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The Crystal Structure of *o*-Phenylenediamine Dihydroiodide

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Synopsis. Crystals of *o*-phenylenediamine dihydroiodide are orthorhombic; $a=7.828(1)$, $b=13.158(1)$, $c=5.043(1)$ Å, $Z=2$, and space group Pmnm. The structure was solved by the heavy-atom method and refined with 1359 diffractometer data points to the final $R=0.052$. It is isostructural with *o*-phenylenediamine dihydrobromide. Protonated amino groups link to iodide ions by hydrogen bonds.

Recently, studies of polyiodides have often been presented in relation to one-dimensional conductors.[1] *o*-Phenylenediamine(OPD)[2] forms many complexes with iodine at various mole ratios and with different crystal systems. In a series of structural studies of OPD–iodine system, we have taken up the crystal structure of OPD dihydroiodide (OPD·2HI). Some OPD–hydrohalides[3] have been studied, but not this one.

Experimental

Colorless a-elongated needle crystals were obtained by mixing an ethanol solution of OPD with an aqueous solution of HI in a nitrogen atmosphere. A crystal with dimensions $0.3\times0.3\times0.25$ mm^3 was sealed in a glass capillary in a nitrogen atmosphere. It was mounted with the a-axis parallel to the ϕ axis of a Rigaku four-circle diffractometer. Intensities and cell parameters were obtained with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.7107$ Å) at room temperature. Intensities of 1620 independent reflections were collected by the 2θ-ω scan method with a scan speed of 4° min^{-1} in 2θ in the range $2\theta\leq75°$, and 1359 intensities ($F_o\geq3\sigma(F)$) were used in the analysis. No absorption correction was applied.

Crystal Data. $C_6H_8N_2\cdot2HI$, $F.W.=364.0$; Orthorhombic, Space group Pmnm, $a=7.828(1)$, $b=13.158(1)$, $c=5.043(1)$ Å, $V=519.4(1)$ Å^3, $D_m=2.27$, $D_x=2.31$ g cm^{-3}, $Z=2$, μ(Mo $K\alpha$)$=59.2$ cm^{-1}, Systematic absences $h0l$ with $h+l=2n+1$.

Structure Determination and Discussion

The structure was solved by the heavy-atom method and refined by full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms, and with anomalous dispersion factors for the iodide ion. The hydrogen atoms bonded to carbon atoms were located in the difference synthesis. These hydrogens were introduced and fixed at those positions with temperature factors B of 4.5 Å^2. The discrepancy index, R, was finally reduced to 0.052.

The atomic scattering factors and anomalous dispersion factors were taken from "International Tables for X-Ray Crystallography."[4] The quantity minimized in the refinement was $\Sigma w(|F_o|-k|F_c|)^2$; $w=1.0$ for all the F's. All the computations were performed at the Computer Centre of the University of Tokyo, using the UNICS program system.[5] The final atomic parameters are shown in Table 1. The tables of F_o-F_c data and anisotropic thermal parameters are kept as Document No. 8210 at the Office of the Chemical Society of Japan.

The crystal consists of OPD$^+$ cations and iodide ions, and is essentially isostructural with OPD·2HBr.[3d] Figure 1 shows the molecular arrangement in a cell and the numbering of atoms. OPD molecule is completely planar with an mm symmetry and parallel to the ab plane, except for the amino hydrogens. Partial intercalation of iodide ions permits relatively wide spacing between OPD$^+$ molecular planes, 5.04 Å ($=c$); this suggests the absence of interaction between cations. The distances and angles of OPD skeleton,

Table 1. Atomic coordinates and their standard deviations

Atom	x	y	z
I(1)	$\frac{1}{4}$	0.52924(6)	$\frac{3}{4}$
I(2)	$\frac{1}{4}$	0.25525(6)	$\frac{1}{4}$
N	0.4405(9)	0.6771(5)	$\frac{1}{4}$
C(1)	0.3421(10)	0.7705(6)	$\frac{1}{4}$
C(2)	0.4284(11)	0.8630(6)	$\frac{1}{4}$
C(3)	0.3407(13)	0.9533(6)	$\frac{1}{4}$
H(2)	0.55	0.85	$\frac{1}{4}$
H(3)	0.43	1.02	$\frac{1}{4}$

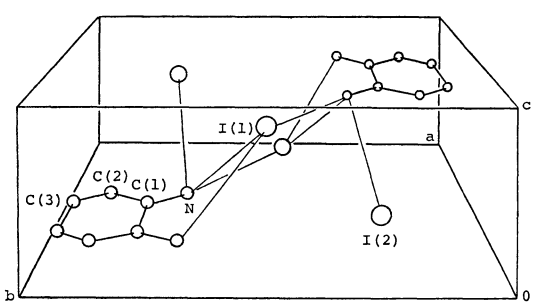

Fig. 1. Perspective view of the non-hydrogen atoms in a cell.

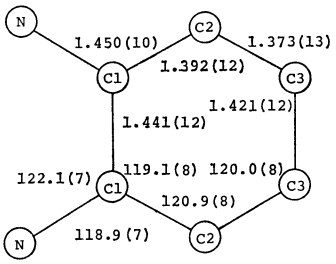

Fig. 2. Bond lengths (Å) and bond angles (°) of OPD^+ skeleton.

shown in Fig. 2, are normal. The C–N length, 1.450 Å, agrees with the C–NH_3^+ bond length, found in the related compounds (1.450—1.501 Å).[3a,3b,3d,6] Domenicano *et al.*[7] proposed that the 'standard' length of the aromatic C–NH_3^+ bond was 1.464 Å, which they calculated as the weighted mean value of 6 ring-substituted anilinium cations. On the other hand, the lengths of reported non-protonated C–NH_2 bond are significantly shorter than those of C–NH_3^+, namely, 1.351—1.391 Å.[3a,6,8] Judging from the C–N bond length, the amino groups in OPD·2HI are protonated. The nitrogen atom is surrounded by 5 iodide ions. Both of the two crystallographically non-equivalent iodide ions, I(1) and I(2), are on the mm symmetry points and surrounded by 4 OPD^+ cations. The I(1) ion has 2 types of I···N distances: 4 equivalent N's to a distance of 3.517 Å and the other 2 equivalent N's at 3.639 Å. The I(2) ion has the only 1 type of 4 I···N distances, 3.608 Å. The reported N···I hydrogen bonding distances are distributed from 3.46 to 4.06 Å.[9]

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2) In this paper, OPD denotes $C_6H_4(NH_2)_2$, and OPD^+ denotes protonated $C_6H_4(NH_3^+)_2$.

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