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Crystal Structure of the 1 : 3 Addition Compound Iodoform-Quinoline

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Details of the crystal structure determination of the 1:3 addition compound iodoform-quinoline are reported. The structure is trigonal rhombohedral with the (hexagonal) lattice parameters:

$$a = 22.40 \text{ Å} \qquad c = 4.59 \text{ Å}$$

both figures with a probable error not exceeding 0.5 %. The primitive (rhombohedral) unit cell contains one molecule of iodoform and three molecules of quinoline. The space group is *R*3. Charge transfer bonds connect every iodine atom with a quinoline nitrogen atom. The I—N distance (3.05 Å) is about 0.60 Å shorter than the van der Waals radius sum of nitrogen and iodine and the C—I—N angle is found equal to 176.8°.

During the last few years the crystal structure of some addition compounds formed by halide molecules and molecules which are known to possess marked electron donor properties have been studied in our laboratory. Among the halides present in the addition compounds studied is iodoform, oxalyl chloride and oxalyl bromide. The donor molecules selected are quinoline, sulphur (S_8), 1,4-dioxan and 1,4-dithiane. In all cases so far examined it has been found that a particular halogen atom of the acceptor molecule is directly linked to an oxygen, sulphur or nitrogen atom belonging to the donor molecule and that the arrangement carbon-halogen-donor atom is approximately *linear* [1,2].

The addition compound between iodoform and quinoline was first prepared by Rhoussopoulos [3]. Dipole moment measurements in carbon tetrachloride solution indicate that the 1:3 complex is present even in dilute solutions[4].

A short communication summing up the main results obtained for the 1:3 compound iodoform-quinoline has been published in 1959 [1]. Here, further details of this investigation will be given and in a forthcoming publication the structure determination of crystals of the 1:3 compound iodoform-sulphur will be described.

The needle-shaped crystals used in the X-ray analysis were obtained from ether solution. The melting point was found equal to 65°C and the measured density was 1.90 g·cm^{-3}. The hexagonal cross section of the needle was about 0.005 mm^2. Corrections for absorption or secondary extinction were not introduced.

The material on which the structure determination is based consists partly of ordinary Weissenberg diagrams taken with CuK radiation (the hexagonal $hk0$ zone) and the multiple film method was employed with visual estimation of the intensities. For the other zones integrated Weissenberg diagrams with Mo$K\alpha$ radiation were obtained and the intensities measured photometrically.

The space group is $R3$ and the primitive rhombohedral unit cell contains one molecule of iodoform and three molecules of quinoline. X-Ray reflections were however, mainly indexed using the triple primitive "hexagonal" unit cell with the lattice constants:

$$a = 22.40 \text{ Å} \qquad c = 4.59 \text{ Å}$$

The structure determination started with the working out of a two-dimensional Fourier projection along the chief axis. Centers of symmetry and symmetry planes are lacking in the structure, but threefold axes are present on which the iodoform molecules must be situated. The quinoline molecules, however, occupy general positions. These conditions and the presence of the heavy iodine atoms simplifies the determination of the approximate x and y coordinates of the latter atoms and the corresponding coordinates of the iodoform carbon atom are fixed. Even with these simplifications the great number of light atoms in general positions made the task of working out a Fourier projection along the trigonal axis somewhat cumbersome. Taking advantage of the detailed information now available regarding the structure of the pyridine molecule it was possible, however, to choose a model of the quinoline molecule which eventually led to a Fourier projection in which the light atoms were sufficiently well resolved to make possible the refinement of the coordinates by least squares computations. These computations were carried out using a Ferranti Mercury computer.

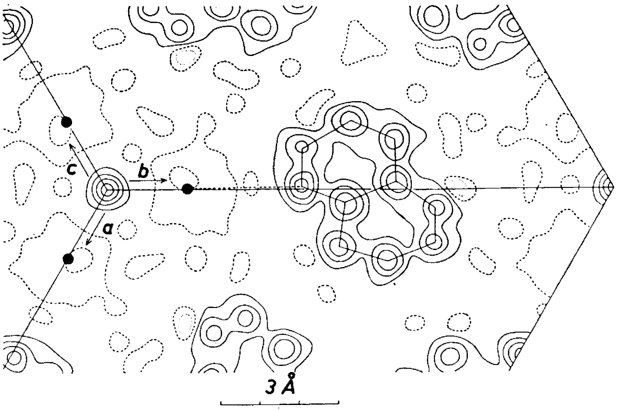

Fig. 1. Electron density projection along the trigonal axis. Contour lines at intervals of 2 e·Å^{-2}. The three axes indicated are the projections of the rhombohedral axes.

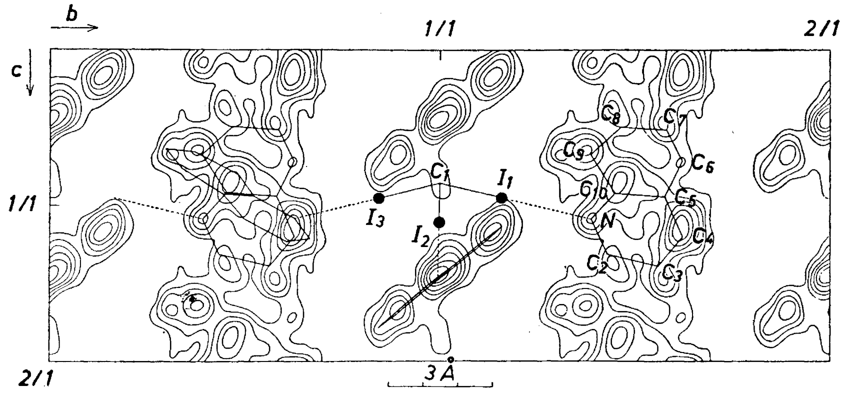

Fig. 2. Electron density projection along [110] (hex. [122]). Contour lines at intervals of 2 e·Å^{-2} from 4 e·Å^{-2} upwards. Contribution from the iodine atoms is subtracted. The axes indicated are the projections of the rhombohedral axes.

The B values of the temperature factor arrived at are as follows: $B_I = 2.14$; $B_N = 1.85$ and B_C (mean value) $= 2.87$. In the final refinement of the coordinates the mean value $B_C = 2.87$ was employed for all carbon atoms. The Fourier map reproduced in Fig. 1 is based on the x and y coordinates thus obtained and by subtracting the contribution from the iodine atoms. The x and y values have been listed in Table 1. The R value corresponding to these coordinates is 0.065 not including unobserved reflections. The number of observed reflections is 107, the number of possible reflections 122.

The results so far (*cf.* Fig. 1) indicated the presence of a bond between each iodoform iodine atom and the nitrogen atom of a particular quinoline molecule and an angle C—I—N of approximately 180°. Final conclusions could not, however, be drawn without determining the z coordinates and a number of two-dimensional Fourier syntheses were therefore worked out with projection along different crystallographic directions. It was found that the most satisfactory resolution could be obtained by choosing the rhombohedral [110] direction (hexagonal [122]).

Table 1.

Atom	x	y	z
I	−0.0531	0.0523	0.0000
N	−0.1302	0.1239	0.2135
C_1	0.0000	0.0000	−0.1249
C_2	−0.1753	0.0810	0.3920
C_3	−0.2398	0.0799	0.4691
C_4	−0.2469	0.1309	0.3268
C_5	−0.1984	0.1813	0.1222
C_6	−0.1931	0.2369	−0.0479
C_7	−0.1530	0.2769	−0.2121
C_8	−0.1003	0.2666	−0.2420
C_9	−0.0852	0.2171	−0.1133
C_{10}	−0.1401	0.1705	0.0874

Table 2. Observed and calculated structure factors and phase angles.

[001] projection

h	k	l	F_o	F_c	a
0	3	0	117	108	67.4
0	6	0	357	396	126.9
0	9	0	128	126	144.4
0	12	0	229	240	243.1
0	15	0	94	87	251.6
0	18	0	139	138	12.3
0	21	0	95	90	358.2
0	24	0	67	81	114.2
1	1	0	193	207	355.6
1	4	0	245	273	123.6
1	7	0	262	258	111.9
1	10	0	142	129	231.0
1	13	0	196	198	243.8
1	16	0	113	111	338.2
1	19	0	119	126	305.1
1	22	0	43	51	77.9
2	2	0	186	204	356.4
2	5	0	270	288	118.2
2	8	0	74	60	90.0
2	11	0	191	192	246.2
2	14	0	79	69	214.3
2	17	0	134	132	6.3
2	20	0	< 49	50	358.2
2	23	0	47	54	132.5
3	3	0	110	102	170.8
3	6	0	142	144	61.3
3	9	0	116	108	305.7
3	12	0	101	93	208.1
3	15	0	54	54	90.0
3	18	0	82	90	347.5
3	21	0	< 42	39	179.6
4	1	0	217	228	255.0
4	4	0	95	99	178.2
4	7	0	140	126	3.7
4	10	0	92	87	337.5
4	13	0	115	96	119.2
4	16	0	< 55	48	99.0
4	19	0	74	69	270.0
4	22	0	< 32	39	219.8
5	2	0	247	264	248.1
5	5	0	214	216	355.2
5	8	0	219	216	3.9
5	11	0	95	90	122.2
5	14	0	138	141	114.3
5	17	0	53	42	211.0
5	20	0	85	96	240.8
6	3	0	129	126	267.3
6	6	0	286	312	4.8
6	9	0	81	90	23.7
6	12	0	182	168	118.2
6	15	0	89	84	115.7
6	18	0	115	123	242.1
7	1	0	262	255	246.6
7	4	0	229	234	357.0
7	7	0	247	255	353.1
7	10	0	127	120	109.3
7	13	0	158	171	120.4
7	16	0	60	57	223.0
7	19	0	86	102	239.1
8	2	0	47	39	248.2
8	5	0	172	162	3.0
8	8	0	99	96	3.5
8	11	0	155	150	118.5
8	14	0	< 54	52	120.2
8	17	0	91	75	238.4
9	3	0	121	114	24.7
9	6	0	124	117	342.0
9	9	0	60	51	11.3
9	12	0	84	81	104.5
9	15	0	< 50	20	316.5
9	18	0	58	54	231.3
10	1	0	156	150	128.8
10	4	0	69	57	31.0
10	7	0	107	90	242.0
10	10	0	< 55	42	174.7
10	13	0	75	72	31.8
10	16	0	49	45	298.1
11	2	0	174	168	115.2
11	5	0	81	78	257.5
11	8	0	150	141	241.4
11	11	0	54	54	0.0
11	14	0	98	105	351.4
11	17	0	< 31	21	102.7
12	3	0	89	81	129.5
12	6	0	193	189	241.5
12	9	0	71	78	247.4
12	12	0	113	117	3.0
12	15	0	66	63	10.3
13	1	0	201	213	116.2
13	4	0	159	147	235.7
13	7	0	155	156	242.5
13	10	0	80	84	336.3
13	13	0	112	123	4.5
14	2	0	73	60	170.5
14	5	0	140	141	242.4
14	8	0	< 54	56	248.9
14	11	0	105	99	358.4
14	14	0	49	51	6.5
15	3	0	< 54	38	275.2
15	6	0	95	96	230.2
15	9	0	50	42	28.1
15	12	0	73	75	348.2
16	1	0	99	102	26.6
16	4	0	77	69	272.2
16	7	0	60	54	153.4
16	10	0	49	39	45.0
17	2	0	101	96	344.7
17	5	0	< 53	44	147.5
17	8	0	82	84	111.0
17	11	0	< 31	15	296.3

Table 2. Continued.

h	*k*	*l*	F_o	F_c	*a*
18	3	0	62	66	39.1
18	6	0	101	105	118.1
18	9	0	41	48	126.0
19	1	0	146	159	357.7
19	4	0	89	93	109.6
19	7	0	86	102	121.0
20	2	0	64	57	2.7
20	5	0	95	108	115.8
21	3	0	< 42	33	166.8
22	1	0	< 43	23	251.9
22	4	0	< 31	43	129.6
23	2	0	51	57	220.2
			[122] projection		
−2	1	0	188	201	4.3
−4	2	0	181	198	3.7
−6	3	0	98	108	188.9
−8	4	0	99	99	183.5
−10	5	0	200	210	5.1
−12	6	0	281	288	354.5
−14	7	0	223	225	7.7
−16	8	0	71	72	355.2
−18	9	0	50	57	173.3
−20	10	0	38	36	194.1
−22	11	0	46	39	0.0
−24	12	0	97	90	356.4
−26	13	0	87	84	356.0
−28	14	0	< 50	27	350.5
28	−15	1	< 50	21	17.7
26	−14	1	78	72	349.1
24	−13	1	88	81	352.4
22	−12	1	< 43	27	34.4
20	−11	1	72	57	135.0
18	−10	1	94	99	132.4
16	−9	1	66	63	43.1
14	−8	1	142	144	6.1
12	−7	1	202	207	0.9
10	−6	1	120	129	26.6
8	−5	1	165	159	125.4
6	−4	1	229	222	140.3
4	−3	1	142	150	40.7
2	−2	1	194	177	15.1
0	−1	1	385	375	346.9
−2	0	1	188	177	14.7
−4	1	1	241	213	134.5
−6	2	1	277	270	141.5
−8	3	1	108	99	131.6
−10	4	1	144	138	28.7
−12	5	1	244	249	353.7
−14	6	1	160	159	3.2
−16	7	1	62	45	58.6
−18	8	1	96	87	143.8
−20	9	1	79	75	136.5
−22	10	1	< 43	24	18.2
−24	11	1	86	81	2.0
−26	12	1	80	72	355.7
−28	13	1	< 50	24	14.8
26	−15	2	< 51	39	350.9
24	−14	2	< 49	42	340.3
22	−13	2	< 46	30	79.2
20	−12	2	117	120	115.9
18	−11	2	105	99	128.1
16	−10	2	79	87	90.0
14	−9	2	93	96	345.1
12	−8	2	122	108	344.2
10	−7	2	87	63	43.6
8	−6	2	105	99	110.0
6	−5	2	253	264	124.5
4	−4	2	95	93	88.2
2	−3	2	131	117	6.3
0	−2	2	186	174	355.3
−2	−1	2	105	96	11.6
−4	0	2	93	96	88.2
−6	1	2	230	240	117.9
−8	2	2	81	87	90.0
−10	3	2	101	93	17.4
−12	4	2	127	132	351.9
−14	5	2	106	108	345.2
−16	6	2	79	78	103.0
−18	7	2	92	93	128.7
−20	8	2	87	87	116.6
−22	9	2	< 46	33	79.2
−24	10	2	58	60	342.5
−26	11	2	51	45	353.3
22	−14	3	< 51	24	119.1
20	−13	3	75	81	123.7
18	−12	3	93	96	124.7
16	−11	3	46	45	135.0
14	−10	3	44	42	293.2
12	−9	3	51	60	293.6
10	−8	3	< 41	30	127.3
8	−7	3	142	138	121.3
6	−6	3	190	201	118.2
4	−5	3	156	159	119.5
2	−4	3	< 38	3	295.4
0	−3	3	59	66	306.8
−2	−2	3	< 38	12	51.6
−4	−1	3	110	105	125.0
−6	0	3	188	201	118.6
−8	1	3	147	159	124.3
−10	2	3	42	30	120.3
−12	3	3	< 43	9	185.5
−14	4	3	< 44	36	289.3
−16	5	3	75	75	113.5
−18	6	3	93	93	127.2
−20	7	3	79	84	119.5
−22	8	3	< 51	21	110.6
16	−12	4	< 51	39	131.7
14	−11	4	< 51	48	250.1

Table 2. Continued.

h	k	l	F_o	F_c	a
12	−10	4	< 51	45	261.2
10	− 9	4	< 49	24	195.0
8	− 8	4	79	99	121.3
6	− 7	4	118	123	115.3
4	− 6	4	63	72	140.9
2	− 5	4	< 46	39	218.2
0	− 4	4	87	102	260.2
− 2	− 3	4	50	57	234.5
− 4	− 2	4	72	72	123.2
− 6	− 1	4	102	117	123.2
− 8	0	4	73	99	119.7
−10	1	4	< 49	30	194.9
−12	2	4	< 51	66	265.9
−14	3	4	< 51	42	258.9
−16	4	4	< 51	15	171.3

The z coordinate of the three iodine atoms belonging to the iodoform molecule could arbitrarily be put equal to zero and the z coordinate of the carbon atom was computed assuming the I—C—I angle to be 113°.[5] It was further assumed that the C—I—N angle is approximately 180° and that the quinoline molecule is planar. With these assumptions and using the information obtained from the projection along the trigonal axis, an approximate determination of the orientation of the quinoline plane became possible. Subsequently trial and error computations led to a conclusive decision between the four alternatives still remaining for the relative position of the three quinoline molecules and the iodoform molecule. Taking advantage of the results obtained also from Fourier projection along other directions it was possible to compute preliminary values of all the atomic coordinates which served as starting values in the least squares computations. In this way the iodine coordinates and the coordinates of a nitrogen and two carbon atoms (N, C_3, and C_7 of Fig. 2) were refined. The B values arrived at were as follows: For I_1 and I_3 2.67, for I_2 3.46 (*cf.* Fig. 2). The B value chosen for the light atoms (3.0) was kept fixed during the process of least squares refinement.

The final Fourier map with projection along the rhombohedral [110] direction and reproduced in Fig. 2 is based on these coordinates and the x and y coordinates of the other light atoms taken from the final Fourier map with projection along the trigonal axis. The z coordinates used for these light atoms were computed using the planar model of the quinoline molecule mentioned above The final atomic coordinates are listed in Table 1. The y coordinates determined from the Fourier projection along [122] are in good agreement with those obtained from the projection along the trigonal axis. We consider the latter to be the more accurate and these values are therefore listed in Table 1. The phase angles of the reflections and a comparison between observed and calculated structure factors have been listed in Table 2. The R factor for the projection along [110] is 0.063, not including unobserved reflections. The number of observed reflections is 85, the number of possible reflections 110.

The chief aim of the present crystal structure investigation was the determination of the I—N distance and the "valence angle" N—I—C. From the atomic coordinates given in Table 1 the values 3.05 Å and 176.8° are obtained respectively. The standard deviation for the I—N distance is 0.034 Å. These findings are in full agreement with the assumption of comparatively strong charge transfer bonds between iodine and nitrogen atoms. Other intermolecular separations all agree with those observed in other crystal structures for purely van der Waals type interactions. The I—I distance within the iodoform molecule is found equal to 3.54 Å.

The charge transfer bonds demonstrated in the iodoform-quinoline compound cannot be regarded as exceptional. Analogous bonds are observed in the corresponding compound with sulphur (S_8) and in the 1:1 compound iodoform-dithiane [2,6,7]. Other halides (oxalyl chloride and oxalyl bromide) form addition compounds with dioxan in which charge transfer bonds connect halogen and oxygen, and such bonds are also observed in solid oxalyl bromide [8].

The correctness of the suggestion put forward a few years ago [9] that the forces holding together iodoform and donor molecules in addition compounds depend on bonds between a particular iodine atom and an electron donating atom belonging to the partner molecule has thus been firmly substantiated.

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