complexes one must also take into account the number of donor-acceptor coordinations when comparing donor or acceptor strengths. In the compound iodoform-diselenane the donor molecule is four-coordinated in the sense that each of the two selenium atoms forms bonds with two acceptor atoms. From the table it is seen that the latter Se−I bonds are weaker than the S−I bonds in the two-coordinated dithiane complex with iodoform. The Se−I bonds are therefore weaker than corresponding bonds with only one free electron pair of each selenium atom involved in charge transfer interaction. This also implies that iodine is a weaker acceptor in C_2I_2 than in C_2I_4 (four-coordinated), and the acceptor strength diminishes in the order:

I_2,ICl>C_2I_4>C_2I_2>CHI_3(two-coordinated)>CHI_3(three-coordinated).

In the iodoform complexes with quinoline and sulphur(S_8) all three iodine atoms belonging to a particular acceptor molecule are linked to different

donor molecules. If the order of donor strengths is considered, these inter-molecular bonds are weak compared with those of the other iodoform complexes with only two of the three iodine atoms involved in donor-acceptor interaction. Thus, the formation of a donor-acceptor bond weakens the acceptor properties of the other two iodine atoms. This can be understood if net charge is transferred from the donor to each of the three iodine atoms. Lengthening of all the three C—I distances may therefore be expected, even in cases where only two of the three iodine atoms are engaged in bond formation.

Infrared or Raman spectra of the dioxan addition compound have not been reported, but the solid state spectra of the dithiane and diselenane analogues agree with the symmetries found from the X-ray analyses.[19] The (C—I) stretching modes are, however, insufficiently affected by the charge transfer interaction to cause splitting which is required if the local symmetry of the iodoform molecule is modified from C_{3v}. Neither are the individual distances in the iodoform molecule found for the complexes studied significantly different from a model with C_{3v} symmetry. The various C—I, respectively I—I distances for the dioxan, diselenane, and dithiane complexes have therefore been averaged to give the molecular parameters. To simplify the calculation of the standard deviation, the iodine coordinate errors were considered uncorrelated to each other and independent of direction. The variance of the average bond lengths are then

$$\sigma^2(C—I) = \tfrac{1}{3}\sigma^2(I)+\sigma^2(C)\ \cos^2\alpha$$
$$\sigma^2(I—I) = \sigma^2(I)$$

where σ (C) is the standard deviation of carbon in the direction of the trigonal axis and α ($\sim$74.0°) is the angle between the trigonal axis and the C—I bond. Standard deviations due to error in unit cell dimensions have also been included in the final values. The latter is the more important source of error for the

Table 8. C—I and I···I distances in the iodoform complexes assuming C_3 symmetry.

Donor molecule	Crystallographic symmetry	Distances (Å)			
		C—I	σ	I···I	σ
Quinoline	C_3	2.124	0.012	3.541	0.007
Diselenane	C_1	2.141	0.010	3.553	0.007
Dithiane	C_{1v}	2.143	0.016	3.531	0.007
Dioxan	C_{1v}	2.141	0.012	3.536	0.005
Sulphur	C_{3v}	—	—	3.553	0.007

long I—I distance. The mean distances and standard deviations have been listed in Table 8. For the complex $CHI_3 \cdot 3S_8$ the accuracy in the C—I distance is rather poor due to overlapping atoms and no value has been quoted in the table.

The mean C—I distance from Table 8 is 2.137(0.006) Å. No accurate structure determination of the gaseous iodoform molecule has been reported in the

literature, but the carbon-iodine bond length is expected to lie between the values 2.134 Å observed in CIF_3 and 2.140 Å observed in CIH_3 in the gas phase.[20,21] This corresponds closely to the $C-I$ distances in Table 8. The latter have not been corrected for vibrational oscillations, however. The lengthening in the $C-I$ distances when the complex is formed, is therefore of the same order of magnitude as the correction due to vibrational oscillation and probably less than 0.01 Å.

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