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Solid-State Coordination Bonding to Polyvalent Iodine— The Structure of 1-acetoxy-1,2-benziodoxolin-3-one

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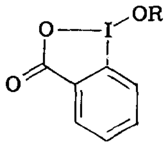
A crystal structure analysis of the mixed anhydride of acetic and *o*-iodosobenzoic acids has verified previous structural assignments as 1-acetoxy-1,2-benziodoxolin-3-one ($a = 16.191$, $b = 7.762$, $c = 7.705$ Å, $\beta = 82.0°$, $Z = 4$, space group $P2_1/a$). The slightly distorted T-like geometry of the three covalent bonds to iodine is similar to that in *o*-iodosobenzoic acid. Intermolecular I–O coordination bonds of markedly constant orientation relative to the covalent iodine bonds occur in this and several other crystal structures of related derivatives.

Introduction

Although recent chemical (*1*) and ir spectroscopic (*2*) evidence has been presented in support of the long-recognized (*3*) possibility that simple esters and mixed anhydrides of *o*-iodosobenzoic acid possess heterocyclic structures, the only published crystallographic data bearing on this problem appears to be the X-ray analysis of the unsubstituted parent acid (*4*), Ia.[1]



(I)

R
(a) H
(b) acetyl
(c) 2′-iodobenzoyl

R
(d) 2′-bromobenzoyl
(e) 2′-chlorobenzoyl
(f) 3′-chlorobenzoyl
(g) benzoyl

Since crystallographic confirmation of the cyclic structures is particularly desirable in view of the unusual *intra*- and *inter*-molecular bonding previously observed in several organic polyvalent iodine compounds,[2] we report here the crystal and molecular structure of 1-acetoxy-1,2-benziodoxolin-3-one, Ib. This acetate is one of several structures (Ib–g and polymorphs) which were determined during studies of the topotactic transformations of the isomeric 2-iododibenzoyl peroxide derivatives (*6*, *7*). All contain the heterocycle. Although their crystal structures exhibit a wide variety of molecular packing modes they all contain intermolecular coordination bonds of remarkably constant orientation with respect to the covalent bonds to the trivalent iodine atoms.

X-Ray Diffraction Studies (*8*) of Ib

Ib was prepared by briefly refluxing acetic anhydride solutions of Ia (*1*). The well-formed prismatic crystals which separate upon cooling are suitable for diffraction studies after recrystallization from the same solvent. The crystal data, $a = 16.191 \pm 0.009$, $b = 7.762 \pm 0.007$, $c = 7.705 \pm 0.006$ Å, $\beta = 82.0 \pm 0.1°$, space group $P2_1/a$, and measured density are consistent with one $C_9H_7IO_4$ formula weight per asymmetric unit. Since the crystals slowly decompose in the X-ray beam, different specimens (approximately 0.06 mm cubes) were used to obtain the diffraction intensities which were visually estimated from equi-inclination

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[1] A brief crystallographic survey of several derivatives of 1-methoxy-1,2-benziodoxolin-3-one (I, R = CH_3) was made (*1*), but apparently no structure analysis was undertaken. In our laboratory, crystals of the simple 1-methoxy derivative have been found to undergo a topotactic transformation which is currently under investigation.

[2] A discussion of iodine bonding in several crystal structures is presented in a review (*5*) of organic polyvalent iodine compounds.

TABLE I

FRACTIONAL ATOMIC COORDINATES FOR (Ib)
(esd's × 10^3 are given in parentheses)

Atom	X	Y	Z
I(1)	0.3287(0.1)	0.0803(0.2)	0.3005(0.2)
C(2)	0.445(2)	−0.016(4)	0.282(4)
C(3)	0.519(2)	0.058(3)	0.204(3)
C(4)	0.593(2)	−0.035(4)	0.212(4)
C(5)	0.591(2)	−0.201(4)	0.297(3)
C(6)	0.523(2)	−0.265(4)	0.381(3)
C(7)	0.447(2)	−0.184(4)	0.371(4)
C(8)	0.367(2)	−0.243(5)	0.448(4)
O(9)	0.361(1)	−0.382(3)	0.529(3)
O(10)	0.300(1)	−0.157(3)	0.434(3)
O(11)	0.391(1)	0.296(3)	0.176(3)
C(12)	0.339(2)	0.390(4)	0.101(4)
O(13)	0.271(2)	0.345(3)	0.090(3)
C(14)	0.377(2)	0.558(4)	0.019(4)

Weissenberg photographs of layers h0l–h3l and hk0, hk1 (CuK_α). The intensities were corrected for absorption and the Lorentz-polarization factors, and correlated to produce the final set of 777 independent nonzero reflections used in the analysis. Patterson and Fourier methods clearly revealed all fourteen nonhydrogen atoms. Several cycles of least squares refinements of all coordinates, anisotropic temperature parameters for iodine and isotropic parameters for the lighter atoms converged to $R = 0.09$ when parameter shifts were less than ~1/5 of the estimated errors. No attempts were made to locate the hydrogen atoms or to refine a totally anisotropic model. The final fractional atomic coordinates are listed in Table I and a list of the observed and calculated structure amplitudes is available.*

The Molecular Structure of Ib

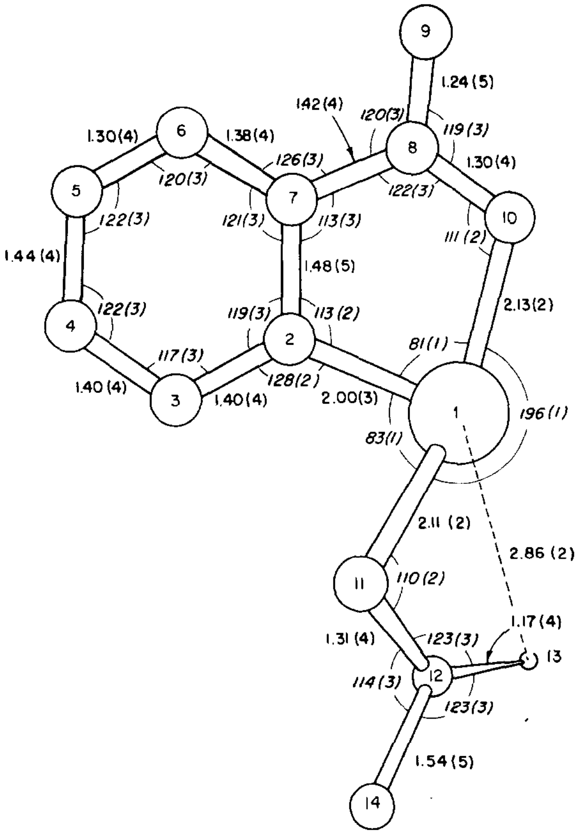

FIG. 1. Calculated bond distances and angles in Ib. The figures in parentheses are least squares estimated uncertainties in the last significant figures.

A perspective drawing of the molecular conformation in the crystal lattice including the calculated bond distances and angles is shown in Fig. 1. Three covalent bonds to iodine are indicated; the I–O bond lengths are somewhat longer than the sum of the single covalent radii (*9*) (2.00 Å) though shorter than the cyclic I–O distance of 2.30 Å reported for the parent acid, Ia. The entire benziodoxolinone moiety is planar within experimental error (rms atomic deviation from the least squares plane is 0.02 Å (plane P_2, Table II)) but O(11) is 0.19 Å out of this plane. The valence angles about the polyvalent iodine suggest deviations from a trigonal bipyramid geometry which are similar in magnitude and direction to those previously observed in Ia.

The planar acetoxy group (atoms 11–14, plane P_3) is rotated about the exocyclic I–O(11) bond through an angle of 24°, resulting in an *intra*molecular I–O(13) distance of 2.86 Å. While this distance suggest possible coordination of O(13) to iodine (*vide infra*), the entire geometry of atoms I, O(11), C(12), and O(13) supports a covalent rather than an appreciably delocalized ionic structure.

Iodine–Oxygen Coordination Bonding

The molecular association of Ib about crystallographic screw axes (Fig. 2) is dominated by an

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* A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01567 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, N.Y. 10022. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

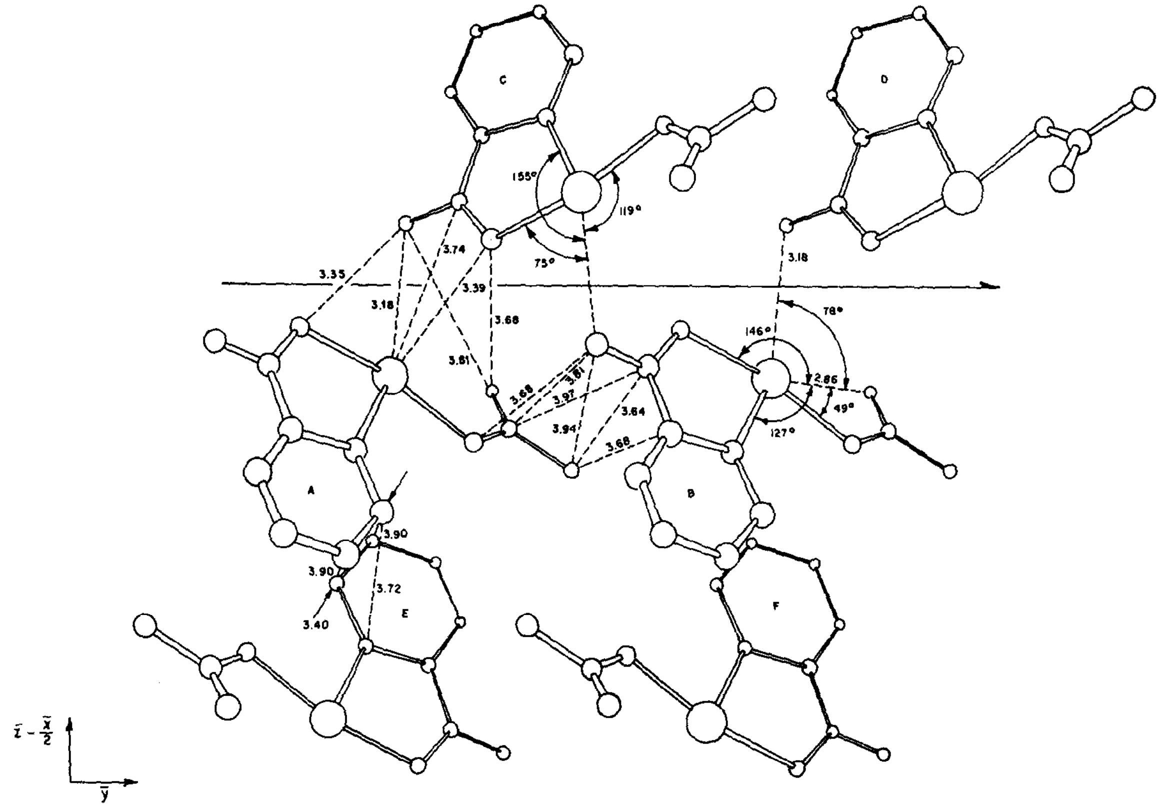

FIG. 2. The intermolecular contacts less than 4 Å in the crystal structure of Ib [(201) projection]. The lettered molecules are related as: A(x, y, z); B($x, 1+y, z$); C($1/2-x, 1/2+y, 1-z$); D($1/2-x, 3/2+y, 1-z$); E($1-x, -y, 1-z$); F($1-x, 1-y, 1-z$).

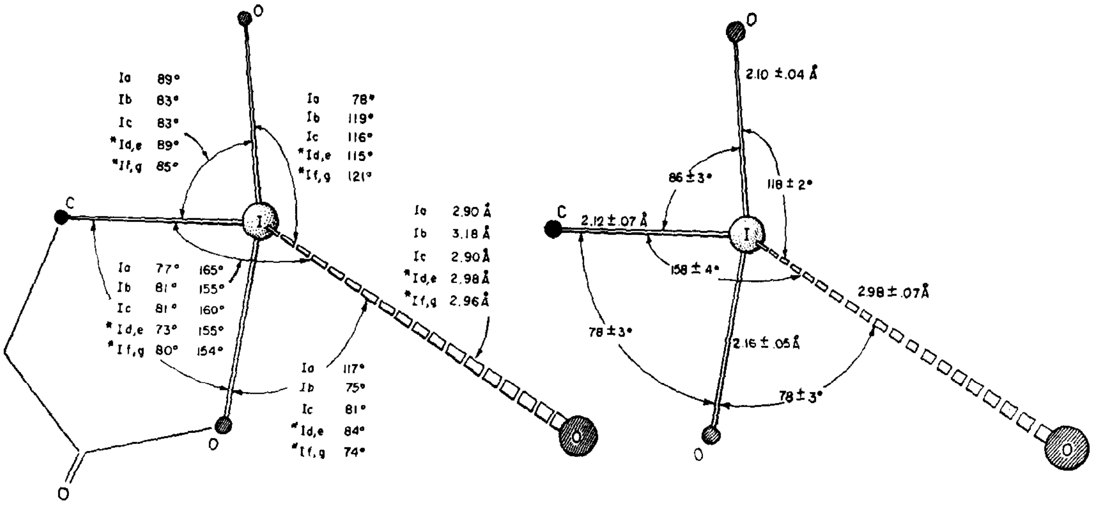

FIG. 3(a; left) The geometry of the recurring intermolecular I–O coordination in some crystal structures of Ia–Ig. Grouped structures marked by an asterisk are crystallographically isostructural.

FIG. 3(b; right) The average of the geometries about iodine in structures Ia–Ig, disregarding the distinction between cyclic and noncyclic covalent I–O bonds. The tolerance figures are average deviations from the average geometrical parameters.

TABLE II

LEAST SQUARES PLANES IN Ib

Plane P_1: $0.233\ X + 0.456\ Y + 0.859\ Z = 3.554$[a]			
	Deviation		Deviation
I(1)[b]	0.01 Å	O(10)[b]	−0.02 Å
C(2)[b]	−0.01	O(11)	0.17
C(7)[b]	0.00	O(13)	−0.70
C(8)[b]	0.02	O(9′)[c]	0.59
Plane P_2: $0.231\ X + 0.467\ Y + 0.853\ Z = 3.522$[a]			
	Deviation		Deviation
I(1)[b]	0.03 Å	C(7)[b]	−0.01 Å
C(2)[b]	−0.01	C(8)[b]	0.00
C(3)[b]	0.00	O(9)[b]	0.01
C(4)[b]	0.00	O(10)[b]	−0.04
C(5)[b]	0.03	O(11)	0.20
C(6)[b]	0.04		
Plane P_3: $-0.189\ X + 0.473\ Y + 0.860\ Z = 1.021$[a]			
	Deviation		Deviation
I(1)	0.18 Å	O(13)[b]	0.00 Å
O(11)[b]	0.00	C(14)[b]	−0.01
C(12)[b]	0.02		

[a] Planes are defined in terms of the orthonormal axes X, Y, Z which are directed along the crystallographic axes a, b, and c^* respectively.

[b] These atoms were used to calculate the plane.

[c] O(9′) is the coordinating atom at

$$(XYZ) = (0.139, 0.118, 0.471).$$

*inter*molecular I–O interaction across a distance (3.18 Å) which is appreciably less than the sum (~3.46 Å) of van der Waals' radii.[3] Similar I–O interactions of remarkably constant geometry are present in crystal structures Ia, and Ic–Ig (*10*) despite their different *R* substituents and different over-all crystal structures (Fig. 3a). In all structures, the coordinated oxygen atom is displaced from a plane through the iodine atom and normal to the vector between the oxygen atoms to which iodine is covalently bonded ("equatorial plane"). The displacement (1.2 Å in Ib) consistently is toward the *cyclic* covalent I–O bond in structures Ib–Ig which have a carbonyl oxygen atom (O(13)) on the *opposite* side of the equatorial plane within coordinating distance of the iodine atom. The angular orientation of the *fifth* atom, O(13), relative to the other atoms [C(2), O(10), O(11) and O(9′)] associated with iodine (see Fig. 2), also is essentially constant in Ib–Ig.

Unlike the above structures, the *inter*molecularly coordinated atom in the crystal structure of the parent acid, Ia, is not a carbonyl but rather the hydroxyl oxygen atom of a screw-axis related neighbor. Moreover, the displacement of the coordinated oxygen atom from the equatorial plane occurs toward the *noncyclic* covalent I–O bond resulting in an apparent interchange of the two angles between the covalent I–O bonds and the coordination bond (Fig. 3a). The opposite displacement appears to be related to the absence of an additional *intra*molecularly proximate carbonyl group and also, to the additional association (hydrogen bonding) of the hydroxyl group with a third, glide-related molecule. No fifth atom appears to be involved in the coordination about iodine in Ia.

The average geometry about the iodine in these structures, disregarding the distinction between *cyclic* and *noncyclic* covalent I–O bonds is shown in Fig. 3b. This unusually consistent coordination geometry suggests strongly directional valence requirements for polyvalent iodine which, by analogy, may define the as yet undetermined geometry about the pentavalent iodine atom in *o*-iodoxybenzoic acid.

Several interesting structural consequences of this coordination mode in the many examples of polymorphism and topotaxy in solid-state reactions of this heterocyclic system will be considered in separate reports.

Acknowledgments

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[3] $2.1 + 1.36 = 3.46$ Å. Our data from several crystal structure analyses of polyvalent iodine systems, particularly a polymorph of Ic which does not contain intermolecular I–O coordination bonds suggest that the commonly accepted van der Waals' radius for monovalent iodine (~2.1 Å) should be reduced to ~1.6 Å for polyvalent iodine species.