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The Crystal Structure of the Phenazine-Iodine Molecular Complex

Tokiko Uchida[*1]

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

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The 1 : 1 molecular complex of phenazine and iodine crystallizes in an orthorhombic system with the space group *Pbcn*. There are four formula units in a unit cell with the dimensions of $a=12.85$, $b=11.69$, and $c=8.30$ Å. The structure was solved by Patterson methods and was refined by two-dimensional Fourier and (F_o-F_c) syntheses. The component molecules are arranged alternately along the b axis, the two nitrogen atoms of the phenazine molecule and the two iodine atoms of the iodine molecule lying on a two-fold axis. The molecules of each component are stacked in individual columns parallel to the c axis, where the mean separations of the molecules satisfy the van der Waals distances. The phenazine molecule is planar within the range of experimental error. The interatomic distance of an iodine molecule is 2.75 Å; this is more from that of a free molecule, but not as large as those of the other iodine complexes. The charge-transfer interaction between phenazine and iodine is a little weakened by the steric hindrance of hydrogen atoms attached to the phenazine nucleus.

Iodine is a well-known electron acceptor which forms molecular complexes with various kinds of electron donors. Many spectroscopic investigations have been made of the iodine complexes,[1-3] and their electronic structures have been successfully explained by Mulliken's charge-transfer theory.[4]

For solid iodine complexes, some interesting physical properties have been reported,[5-7] such as electrical conductivity or paramagnetic resonance absorption. However, their electronic states have not been discussed, since their crystal structures have not been systematically studied except for the work by Hassel and his coworkers.[8]

In this paper, the crystal structure of the molecular complex between phenazine and iodine will be reported.

Experimental

The phenazine was recrystallized from ethanol and then from benzene repeatedly, until the orange-colored fluorescence disappeared. The iodine was purified by sublimation. The molecular complex was prepared by adding an excess amount of iodine to phenazine dissolved in ether, and was then recrystallized from chloroform. The crystals are red rectangular plates with well-developed (100) faces. They decompose very slowly in the open air.

The crystal data are as follows:
$C_{12}H_8N_2{\cdot}I_2$; $M=434.02$; mp 198°C (uncorr.)
Orthorhombic:
$a=12.85\pm0.01$, $b=11.69\pm0.01$, $c=8.30\pm0.01$ Å.
Density observed: 2.30 g/cm^3.
Density calculated: 2.31 g/cm^3.
Four formula units per unit cell.
Systematic absences: $hk0$ with $h+k$ odd,
$h0l$ with l odd,
$0kl$ with k odd.
Space group: *Pbcn*.
Total number of electrons per unit cell:
$F(000)=800$.

The cell dimensions were calculated by the least-squares method from 13 powder reflections recorded with a diffractometer; powder lines of quartz were used as a reference. The density was determined by floatation in an aqueous mercury(II) potassium iodide solution.

The intensity data for $hk0$, $h0l$, and $0kl$ zones were collected from Weissenberg films by the multiple-film technique, and were estimated visually by means of a calibration strip. From the 102, 69, and 66 possible reflections, 86, 48, and 62 non-zero reflections were observed for the $hk0$, $h0l$, and $0kl$ zones respectively. Crystals with cross-sections of about 0.05×0.1 mm^2 were used, and the three sets of two-dimensional data were scaled by comparing the common reflections. Lorentz and polarization corrections were applied,

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[*1] Present address: Faculty of Science and Technology, the Science University of Tokyo, Noda, Chiba.

1) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

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3) S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958).

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Table 1. Observed and calculated structure factors

h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0*	415.6	385.7	6	8	0	169.8	−174.6
4	0	0*	373.0	372.6	8	8	0	102.9	−118.7
6	0	0	249.7	265.1	10	8	0	82.2	−86.7
8	0	0	234.7	216.0	12	8	0	77.4	−66.7
10	0	0	150.8	140.5	1	9	0	189.2	−150.6
12	0	0	156.1	140.7	3	9	0	164.7	−145.6
14	0	0	114.0	102.7	5	9	0	109.1	−115.5
16	0	0	41.5	57.2	7	9	0	54.9	−70.7
1	1	0*	112.5	132.5	9	9	0	92.0	−90.8
3	1	0*	217.8	280.4	11	9	0	65.7	−61.0
5	1	0	170.9	183.4	13	9	0	52.1	−53.0
7	1	0	188.7	178.9	0	10	0	45.4	−32.6
9	1	0	146.1	121.7	2	10	0	59.0	−50.7
11	1	0	108.9	98.6	4	10	0	45.0	−36.8
13	1	0	26.5	38.9	6	10	0	62.8	−58.3
15	1	0	48.9	46.2	8	10	0	35.9	−37.6
0	2	0	69.3	121.8	10	10	0	30.1	−28.5
2	2	0	4.3	8.1	12	10	0	16.2	−18.9
4	2	0	30.5	39.9	1	11	0	7.1	2.4
6	2	0	10.9	−15.3	3	11	0	17.2	13.3
8	2	0	8.4	9.4	5	11	0	9.6	8.3
12	2	0	15.9	15.2	7	11	0	6.3	10.5
14	2	0	13.7	13.6	9	11	0	7.4	6.8
1	3	0	70.8	−84.8	0	12	0	45.2	35.6
3	3	0	84.9	−92.9	2	12	0	34.8	26.2
5	3	0	41.8	−60.1	4	12	0	28.7	22.9
7	3	0	15.9	−31.0	6	12	0	30.3	25.0
9	3	0	35.8	−42.0	8	12	0	25.0	18.2
11	3	0	22.4	−25.5	0	14	0	16.2	−8.6
13	3	0	14.9	−19.1	2	14	0	13.3	−8.9
0	4	0	45.3	−54.8	4	14	0	10.9	−7.3
2	4	0	31.6	−37.6	0	0	2*	403.8	−382.7
4	4	0	20.8	−28.5	1	0	2	69.5	−114.2
6	4	0	21.1	−34.8	2	0	2*	495.6	−479.9
8	4	0	12.7	−23.4	3	0	2	44.0	−30.4
1	5	0	41.2	45.6	4	0	2	215.9	−293.6
3	5	0	38.9	50.0	6	0	2	226.5	−262.6
5	5	0	26.7	38.2	8	0	2	170.5	−179.7
7	5	0	19.6	30.9	10	0	2	168.0	−161.4
9	5	0	16.9	26.8	11	0	2	26.0	25.0
0	6	0	65.5	59.1	12	0	2	123.0	−118.6
2	6	0	25.3	26.5	14	0	2	90.5	−87.2
4	6	0	30.6	32.3	16	0	2	54.7	−62.4
6	6	0	8.8	13.6	0	0	4	262.2	271.1
8	6	0	6.9	15.8	1	0	4	17.7	−25.9
1	7	0	87.1	−77.7	2	0	4	220.8	266.5
3	7	0	67.1	−67.8	3	0	4	32.8	56.6
5	7	0	47.0	−52.3	4	0	4	249.3	281.7
7	7	0	15.3	−21.3	5	0	4	41.6	13.5
9	7	0	31.8	−43.4	6	0	4	185.0	177.5
11	7	0	25.8	−26.1	8	0	4	190.5	170.7
13	7	0	30.0	−29.0	9	0	4	25.6	−21.5
0	8	0	180.0	−157.3	10	0	4	141.8	137.1
2	8	0	188.1	−173.6	12	0	4	93.3	90.5
4	8	0	139.4	−135.0	14	0	4	65.6	66.4

TABLE 1 (Continued)

h	k	l	F_o	F_c
0	0	6	200.3	−177.2
2	0	6	211.0	−168.9
4	0	6	174.0	−159.1
6	0	6	181.2	−162.7
8	0	6	133.7	−126.9
10	0	6	92.0	−91.2
12	0	6	79.8	−69.5
0	0	8	128.9	107.9
2	0	8	122.4	105.8
4	0	8	125.2	98.4
6	0	8	104.8	108.6
8	0	8	98.1	83.3
10	0	8	67.1	59.8
0	0	10	67.6	−62.7
2	0	10	74.7	−60.8
4	0	10	62.0	−68.3
0	2	1	20.9	64.2
0	2	2	7.3	−14.1
0	2	3	10.0	−5.2
0	2	4	24.6	25.5
0	2	6	11.3	−3.0
0	2	8	7.9	1.1
0	2	9	7.0	1.1
0	4	1*	283.2	−371.2
0	4	2	20.2	37.4
0	4	3	161.0	241.9
0	4	4	21.1	−23.3
0	4	5	165.3	−184.9
0	4	6	25.7	20.9
0	4	7	142.8	140.1
0	4	8	14.1	−13.2
0	4	9	95.3	−76.7
0	4	10	4.3	5.7
0	6	1	70.1	−78.0
0	6	2	21.4	−26.8
0	6	3	31.7	35.3
0	6	4	22.6	23.6
0	6	5	25.5	−37.1
0	6	6	8.0	−11.3
0	6	7	14.5	13.2
0	6	8	12.9	5.4
0	6	9	17.4	−14.9
0	8	1	40.8	39.6
0	8	2	160.7	166.7
0	8	3	31.0	−33.1
0	8	4	110.9	−115.1
0	8	5	29.4	24.7
0	8	6	123.7	112.7
0	8	7	29.2	−28.1
0	8	8	86.9	−77.2
0	10	1	28.1	−18.0
0	10	2	54.0	48.3
0	10	3	28.3	18.3
0	10	4	37.5	−32.9
0	10	5	15.7	−12.2
0	10	6	57.7	37.2
0	10	7	15.4	13.0
0	12	1	97.0	85.3
0	12	2	29.5	−26.1
0	12	3	89.1	−64.2
0	12	4	27.8	18.6
0	12	5	80.0	54.0
0	12	6	22.2	−16.9
0	14	1	40.6	31.3
0	14	2	14.2	8.6
0	14	3	35.2	−28.7

but no absorption corrections were made ($\mu=426\ \text{cm}^{-1}$). Nickel-filtered Cu$K\alpha$ radiation ($\lambda=1.5418$ Å) was used throughout.

Determination of the Structure

The Patterson projections, $P(uv)$ and $P(vw)$, showed that all the iodine atoms are in four-fold special positions (c), $(0, y, \frac{1}{4};\ 0, \bar{y}, \frac{3}{4};\ \frac{1}{2}, \frac{1}{2}+y, \frac{1}{4};\ \frac{1}{2}, \frac{1}{2}-y, \frac{3}{4})$, *i. e.*, on the two-fold axes at $z=\frac{1}{4}$ and $\frac{3}{4}$ ($x=0$ and $\frac{1}{2}$). When the molecular axis of phenazine, containing two nitrogen atoms, is placed on the two-fold axis and a linear chain of alternating phenazine and iodine molecules, $>$N···I–I···N$<$,[*2] is constructed in the same way as in other halogen complexes,8) the structure well satisfying the packing consideration. The Fourier projection along the c axis was synthesized with the signs of the structure factors calculated for the iodine atoms alone, the y parameters of which were easily found from the Patterson projection, $P(uv)$. This projection gave the approximate positions of all the atoms; they agreed with the presumed model. The approximate parameters of all the atoms were refined by successive Fourier and difference Fourier syntheses for the three sets of two-dimensional data. At this stage, the reliability factors, $\sum\|F_o|-|F_c\|/\sum|F_o|$, were 0.19, 0.19, and 0.24 for the $hk0$, $h0l$, and $0kl$ zones respectively.

During the refinement of the xy projection, it became evident that the strong intensities with low indices showed systematically high calculated values. It was presumed that this discrepancy was caused by extinction,9) and an empirical correction for it was made according to the method of Pinnock, Taylor, and Lipson,10) who developed it

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[*2] In this paper, a solid line, I–I, denotes a covalent bond, whereas a broken line, N···I, represents an intermolecular contact.

9) C. G. Darwin, *Phil. Mag.*, **43**, 800 (1922).
10) P. R. Pinnock, C. A. Taylor and H. Lipson, *Acta Cryst.*, **9**, 173 (1956).

in their study of triphenylene. The reliability factors were decreased through this correction to 0.145, 0.104, and 0.186 for the *hk*0, *h*0*l*, and 0*kl* zones respectively. The observed and calculated structure factors are shown in Table 1. The structure factors corrected for extinction are marked with asterisks.

The final atomic parameters are listed in Table 2. The parameters of nitrogen and carbon atoms were determined from the difference syntheses, in which the calculated structure factors for the iodine atoms were subtracted from the observed structure factors. Because of the large amount of overlap in the *yz* and *xz* projections, the *z* parameters of carbon atoms are the least accurate of all. The electron density projection along the c axis is shown in Fig. 1.

TABLE 2. THE ATOMIC PARAMETER

Atom	x	y	z
I(1)	0.000	0.060	0.250
I(2)	0.000	−0.175	0.250
N(1)	0.000	0.310	0.250
N(2)	0.000	0.576	0.250
C(1)	0.073	0.385	0.184
C(2)	0.070	0.503	0.184
C(3)	0.155	0.326	0.110
C(4)	0.155	0.565	0.110
C(5)	0.230	0.384	0.038
C(6)	0.231	0.505	0.038

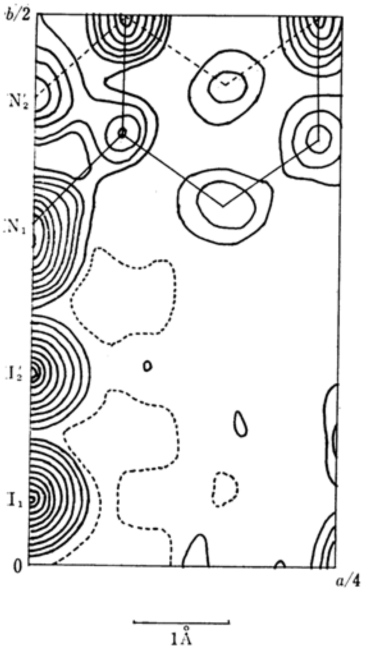

Fig. 1. The electron density projection along the c axis. Contour intervals: 2 eA^{-2} for carbon and nitrogen; 10 eA^{-2} for iodine. First contour at 4 eA^{-2} for carbon and nitrogen, 10 eA^{-2} for iodine. The broken lines indicate negative areas.

The phenazine molecule forms a plane parallel to the b axis, and the best calculated least-squares plane has the following equation:

$$0.0222x + 0.0581z = 1.$$

The deviations of atoms from this plane, shown in Table 3, are all within the range of experimental error. The angle between this plane and (001) is 30.5°.

TABLE 3. DISTANCE TO THE BEST PLANE FROM THE ATOMS

Atom	Distance, Å
N(1)	0.000
N(2)	0.000
C(1)	0.006
C(2)	−0.014
C(3)	0.013
C(4)	0.013
C(5)	−0.011
C(6)	0.004

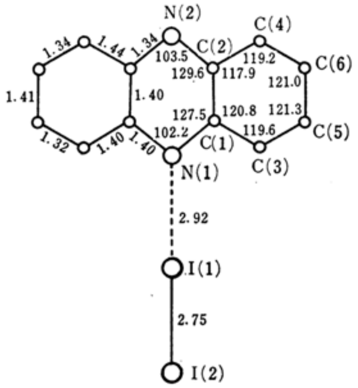

Fig. 2. The bond lengths and bond angles (Å, degree).

The bond lengths and angles are summarized in Fig. 2. The average deviations of C–C and C–N distances are about 0.1 Å at the present stage of refinement. In spite of the fairly large errors (because of the disturbance of heavy iodine atoms), it may be said that the nitrogen atoms of phenazine are slightly deviated from their normal positions towards the iodine molecules. The other bond lengths and angles of phenazine are normal.11)

The computations were performed in the initial stage on the PC-2 computer at the Data Processing Centre of the University of Tokyo, and later on the HITAC 5020E computer at the Computer Centre of the same University. The programmes for the PC-2 computer were kindly offered by Professor Y. Iitaka.

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11) F. H. Herbstein and G. M. J. Schmidt, *Acta Cryst.*, **8**, 399, 406 (1955).

Table 4. The atomic distances observed in some molecular complexes

Molecular complex	Bond	Distance observed	Bond	Distance observed	Ref.
4-Picoline-I_2	N···I	2.31 Å	I-I (I_2)	2.83 Å	13
$(CH_3)_3N$-I_2	N···I	2.27	I-I (I_2)	2.83	14
Pyridine-2I_2	N—I	2.16	I-I (I_3^-)	2.93	16
	(cation)		I-I (I_2)	2.74	16
Phenazine-I_2	N···I	2.9	I-I (I_2)	2.75	this work
I_2 (free molecule)			I-I	2.67	15

Results and Discussion

The packing of the molecules in the crystal is illustrated in Fig. 3. The straight-chain configuration of alternating phenazine and iodine molecules, parallel to the b axis, is explained by the charge-transfer interaction. In the direction of the c axis, on the other hand, the phenazine molecules are stacked in a plane-to-plane manner, arranged in columns, and the mean separation of the molecules is 3.57 Å. The iodine molecules are arranged in another kind of column, parallel to the c axis, and the average distance of intermolecular atoms is 4.38 Å. These values are almost equal to the van der Waals separations.[12] As a whole, the structure of this complex consists of infinite straight chains of alternate donor and acceptor molecules; the chains are then arranged in an approximately close-packed array.

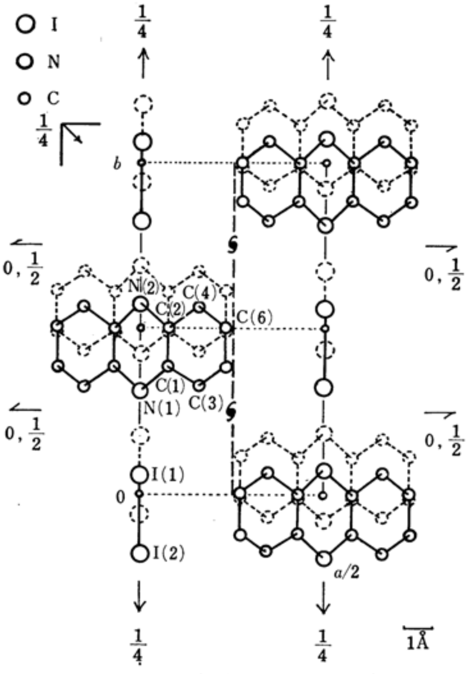

Fig. 3. Projection of the structure along the c axis.

Table 4 shows the intermolecular N···I distances and the intramolecular I–I distances in several iodine complexes, in which the charge-transfer interaction takes place from the lone pair electrons of the nitrogen atom of the donor to the iodine molecule. In 4-picoline-I_2[13] and trimethylamine-I_2[14] complexes, the N···I distance, about 2.3 Å, is much shorter than the sum of van der Waals radii, 3.65 Å. On the other hand, the intramolecular I–I distance, 2.83 Å, is longer than that of free iodine,[15] 2.67 Å. These deviations of atomic distances relate to the donor-acceptor interaction: the decrease in N···I distance is explained by the increase in the contribution of covalent character between the nitrogen and iodine atoms, whereas the elongation of the I–I distance indicates the increase in the ionic character of the bond.[8]

In the pyridine-2I_2 complex, three kinds of iodine have been observed by Hassel and Hope.[16] The first is an iodine atom combined covalently to two nitrogen atoms of two pyridine molecules (N–I distance of 2.16 Å); they form a cation.*3 The second forms a completely ionized triiodide ion, I_3^-, while the third is an iodine molecule possessing less ionic character than the second: the I–I bond distance in Table 4 clearly corresponds to these characters. In the phenazine-I_2 complex, the observed distances of N···I and I–I are 2.9 and 2.75 Å respectively. The longer N···I distance in phenazine-I_2 than that in 4-picoline-I_2 or trimethylamine-I_2 may be explained by the steric hindrance of hydrogen atoms attached to the C(3) and C(4) atoms of the phenazine nucleus. This steric hindrance is connected with a weakening of the donor-acceptor interaction, resulting in a decrease of the ionic character of the I–I bond.

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12) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Itaca, New York (1960).

13) O. Hassel, Chr. Rømming and T. Tufte, *Acta Chem. Scand.*, **15**, 967 (1961).

14) K. O. Strømme, *ibid.*, **13**, 268 (1959).

15) O. Hassel and H. Viervoll, *ibid.*, **1**, 149 (1947).

16) O. Hassel and H. Hope, *ibid.*, **15**, 407 (1961).

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