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Structure of the Solid Compound Formed by Addition of Two Molecules of Iodine to One Molecule of Pyridine

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The crystal structure of the compound pyridine · $2I_2$ has been investigated. The crystals are *monoclinic*, space group $P2_1/c$, with the lattice constants

$a = 4.42$ $b = 15.37$ $c = 17.65$ $\beta = 103.8°$

The unit cell contains four molecules of pyridine and sixteen atoms of iodine. Centrosymmetrical cations — Py_2I^+ — are present which appear to be at least nearly planar.

The remaining iodine atoms form a network built up of centrosymmetrical triiodide ions with an I—I distance of 2.93 Å and of iodine molecules (I—I = 2.74 Å). Each of the "outer" atoms of the I^-_3 ions is linked to two iodine atoms belonging to iodine molecules by bonds of length 3.44 Å. The anionic arrangement closely resembles that found in tetraethyl-ammonium heptaiodide [7]. The N—I distance in the cation (2.16 Å) appears to be a little shorter than the N—I bond observed in simple addition compounds formed by tertiary amines and iodine.

The substance investigated may properly be regarded as dipyridineiodine heptaiodide.

Crystal structure determination of a number of 1:1 addition compounds formed by amines and halogens have been carried out during the last years [1]. The results are consistent and show that such compounds are true "charge transfer" compounds in which one particular halogen atom is linked to the donor (nitrogen) atom, the second halogen atom pointing away from the donor atom. The arrangement N-Hal-Hal has always been found to be *linear* or at least very nearly so. These findings thus contradict the suggestion put forward by Hantzsch [2] that the addition compounds in question should be regarded as salt-like compounds containing halogen substituted ammonium cations and halogen anions. However, no structure determinations of addition compounds formed by amines and halogen with a molar ratio other than 1:1 appears to have been carried out. It was felt that at least one compound containing more halogen molecules than amine molecules should be investigated. From state-

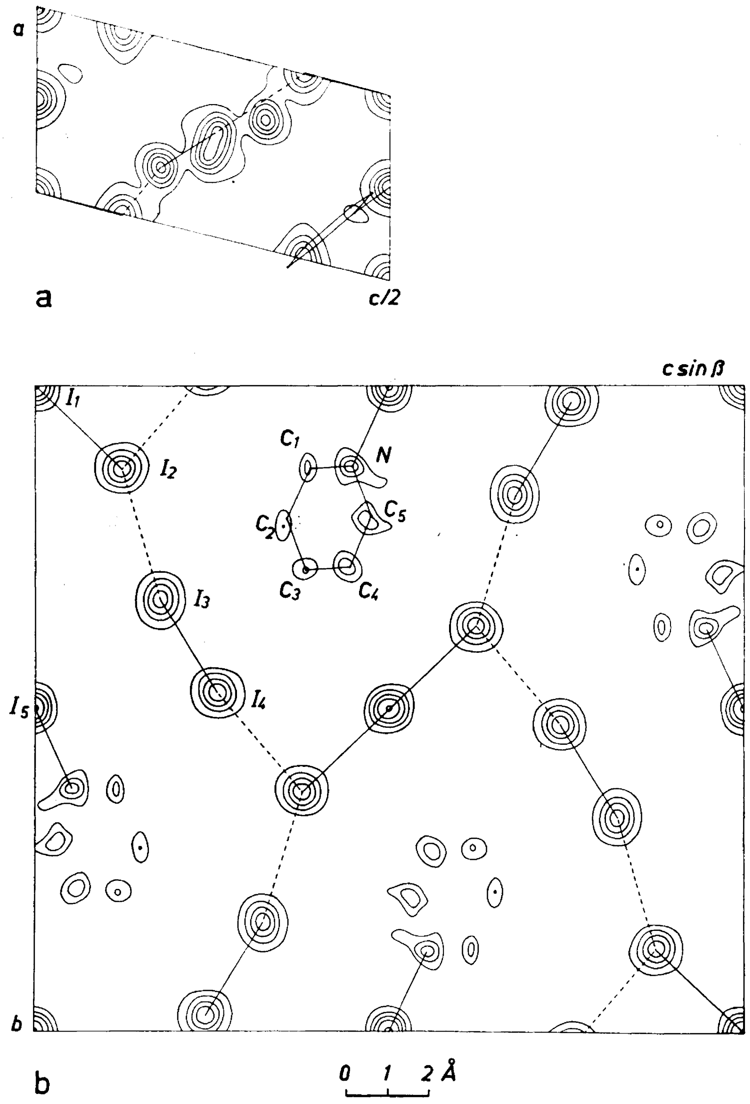

Fig. 1. Electron density maps a) projection along [010] b) projection along [100]. Contours at 10, 30, 50 . . . eÅ^{-2} (iodine) and 4, 6, 8 eÅ^{-2} (light atoms).

ments available in the literature we expected the compound pyridine · $2I_2$ to be sufficiently stable to allow single crystal work to be carried out. This substance was first prepared by Prescott and Trowbridge [3] by adding 1 mole of pyridine to an alcoholic solution containing two moles of iodine, whereby a crystalline substance having the composition $C_5H_5NI_4$ was formed. This substance may be recrystallized using different solvents, *e.g.* benzene, chloroform, or alcohol.

EXPERIMENTAL

The crystals used in the X-ray analysis were obtained from alcoholic solutions in the form of thin needles.

During the X-ray exposure, which was carried out at room temperature, the crystals were kept in sealed, thin-walled capillary tubes. The intensity data referring to the (0*kl*) zone were obtained using filtered Cu*K*α radiation, and an integrating Weissenberg camera. The intensities were measured with a microphotometer. The cross section of the crystals was approximately 0.05 × 0.08 mm². The intensity data of the (*h*0*l*) zone were obtained from precession diagrams of crystals having a cross section of about 0.15 × 0.15 mm² using filtered Mo*K*α radiation. The intensities were measured with a recording photometer. As the spots appeared to be of nearly the same shape, the peak heights were taken as the relative intensities.

248 independent (0*kl*) reflexions, and 97 (*h*0*l*) reflexions were observed. The maximum numbers compatible with the experimental conditions chosen are 331 and 119, respectively.

RESULTS

The crystals are monoclinic, with the space group $P2_1/c$. The unit cell containing four molecules of pyridine and sixteen iodine atoms has the following parameters:

$$a = 4.42 \text{ Å}; \qquad b = 15.37 \text{ Å}; \qquad c = 17.65 \text{ Å}; \qquad \beta = 103.8^0$$

A Patterson projection along [100] revealed that isolated iodine atoms were situated in centers of symmetry, and that centrosymmetric I_3 groups were also present. Approximate co-ordinates for the remaining two iodine atoms of the asymmetric unit could also be determined.

This interpretation of the Patterson projection indicated that the crystals are built up of centrosymmetrical Py_2I^+ resp. I^-_3 ions, the latter being connected by iodine molecules into a network.

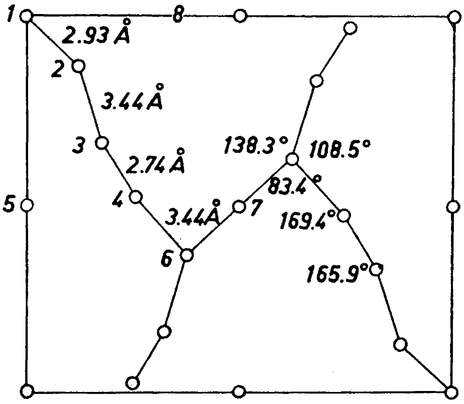

Fig. 2. Distances and angles within the anionic network (compare Fig. 1 b). Estimated standard deviations: I_1-I_2 0.01 Å, other I—I distances 0.02 Å.

Table 1. Final atomic parameters. The anisotropic temperature factor is $\exp(-uh^2-vhk-wk^2)$ (h,k, two-dimensional indices of the reflexions). The isotropic temperature factor is $\exp\left(-B\,\frac{\sin^2\Theta}{\lambda^2}\right)$. For iodine $B = \sqrt{B_{\max}\cdot B_{\min}}$.

	x	y	z	B	u	v	w
I_1		0	0	2.49	0.00205	0.00123	0.00290
I_1	0		0	3.72	0.04362	0.01097	0.01449
I_2		0.1288	0.1219	2.99	0.00226	−0.00054	0.00360
I_2'	0.0078		0.3781	5.08	0.07591	0.00803	0.01503
I_3		0.3312	0.1776	3.86	0.00490	−0.00034	0.00274
I_3	0.3010		0.1774	3.30	0.04704	0.00719	0.01039
I_4		0.4752	0.2581	3.27	0.00307	0.00062	0.00316
I_4'	0.4294		0.2419	3.80	0.04831	−0.00179	0.01304
I_5		0	0.5	2.14	0.00180	0.00078	0.00237
I_5'	0.5		0	3.26	0.04218	0.00713	0.01131
N	0.319	0.123	0.449	4.0			
C_1	0.069	0.126	0.389	4.5			
C_2	−0.067	0.202	0.354	4.5			
C_3	0.083	0.282	0.382	4.5			
C_4	0.342	0.278	0.444	4.5			
C_5	0.444	0.199	0.474	4.5			

In the corresponding Fourier map, obtained by using the signs derived from the Patterson synthesis, peaks due to the iodine atoms appeared near the expected positions, but the lighter atoms did not show up. With the help of the results from the [100] projection a sharpened Patterson projection along [010] was readily interpreted and the corresponding Fourier synthesis worked out (Fig. 1 a).

Using the coordinates obtained from the Fourier syntheses and a temperature factor with $B = 3$ Å^2, the R factors obtained for both projections were about 0.16. The coordinates were therefore considered sufficiently accurate to serve as starting values for least squares refinement. The Least Squares Programme used was designed by Curtis for the Ferranti Mercury Computer[4]. Two cycles of refinement of the coordinates and isotropic temperature factors of the [100] projection were first carried out. A Fourier map based on the structure factor signs thus derived revealed, beside the peaks corresponding to the iodine atoms, five additional peaks which clearly indicated the presence of atoms belonging to the pyridine ring. A sixth atom was also indicated, but the height of this peak was considerably lower.

Approximate coordinates of the light atoms were chosen from this Fourier synthesis combined with a model based on the structure of the pyridine molecule[5,6]. Keeping these coordinates fixed, three cycles of least squares refinement of the coordinates of the iodine atoms were carried out, introducing anisotropic temperature factors. The structure factor signs thus obtained served as a basis for the calculation of the Fourier map reproduced in Fig. 1 b. A $F_{\text{obs}}-F_{\text{I}}$ synthesis based on the final parameters was also computed. The pyridine ring was clearly brought out with reasonable peak heigths. The

Table 2. Calculated and observed structure factors in the (0*kl*) zone.

k	*l*	F_c	$\|F_o\|$
0	2	-56	79
	4	110	113
	6	132	144
	8	266	255
	10	42	37
	12	127	125
	14	-69	65
	16	170	153
	18	53	51
	20	-2	< 20
1	1	34	40
	2	-192	238
	3	-29	20
	4	180	176
	5	-107	110
	6	64	68
	7	4	< 16
	8	-32	23
	9	163	170
	10	44	37
	11	-127	127
	12	-81	91
	13	18	< 24
	14	35	40
	15	-8	< 25
	16	41	42
	17	29	< 24
	18	-56	51
	19	-28	25
	20	1	< 20
	21	6	20
2	0	204	249
	1	49	51
	2	46	51
	3	-262	232
	4	389	345
	5	51	54
	6	-58	68
	7	180	184
	8	290	289
	9	-100	102
	10	21	25
	11	-126	127
	12	133	125
	13	115	116
	14	64	65
	15	-12	< 25
	16	72	62
	17	0	< 25
	18	15	< 23
	19	-8	< 22
	20	66	57
	21	-14	< 20
3	1	20	20
	2	-128	122
	3	-105	110
	4	-30	25
	5	252	243
	6	117	122
	7	-90	93
	8	-20	23
	9	-121	130
	10	-54	51
	11	71	74
	12	-28	25
	13	52	45
	14	50	40
	15	-90	91
	16	-15	< 25
	17	44	40
	18	-10	< 23
	19	-45	40
	20	-18	< 20
	21	26	< 20
4	0	67	37
	1	-20	20
	2	72	74
	3	-60	65
	4	468	430
	5	154	170
	6	4	< 15
	7	-185	184
	8	147	147
	9	126	127
	10	11	< 21
	11	-14	< 22
	12	184	187
	13	-25	28
	14	81	79
	15	23	28
	16	29	< 25
	17	13	< 24
	18	7	< 23
	19	-34	40
	20	77	74
	21	30	28
5	1	-90	93
	2	237	229
	3	130	119
	4	-133	133
	5	11	28
	6	-41	45
	7	-100	99
	8	-5	< 19
	9	26	23
	10	17	< 21
	11	-55	65
	12	25	34
	13	66	79
	14	-15	< 25
	15	-30	37
	16	-70	68

k	*l*	F_c	$\|F_o\|$
	17	−15	< 24
	18	68	65
	19	4	< 20
	20	−18	< 19
6	0	411	394
	1	252	246
	2	−18	17
	3	20	25
	4	175	176
	5	27	25
	6	168	176
	7	−176	190
	8	97	96
	9	110	122
	10	71	74
	11	10	< 23
	12	153	156
	13	7	< 25
	14	−19	28
	15	−89	88
	16	96	91
	17	33	< 23
	18	44	40
	19	13	25
	20	10	25
7	1	47	48
	2	−7	< 17
	3	−36	34
	4	68	76
	5	−81	82
	6	−84	88
	7	38	40
	8	−78	79
	9	107	119
	10	144	153
	11	−79	82
	12	−75	71
	13	−10	< 25
	14	−3	< 25
	15	5	< 25
	16	1	< 24
	17	12	< 22
	18	4	< 21
	19	−18	< 19
	20	−12	20
8	0	246	241
	1	178	178
	2	144	144
	3	−156	159
	4	52	51
	5	55	57
	6	9	< 21
	7	6	< 22
	8	249	263
	9	32	28
	10	72	79
	11	−86	88
	12	2	< 25
	13	88	91
	14	63	68
	15	−47	51
	16	79	82
	17	23	< 21
	18	44	42
	19	−7	25
9	1	86	91
	2	−83	82
	3	−139	144
	4	−38	40
	5	25	28
	6	110	113
	7	23	23
	8	−30	25
	9	−14	25
	10	−43	45
	11	22	31
	12	−46	48
	13	−35	40
	14	53	57
	15	−17	< 24
	16	−29	< 22
	17	49	48
	18	−1	< 19
	19	−31	31
10	0	72	76
	1	−44	45
	2	132	130
	3	−158	153
	4	136	139
	5	188	190
	6	81	85
	7	−74	85
	8	92	93
	9	52	54
	10	65	65
	11	−87	88
	12	59	65
	13	24	28
	14	76	74
	15	32	31
	16	29	29
	17	4	< 20
	18	27	31
11	1	−86	85
	2	18	23
	3	95	96
	4	−67	65
	5	25	25
	6	78	88
	7	−43	48
	8	−4	< 25
	9	−25	< 25
	10	−42	54
	11	−3	< 25
	12	−16	< 25
	13	40	42

k	l	F_c	$\|F_o\|$
	14	40	45
	15	− 8	< 21
	16	− 47	42
	17	− 40	40
12	0	25	28
	1	98	99
	2	69	65
	3	− 64	65
	4	138	136
	5	46	45
	6	161	164
	7	− 72	68
	8	− 50	48
	9	45	45
	10	82	85
	11	− 27	< 25
	12	117	116
	13	31	37
	14	39	42
	15	− 36	42
	16	17	23
	17	16	20
13	1	− 25	28
	2	27	< 25
	3	45	42
	4	29	< 25
	5	3	< 25
	6	− 66	68
	7	− 18	< 25
	8	− 59	57
	9	− 19	< 25
	10	89	85
	11	4	< 24
	12	− 41	48
	13	3	< 21
	14	− 16	< 20
	15	0	< 19
	16	− 16	< 18
14	0	45	42
	1	137	125
	2	136	127
	3	3	< 25
	4	22	< 25
	5	− 14	< 25
	6	72	68
	7	− 54	51
	8	76	76
	9	51	45
	10	80	79
	11	1	< 22
	12	6	< 20
	13	16	< 20
	14	64	59
	15	− 52	42
15	1	48	45
	2	37	37
	3	− 71	68
	4	− 21	28
	5	− 26	28
	6	− 16	< 24
	7	36	34
	8	− 20	< 23
	9	2	< 22
	10	21	< 21
	11	15	< 20
	12	− 19	< 19
	13	− 45	45
16	0	75	71
	1	− 14	< 24
	2	112	110
	3	− 42	40
	4	− 22	28
	5	54	54
	6	79	82
	7	− 33	42
	8	73	68
	9	21	28
	10	77	71
	11	− 23	28
	12	− 13	20
17	1	2	< 22
	2	− 34	45
	3	5	< 22
	4	− 30	28
	5	− 33	25
	6	51	54
	7	21	< 20
	8	1	< 19
	9	6	< 19
	10	− 42	37
18	0	19	23
	1	− 15	20
	2	75	79
	3	− 47	48
	4	32	40
	5	31	45
	6	96	85
	7	23	< 19
	8	− 11	< 19
19	1	− 33	28
	2	− 25	25
	3	32	28
	4	12	< 18

Calculated and observed structure factors in the (*h*0*l*) zone. Half the absolute F values are given.

h	l'	F_c	$\|F_o\|$
0	1	−28	40
	2	54	62
	3	65	86
	4	129	148
	5	18	18
	6	61	68
	7	−39	39
	8	80	75
	9	23	25
	10	−5	12
	11	13	11
	12	13	12
1	−12	9	10
	−11	−10	8
	−10	−25	23
	−9	−38	36
	−8	−28	31
	−7	41	46
	−6	−56	64
	−5	3	< 6
	−4	57	65
	−3	63	75
	−2	−286	261
	−1	138	133
	0	−16	21
	1	34	34
	2	−66	79
	3	0	< 6
	4	12	21
	5	82	88
	6	−88	95
	7	5	< 8
	8	21	22
	9	−13	14
	10	−2	< 7
	11	−1	< 6
2	−12	12	11
	−11	−4	< 7
	−10	30	30
	−9	−14	13
	−8	64	68
	−7	24	20
	−6	−7	< 7
	−5	35	35
	−4	183	171
	−3	−27	30
	−2	108	98
	−1	21	25
	0	121	125
	1	92	92
	2	3	< 6
	3	−11	15
	4	129	141
	5	14	16
	6	8	10
	7	36	36
	8	6	10
	9	24	20
	10	6	< 6
3	−11	15	12
	−10	−24	23
	−9	7	11
	−8	22	20
	−7	−9	8
	−6	−42	40
	−5	36	40
	−4	−32	35
	−3	41	33
	−2	−40	43
	−1	−32	29
	0	64	65
	1	15	10
	2	−57	58
	3	20	29
	4	7	8
	5	−14	15
	6	16	12
	7	−27	20
	8	12	10
	9	4	< 5
4	−11	0	< 4
	−10	2	< 7
	−9	20	18
	−8	20	18
	−7	12	11
	−6	36	35
	−5	−1	< 8
	−4	55	54
	−3	46	41
	−2	−18	22
	−1	43	49
	0	46	46
	1	16	15
	2	24	26
	3	27	28
	4	3	< 8
	5	45	36
	6	−10	10
	7	11	10
5	−9	−3	< 6
	−8	−3	< 7
	−7	11	11
	−6	−16	17
	−5	−4	8
	−4	24	29
	−3	−17	22
	−2	4	< 8
	−1	−1	< 8
	0	−2	< 8
	1	0	< 8

h	l'	F_c	$\|F_o\|$
5	2	8	< 8
	3	− 24	18
	4	22	20
6	− 5	19	22
	− 4	2	< 6
	− 3	15	18
	− 2	10	12
	− 1	8	8
	0	8	10

final coordinates of the light atoms (given in Table 1) were derived from the difference synthesis combined with the pyridine model just mentioned.

Returning to the [010] projection three cycles of least squares refinement were carried out using the x coordinates of the iodine atoms obtained from the [010] Fourier projection and the final z coordinates derived from the [100] projection as initial values. Anisotropic temperature factors for the iodine atoms were introduced. From the pyridine model and the data from the [100] projection the x coordinates of the light atoms were estimated. These coordinates and the temperature factors with $B = 4.0$ Å^2 (nitrogen), and $B = 4.5$ Å^2 (carbon) were not refined. Due to overlapping the z coordinate of I_4 was not refined.

The final parameters listed in Table 1 were used in calculating F_c in Table 2, in which a comparison of calculated and observed F values is given. The R factor for the (100)-zone is 0.07. If the contribution from the light atoms is disregarded the R factor becomes 0.09. For the (010)-zone the R factor is 0.11. All R factors were computed excluding unobserved reflexions.

The I—I distances and I—I—I angles are given in Fig. 2 which corresponds to the [100] projection (Fig. 1 b). The I—I distance within the I^-_3 ion (2.93 Å) is approximately that previously found in other crystals. The distance between the two iodine atoms of the I_2 molecule (2.74 Å) is only slightly larger than in the free molecule. As would be expected the two distances between an iodine atom belonging to an I^-_3 ion and the two nearest iodine atoms belonging to I_2 molecules are considerably larger. These two I—I distances were both found equal to 3.44 Å.

The shortest distance between a C atom of the pyridine ring and an I atom is 4.3 Å. The whole anionic arrangement of I^-_3 ions connected by iodine molecules into a network very much resembles that found by Havinga in tetraethyl-ammonium heptaiodide [7].

The structure of the Py_2I^+ ion is of considerable interest. The present compound in which the iodine atoms contribute so heavily to the reflexion of X-ray is not very well suited for an accurate determination of the positions of the carbon and nitrogen atoms, but it appears certain from our results that the ion, besides having a center of symmetry, is nearly planar. The N—I distance cannot, however, be determined very accurately. The value deduced from the coordinates listed in Table 1 (2.16 Å) may therefore have an error of ± 0.1 Å. We think, however, that the N—I separation is probably shorter than that observed in simple addition compounds formed by tertiary amines and iodine (2.30 Å). The existence of the Py_2I^+ ion suggested by Carlsohn [8] has been confirmed by the present investigation. It would appear interesting to study the structure of this ion in a simple salt like the nitrate or perchlorate.

Structure determinations so far carried out seem to indicate that the ion PyI^+ is rather unstable.

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