

## Crystal Structure of the 1:1 Addition Compound Formed by 4-Picoline and Iodine

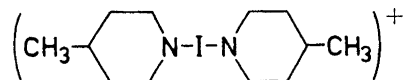
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The crystal structure of an equimolecular addition compound of 4-picoline and iodine has been determined by X-ray methods at temperatures about  $-40^{\circ}\text{C}$ . The space group is  $P2_1/c$ , the lattice parameters:  $a = 4.72 \text{ \AA}$ ;  $b = 9.05 \text{ \AA}$ ;  $c = 21.55 \text{ \AA}$ ;  $\beta = 101^{\circ}$ . The I-I-N arrangement is linear with the I-I distance  $2.83 \text{ \AA}$  and the I-N distance  $2.31 \text{ \AA}$ .

Glusker and Miller<sup>1</sup> have examined two different solid compounds formed by 4-picoline and iodine. One compound (I),  $(\text{C}_6\text{H}_7\text{N})_2\text{I}_2$ , is water-soluble, alcohol-insoluble, and has a melting point of  $244^{\circ}\text{C}$ . The second compound (II),  $\text{C}_6\text{H}_7\text{N}\cdot\text{I}_2$  is insoluble in water and its melting point is  $83^{\circ}\text{C}$ . For both substances radial distribution functions were worked out, based on intensities collected from X-ray powder experiments. The conclusions drawn from the radial distribution curves were that compound I contains no I-I distance shorter than  $3 \text{ \AA}$  and that compound II contains one I-I distance between  $1.9 \text{ \AA}$  and  $3.0 \text{ \AA}$  per molecule picoline. They were thus led to the conclusion that the compound I has an ionic structure while the compound II is a molecular addition compound.

Recently Hassel and Hope<sup>2</sup> by carrying out a structure determination of a reaction product of pyridine and iodine demonstrated the existence of a centrosymmetric  $(\text{C}_6\text{H}_5\text{N})_2\text{I}^+$  ion. It appears very probable that the cation of compound I has a similar structure:



rather than the  $\alpha$ -addition arrangement proposed by Glusker and Miller.

We also found Glusker and Miller's argument regarding the structure of compound II somewhat inconclusive. One alternative explanation of the radial distribution curve might, *e.g.*, be given by assuming the presence of (4-picoline)<sub>2</sub>I<sup>+</sup> and I<sub>3</sub><sup>-</sup> ions.

A single crystal X-ray investigation of the 1:1 compound (II) has now been carried out in order to determine the spatial arrangement of the atoms.

### EXPERIMENTAL

A solution of iodine in ethyl ether was added to an equimolecular amount of 4-picoline and the solvent slowly evaporated at  $-30^{\circ}\text{C}$ . The crystals thus obtained were either plates or needles, those having the latter habit were preferred for use in the X-ray examination. They were kept in sealed, thin-walled capillary tubes. Also during the preparation and mounting of the crystals care was taken to avoid moisture, and during the X-ray exposure they were cooled to temperatures below  $-40^{\circ}\text{C}$ .

The melting point of the compound was found equal to  $83^{\circ}\text{C}$  and the density measured by the flotation method  $2.4\text{ g/cm}^3$ . This is in good agreement with the figures reported by Glusker and Miller for compound II.

Oscillation and Weissenberg photographs (CuK $\alpha$  radiation) with rotation about two crystallographic axes were taken in order to determine the unit cell dimensions and the space groups. The  $0kl$  and  $h0l$  intensities were estimated partly from Weissenberg diagrams by visual comparison with a standard scale and partly from measurements on a microphotometer of films taken with an integrating Weissenberg camera. 128  $0kl$  reflexions and 116  $h0l$  reflexions were recorded, the maximum numbers obtainable with CuK $\alpha$ -radiation are 230 and 128, respectively. The intensities were corrected for Lorentz and polarization effects and eventually for secondary extinction using a method given by Pincock, Taylor and Lipson<sup>3</sup>. No absorption corrections were applied.

The computations involved in the present investigation were carried out on a Ferranti Mercury computer; the least squares programme used has been designed by Curtis<sup>4</sup>. The atomic scattering factors used to suit this programme are given as an analytical approximation by Forsyth and Wells<sup>5</sup>.

### RESULTS

The crystals were found to be monoclinic, space group  $P2_1/c$  with the unit cell dimensions:

$$a = 4.72 \text{ \AA}; b = 9.05 \text{ \AA}; c = 21.55 \text{ \AA}; \beta = 101^{\circ}$$

With four molecules per unit cell the calculated density is  $2.55\text{ g/cm}^3$ .

Patterson syntheses based on the  $0kl$  and  $h0l$  intensities were worked out and the parameters of the two independent iodine atoms determined. The corresponding electron density Fourier maps were evaluated from experimental structure factors with signs based on the iodine parameters. From the Fourier maps more accurate iodine parameters could be determined and indications regarding the position of the light atoms were also obtained. The organic part of the compound was well resolved in the projection along the  $a$  axis. In the projection along the  $b$  axis, however, overlapping occurred for two pairs of carbon atoms of the six-membered ring. A normal series of Fourier refinements could then be performed. At the stage at which no further structure factor signs changed, the reliability index  $R$  for the two zones were 0.17 and 0.18, respectively. The intensities were corrected for secondary extinction, and the refinement of the parameters was continued with the method of least squares.

Table 1. Atomic coordinates as fractions of the cell-edges.

Atom	$x$	$y$	$z$
I <sub>1</sub>	0.1821	0.1388	0.0837
I <sub>2</sub>	0.5456	0.1431	0.2040
N	0.875	0.144	0.299
C <sub>2</sub>	0.003	0.005	0.320
C <sub>3</sub>	0.003	0.275	0.326
C <sub>4</sub>	0.250	0.019	0.373
C <sub>5</sub>	0.250	0.019	0.373
C <sub>6</sub>	0.372	0.141	0.408
C <sub>7</sub> (methyl)	0.630	0.153	0.458

The atomic coordinates eventually arrived at using this method are listed in Table 1, the  $z$ -coordinate being in each case the mean of values derived from the two projections. The mean  $B$  values in the temperature factor expression were  $2.2 \text{ \AA}^2$  for the "outer" iodine atom,  $1.1 \text{ \AA}^2$  for the iodine atom linked to the nitrogen atom and  $2.7 \text{ \AA}^2$  for nitrogen and carbon atoms. The final  $R$  values were 0.12 and 0.16 in the  $0kl$  and the  $h0l$  zones, respectively. A compari-

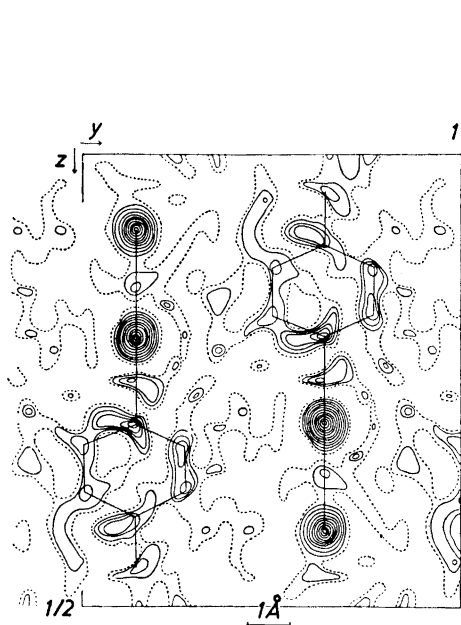


Fig. 1. Projection along the  $a$ -axis. Contours at intervals of  $10 e \cdot \text{\AA}^{-2}$  in the iodine peaks and of  $2 e \cdot \text{\AA}^{-2}$  in the rest of the map. The  $2 e \cdot \text{\AA}^{-2}$  is dotted.

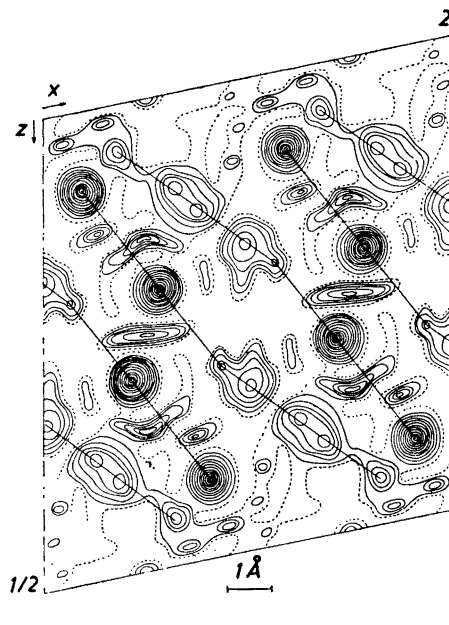


Fig. 2. Projection along the  $b$ -axis. Contour lines as in Fig. 1.

Table 2.

$h k l$	$F_{\text{obs}}$	$F_{\text{calc}}$	$h k l$	$F_{\text{obs}}$	$F_{\text{calc}}$
0 0 2	5.0	- 9.4	2	33.6	-31.6
4	7.0	- 6.8	4	11.4	10.0
6	12.0	-12.1	6	7.6	5.0
8	18.6	-21.0	8	10.4	8.6
10	22.2	22.6	10	10.8	11.8
12	1.4	- 2.4	12	14.6	-15.0
14	12.8	11.0	14	< 1.4	- 1.5
16	7.4	- 3.8	16	11.8	- 9.2
18	15.2	-12.4	18	9.2	5.4
20	5.4	3.2	20	12.4	8.6
22	6.4	- 4.4	22	4.4	- 4.4
24	13.0	11.2	24	3.4	3.4
26	1.8	0.0	3 0 $\overline{26}$	6.8	- 5.6
28	< 0.2	0.4	$\overline{24}$	4.2	- 4.8
1 0 $\overline{28}$	< 0.3	0.6	$\overline{22}$	2.8	4.0
$\overline{26}$	4.4	4.2	$\overline{20}$	5.4	- 3.6
$\overline{24}$	2.8	- 2.6	$\overline{18}$	13.4	-15.2
$\overline{22}$	5.8	4.0	$\overline{16}$	5.6	- 3.8
$\overline{20}$	19.0	-16.8	$\overline{14}$	8.0	- 8.0
$\overline{18}$	5.4	2.6	$\overline{12}$	5.8	- 4.2
$\overline{16}$	6.8	5.2	$\overline{10}$	10.6	- 9.0
$\overline{14}$	6.6	6.0	$\overline{8}$	16.8	18.0
$\overline{12}$	14.6	16.2	$\overline{6}$	1.8	0.8
$\overline{10}$	20.0	-23.2	$\overline{4}$	7.6	6.8
$\overline{8}$	3.8	- 4.2	$\overline{2}$	7.0	- 5.4
$\overline{6}$	3.8	- 3.8	0	16.0	-16.2
$\overline{4}$	9.4	8.0	2	9.4	8.0
$\overline{2}$	22.0	22.0	4	3.4	- 4.4
0	8.8	- 7.6	6	17.8	17.0
2	7.0	6.0	8	< 1.3	- 0.6
4	24.8	-28.2	10	13.0	-11.6
6	6.8	- 6.6	12	2.0	1.8
8	9.4	11.6	14	11.0	-10.2
10	4.8	3.2	16	12.4	9.4
12	17.6	18.6	18	4.8	2.8
14	18.0	-14.8	20	< 0.6	0.9
16	7.0	- 4.4	22	< 0.2	1.8
18	2.8	- 0.6	4 0 $\overline{22}$	1.8	2.6
20	7.4	- 3.4	$\overline{20}$	5.8	7.2
22	14.2	12.4	$\overline{18}$	5.8	- 7.0
24	4.4	- 3.2	$\overline{16}$	5.0	4.0
26	< 0.5	0.1	$\overline{14}$	8.2	-10.2
2 0 $\overline{26}$	1.8	1.8	$\overline{12}$	< 1.4	- 0.3
$\overline{24}$	2.2	- 2.2	$\overline{10}$	9.0	11.6
$\overline{22}$	11.2	-10.0	$\overline{8}$	< 1.4	0.6
$\overline{20}$	7.8	6.8	$\overline{6}$	10.6	11.4
$\overline{18}$	4.0	- 2.8	$\overline{4}$	12.4	-13.2
$\overline{16}$	12.4	13.8	$\overline{2}$	7.0	- 7.4
$\overline{14}$	5.2	2.0	0	3.4	3.4
$\overline{12}$	10.0	-11.2	2	< 1.4	- 0.9
$\overline{10}$	2.0	1.4	4	15.4	14.2
$\overline{8}$	22.0	-23.6	6	5.8	- 4.8
$\overline{6}$	18.4	20.6	8	2.4	- 1.4
$\overline{4}$	12.4	12.2	10	5.8	- 5.2
$\overline{2}$	4.2	- 2.4	12	4.8	- 5.2
0	5.6	3.4	14	11.4	10.2

Table 2. Continued.

<i>h k l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	<i>h k l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$
			24	< 4.3	2.3
5 0 $\overline{18}$	< 0.6	1.3	25	4.0	5.0
	1.8	1.6	26	5.2	- 6.4
	5.8	- 9.0	0 2 0	8.6	- 8.0
	3.4	4.0	1	27.7	-30.8
	2.4	3.6	2	3.1	2.2
	1.8	2.0	3	7.4	- 8.6
	4.2	4.4	4	< 2.4	- 0.4
	9.8	-11.8	5	11.1	-11.9
	1.8	1.8	6	< 3.0	1.7
	4.8	- 4.6	7	< 3.7	1.2
	3.4	4.8	8	< 3.4	3.6
	2	10.6	9	22.5	28.0
	4	- 7.6	10	< 3.7	- 3.5
	6	3.0	11	8.3	- 8.7
	8	- 4.0	12	< 4.3	0.9
6 0 $\overline{8}$	< 0.9	0.6	13	4.3	4.0
	< 0.2	- 0.1	14	< 4.6	- 2.3
	< 0.3	0.2	15	14.5	-13.6
	< 0.3	0.1	16	< 4.9	1.1
	< 0.2	- 0.1	17	7.7	- 5.8
0 0 2	7.4	- 9.2	18	< 5.5	1.9
	8.3	7.4	19	13.5	12.3
	6	-12.5	20	< 5.2	- 1.1
	8	-21.0	21	< 5.2	- 0.3
	10	23.5	22	< 4.9	1.0
	12	0.9	23	8.6	8.8
	14	12.3	24	< 4.0	- 2.2
	16	- 4.7	25	5.8	- 8.1
	18	-14.1	0 3 1	16.9	-16.7
	20	3.9	2	10.8	-10.8
	22	- 2.5	3	15.7	14.2
	24	13.2	4	< 3.0	0.9
	26	0.6	5	< 3.0	- 1.4
0 1 1	8.6	8.9	6	5.2	- 4.8
	2	-14.4	7	20.3	20.4
	3	- 5.4	8	7.7	8.4
	4	- 0.2	9	6.2	- 7.3
	5	0.8	10	2.5	2.7
	6	-12.5	11	8.0	- 9.0
	7	-17.6	12	< 4.6	- 1.6
	8	20.5	13	< 4.6	- 2.3
	9	5.4	14	< 4.6	- 0.9
	10	5.2	15	8.0	- 8.5
	11	6.7	16	6.8	- 6.8
	12	- 2.4	17	14.2	13.6
	13	2.8	18	< 5.2	2.4
	14	- 2.2	19	< 5.2	1.5
	15	5.8	20	< 5.2	1.5
	16	-14.5	21	< 4.9	1.1
	17	-10.9	22	< 4.6	2.8
	18	8.3	23	< 4.3	- 3.3
	19	- 3.3	24	< 3.7	0.9
	20	2.2	25	6.2	- 7.6
	21	- 0.8	0 4 0	23.9	-26.8
	22	2.4	1	8.9	8.2
	23	1.9			

Table 2. Continued.

<i>h k l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>	<i>h k l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>
2	5.2	3.5	12	< 5.2	- 1.6
3	< 3.4	0.1	13	< 5.2	- 1.0
4	< 3.7	- 0.7	14	< 5.2	4.5
5	3.7	4.0	15	6.8	8.4
6	14.2	12.4	16	< 5.2	- 1.9
7	< 4.0	0.9	17	4.0	3.4
8	17.5	15.8	18	4.0	- 4.1
9	8.0	- 8.2	19	7.7	- 7.9
10	18.2	-17.6	0 7 1	9.5	9.7
11	3.7	4.0	2	< 4.8	- 0.9
12	< 4.0	- 0.5	3	8.6	- 6.8
13	< 4.6	- 2.5	4	< 4.9	1.4
14	< 10.2	- 9.9	5	< 5.2	- 0.2
15	< 4.9	4.2	6	< 5.2	0.3
16	8.0	7.0	7	16.6	-16.1
17	< 5.2	1.6	8	< 5.2	- 0.8
18	12.6	11.4	9	6.2	6.2
19	< 5.2	- 3.8	10	< 5.2	- 1.0
20	6.5	- 6.7	11	6.8	6.2
21	< 5.2	1.2	12	< 5.2	- 0.2
22	4.3	3.5	13	< 5.2	2.6
23	< 4.6	- 3.0	14	< 5.2	0.7
24	7.1	- 8.7	15	6.5	6.9
0 5 1	6.2	- 3.6	16	< 4.6	0.8
2	20.6	18.5	17	11.4	-13.4
3	< 4.0	2.4	0 8 0	15.7	14.4
4	4.6	2.8	1	13.2	-10.6
5	< 4.3	0.7	2	5.2	- 2.5
6	11.1	9.6	3	< 5.2	- 0.8
7	5.5	3.5	4	< 5.2	- 1.8
8	18.2	-17.3	5	< 5.2	- 2.9
9	< 4.6	- 1.2	6	< 5.2	- 4.7
10	5.5	- 3.9	7	5.2	- 1.0
11	< 4.9	- 2.2	8	6.8	- 5.9
12	4.0	3.3	9	9.2	9.4
13	< 5.2	- 0.9	10	6.8	8.2
15	< 5.2	- 1.8	11	5.8	- 5.4
16	14.2	14.4	12	< 4.9	0.8
17	< 5.2	3.1	13	4.0	4.3
18	< 7.7	- 6.5	14	< 4.6	4.0
19	< 4.9	1.1	15	4.3	- 3.4
20	< 4.6	- 2.5	16	< 4.0	- 2.3
21	< 4.3	0.2	17	< 3.7	- 2.3
22	7.1	- 4.7	0 9 1	< 5.2	- 0.5
0 6 0	14.2	12.8	2	9.9	- 9.0
1	16.0	15.1	3	< 5.2	1.4
2	5.8	- 4.2	4	< 5.2	- 0.3
3	4.6	3.0	5	< 5.2	- 1.1
4	< 4.6	0.8	6	9.5	- 8.2
5	6.8	5.7	7	< 4.9	1.2
6	4.6	- 3.0	8	11.7	11.8
7	< 4.9	- 0.4	9	< 4.6	- 1.1
8	6.5	- 7.3	10	< 4.6	4.0
9	17.5	-16.7	11	< 4.3	- 0.3
10	8.0	8.2	12	< 4.3	- 2.1
11	5.2	4.5	13	< 4.0	0.6

Table 2. Continued.

<i>h k l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	<i>h k l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$
14	< 3.7	— 1.8	8	4.0	5.7
15	< 3.4	— 1.0	9	3.1	5.0
16	< 3.0	— 8.3	10	8.0	— 6.8
17	4.0	3.6	0 11 1	4.0	— 6.6
0 10 0	11.7	—10.5	2	< 3.4	1.9
1	4.6	— 5.0	3	4.9	5.1
2	3.7	4.7	4	< 3.4	— 1.3
3	< 4.6	— 2.2	5	< 3.4	0.2
4	< 4.6	— 0.1	6	< 3.0	1.7
5	< 4.3	— 2.0	7	< 2.8	7.4
6	< 4.3	3.4	8	4.3	— 4.3
7	< 4.3	1.2			

son between observed and calculated structure factors is given in Table 2. The two electron density maps are reproduced in Figs. 1 and 2.

The structure determination proves that the compound II is a molecular addition compound. The atoms  $I_1$ - $I_2$ -N form, within the accuracy of the measurements, a straight line. The  $I_1$ - $I_2$  distance is 2.83 Å (standard deviation <sup>6</sup> 0.003) Å which implies a lengthening of about 0.17 Å compared with the distance in the free iodine molecule. The  $I_2$ -N distance is 2.31 Å (standard deviation 0.02 Å). These results are in good agreement with measurements on similar compounds already investigated as may be seen from Table 3.

The distance between the light atoms deduced from the atomic coordinates given in Table 1 are certainly not very accurate in a structure like the present one containing atoms as heavy as iodine. The greatest deviations from the corresponding figures in the pyridine molecule are as large as 0.08 Å.

A line drawn through  $I_1$ ,  $I_2$ , and N is forming an angle of 13° with the plane of the picoline ring and the plane defined by this line and the  $C_4$ -atom is approximately normal to the plane containing the light atoms. One would perhaps have expected the line to pass through the  $C_4$ -atom, but intermolecular forces are evidently strong enough to distort the planar configuration.

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Table 3. A comparison of bond lengths in various addition compounds containing iodine.

Compound	Ref.	I-I (Å)	I-N (Å)
Trimethylamine · $I_2$	7	2.83	2.27
Dithiane · $I_2$	8	2.79	
Benzylsulphide · $I_2$	9	2.82	
Pyridine · ICl	10		2.26
Trimethylamine · ICl	11		2.30
4-Picoline · $I_2$	present examination	2.83	2.31

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