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Solid-State Chemistry of Organic Polyvalent Iodine Compounds. V. The Crystal Structures of 3-oxo-3H-2,1-benzoxiodol-1-yl *o*-Bromobenzoate (Two Polymorphs) and 3-oxo-3H-2,1-benzoxiodol-1-yl *o*-Chlorobenzoate

J. ZANOS GOUGOUTAS AND D. G. NAAE*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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Single-crystal transformations of 2-iodo-2′-bromo-, and 2-iodo-2′-chlorodibenzoyl peroxides (IIa and IIb) yield topotactically aligned crystal structures of their respective isomers: 3-oxo-3H-2,1-benzoxiodol-1-yl *o*-bromobenzoate (Ia) and its *o*-chlorobenzoate analog (Ib). Two of the polymorphic forms of Ia ($C_{14}H_8IBrO_4$) which are formed in crystalline IIa can also be obtained by crystallizing Ia from various solvents: (Ia-β), $\mathbf{a} = 7.474$, $\mathbf{b} = 13.994$, $\mathbf{c} = 13.152$ Å, $\beta = 102.4°$, $Z = 4$, $P2_1/a$, and a disordered acicular form (Ia-α) which appears to be orthorhombic, $\mathbf{a} = 3.99$, $\mathbf{b} = 26.553$, $\mathbf{c} = 26.008$, $Z = 8$, ($Pbc2_1$?). The only form of Ib ($C_{14}H_8IClO_4$) obtained by crystallizations from solvents is also formed in crystalline IIb.

The crystal structures of the isostructural Ia-β and Ib have been determined but only the latter has been refined ($R = 0.059$ for 2085 "observed" intensities). The derivative crystal structure of Ia-α has been determined only in (100) projection ($R = 0.08$ for 156 "observed" intensities). The three structures contain similar chains of bimolecular units or "dimers." The "dimers" are analogous to those found in crystal structures of the benzoate, *m*-chlorobenzoate, *o*-iodobenzoate, and *o*-fluorobenzoate analogs of I.

Novel polymorphs (X_a and X_b) of Ia and Ib are formed during the solid state peroxide isomerizations. The isostructural X_a and X_b consist of chains of "dimers" which are similar to those in Ia and Ib.

Introduction

The crystal structures of several benzoxiodolin-3-one derivatives, Ia-f, have been determined as part of our studies of their topotactic formation from the corresponding isomeric derivatives of 2-iododibenzoyl peroxide, II. Single crystals of these and other closely related polyvalent iodine structures, whether from topotactic solid-state peroxide rearrangement or from independent chemical synthesis and crystallization from solvents, further have been found to undergo solid-state hydrolytic and photochemical degradations resulting in topotactically oriented crystal structures of the various chemical products (*1*).

The polymorphism which is very common in this class of compounds reflects the ability of several nucleophilic atoms in these molecules to coordinate *inter*molecularly with the relatively electropositive trivalent iodine, I^{III}. We have identified four types of crystal structures among the various crystals of 1-substituted benzoxiodolin-3-one derivatives grown from solvents. Each type is characterized by a specific mode of *inter*molecular coordination involving I^{III}: (1) acyclic-

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* Present address: Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506.

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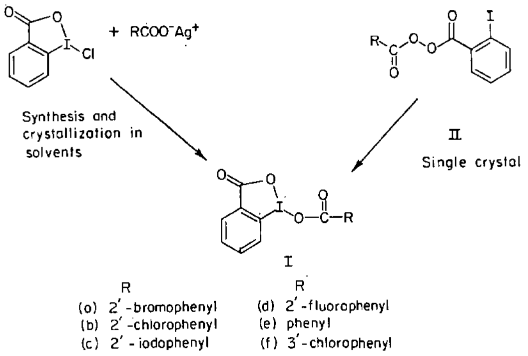

SCHEME 1

$C{=}O\cdots I^{III}$; (2) cyclic-$C{=}O\cdots I^{III}$; (3) monovalent halogen$\cdots I^{III}$; (4) $>O\cdots I^{III}$ (Fig. 1). The previously reported crystal structure of *o*-iodosobenzoic acid (*2*), and its acetate (*3*) (structure I with $R = CH_3$) are representatives of Types 4 and 2, respectively. Each of the derivatives Ia–f crystallizes in at least one crystal structure of Type 1. Only one crystalline modification has been obtained from solvent crystallizations of Ib, Id (*4*), and Ie (*5*) while structures Ia, Ic (*6*), and If (*5*) crystallize in two polymorphic modifications with the second forms of Ic and If exhibiting Type 3 intermolecular coordination modes. In this paper, we describe the crystal structures of the two forms of Ia and the sole structure of Ib obtained from solvents. Unlike the two polymorphs of Ic and If, both forms of Ia exhibit Type 1 coordination modes; Ib is isostructural with one of the forms of Ia.

Without exception, we have found that Type 1 coordination is *mutually established* between two centrically or pseudocentrically related molecules such that the I^{III} and O atoms of one molecule are coordinated with the corresponding O and I^{III} atoms of the other. These internally coordinated "dimers," which further characterize the Type 1 polymorphs, are of special interest in our studies of the isomerizations II → I, for it has been observed that only Type 1 polymorphs crystallize as oriented phases during the topotactic solid-state rearrangements. Thus, both Type 1 polymorphs of Ia crystallize topotactically during the solid-state isomerization of 2-iodo-2′-bromodibenzoyl peroxide, but the topotactic isomerizations of bis-(orthoiodobenzoyl) peroxide to Ic, and 2-iodo-3′-chlorodibenzoyl peroxide to If, yield the corresponding Type 1, but not Type 3 polymorphs.

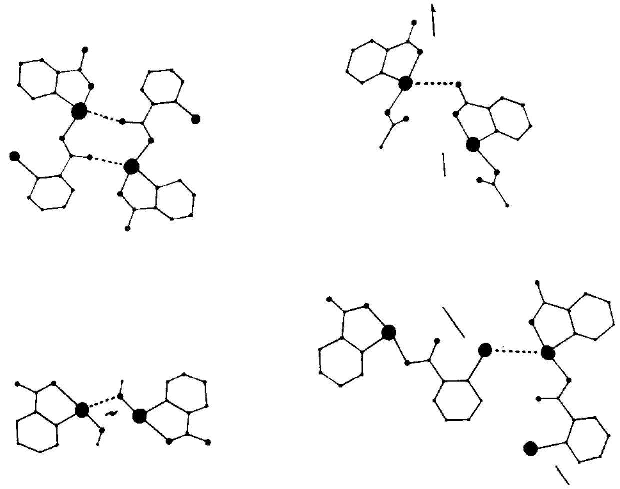

FIG. 1. The four types of observed *inter*molecular coordination bonding to trivalent iodine atoms of benzoxiodolinones: Type 1 (top left) is characterized by "dimers" containing two coordination bonds involving the acyclic carbonyl oxygens; type 2 coordination (top right) occurs along screw axes and involves the heterocyclic carbonyl oxygens; type 3 coordination (bottom right) involves nucleophilic halogen atoms; type 4 coordination (bottom left) involves oxygen atoms which are not covalently bonded to other atoms through π bonds. (Large atoms are halogens.)

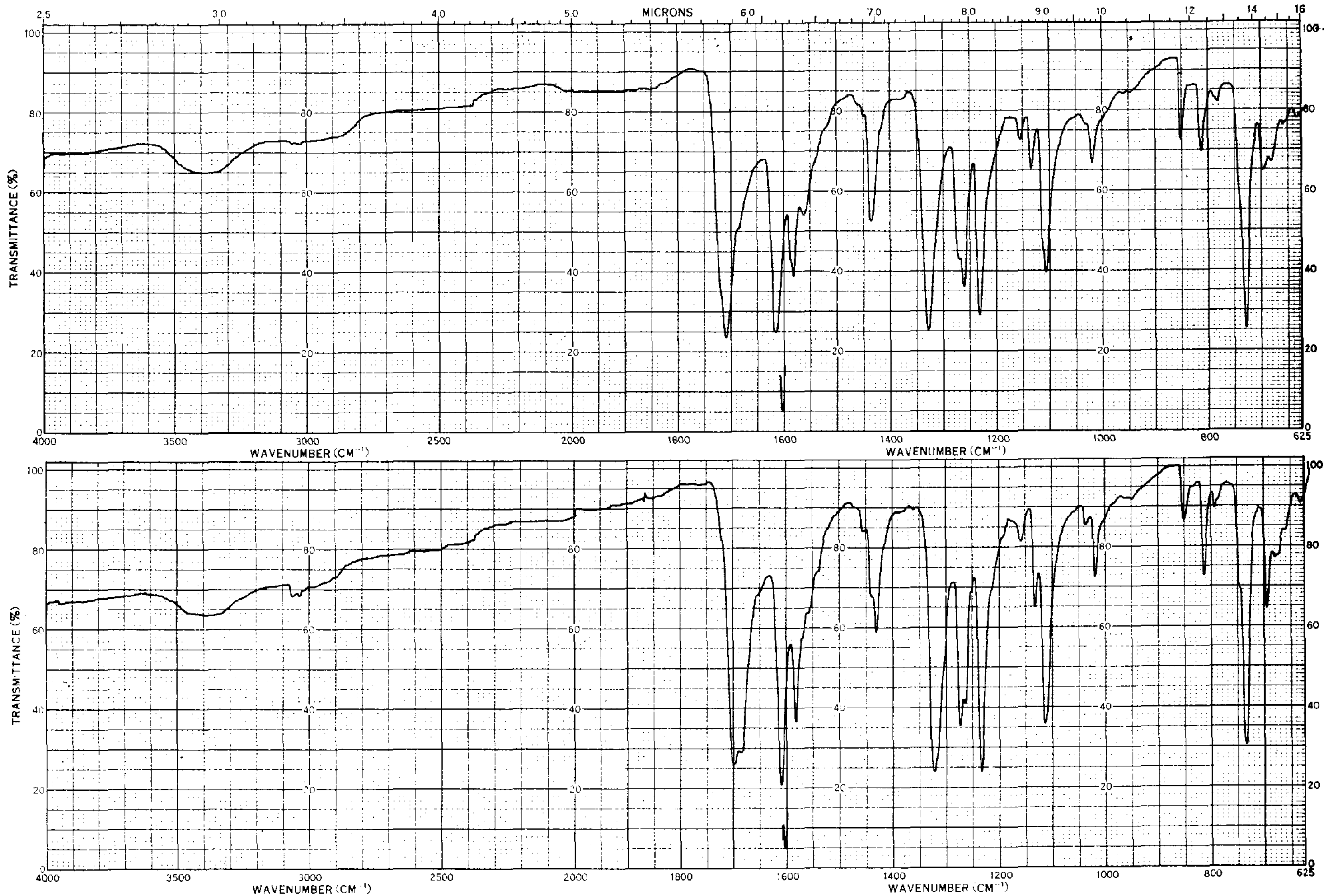

FIG. 2. The infrared spectra of 3-oxo-3H-2,1-benzoxiodol-1-yl *o*-bromobenzoate in KBr pellets. (Top) The acicular polymorph Ia-α. (Bottom) The prismatic form, Ia-β. The calibration band in each spectrum is the 6.24 μ absorption of polystyrene.

Experimental

Ia and Ib were synthesized according to the previously described procedure (*5*) and crystallized in the temperature range 25–0°C from either chloroform, toluene, or *o*-dichlorobenzene. In the case of Ia, an acicular (Ia-α) and an elongated prismatic (Ia-β) form usually crystallize together. Rapid cooling of supersaturated solutions appears to favor crystallization of Ia-α. Only a prismatic form of Ib has been obtained from these and other solvents. The close similarity of the ir spectra of Ia-α and Ia-β (Fig. 2) first suggested the close correspondence in their intermolecular coordination modes. (The ir spectrum of Ib corresponds closely with that of Ia-β.) By comparison, the two polymorphs of Ic (and If) exhibit markedly different ir carbonyl absorption frequencies.

All crystals of the prismatic forms of Ia and Ib were found to be twinned across (001). Single-crystal specimens for the intensity measurements were obtained from twins by cleavage with a razor blade under the polarizing microscope. Unit cell parameters (Table I) were derived from least-squares analyses of Weissenberg and precession photographs calibrated with Al powder reflections. Space groups were assigned on the basis of systematic extinctions; crystal densities were measured by flotation in mixtures of 1,3-dibromopropane and methylene bromide. The isostructural relationship between Ia-β and Ib was readily apparent from their virtually identical diffraction intensities and unit cell parameters.

The Crystal Structure of Prismatic Ia-β and Ib

Initially, the approximate structure of Ia-β was determined by Patterson and Fourier methods based on 1541 intensities (Cu$K\alpha$) measured on a PAILRED diffractometer. Although all nonhydrogen atoms were located, the analysis was terminated at $R = 0.15$ and it was decided to concentrate on the isostructural Ib.

Intensity data from two crystal segments of Ib of average dimensions 0.46 × 0.30 × 0.17 mm were measured on the PAILRED using monochromatic Mo$K\alpha$ X-rays (~22°C; $\lambda = 0.7107$ Å). The segment used for levels $h0l$–$h7l$ showed no detectable twinning. The small amount (<3%) of twin member in the segment used for levels $0kl$–$4kl$ was ignored since only the last level contains erroneously coincident reflections from both members. The data were corrected for absorption (*10*), reduced to $|F|^2$, and correlated to produce 3165 symmetry independent reflections. Of these, 2085 had intensity $I > 3\sigma(I)$, where $\sigma(I)$ is given by the square root of the sum of background and peak counts.

Quantitative verification of the isostructural relationship between Ia-β and Ib was obtained when 693 observed low angle ($\sin\theta/\lambda < 0.33$ Å^{-1}) structure factors for Ib agreed to

TABLE I

CRYSTAL DATA[a]

Structure	a (Å)	b (Å)	c (Å)	β (degrees)	Z	D_m (g/cm^3)	D_{calc} (g/cm^3)	V (Å^3)	Space group	Mp (°C)	μ (cm^{-1})
Ia-α[b]	3.99(2)	26.553(5)	26.008(5)	—	8	2.15	2.15	2755	$Pbc2_1$ (?)	179–182	225 (Cu$K\alpha$)
Ia-β[b]	7.474(3)	13.994(5)	13.152(5)	102.4(1)	4	2.21	2.21	1344	$P2_1/a$	180–183	231 (Cu$K\alpha$)
Ib[b]	7.442(3)	13.877(3)	13.127(4)	102.1(1)	4	2.01	2.01	1325	$P2_1/a$	185–187	26.5 (Mo$K\alpha$)
Id[b]	4.08(1)	12.00(3)	26.25(5)	90.5(1)	4	1.995	1.995	1285	$P2_1/c$	194–196	202 (Cu$K\alpha$)

[a] All crystal data determined at 22°C.

[b] The crystals are elongated along the crystallographic a axis.

$R = 0.13$ with F's calculated from the approximately determined structure of Ia-β with Br replaced by Cl. Introduction of the dispersion corrections $\Delta f'$ and $\Delta f''$ for I and Cl followed by two cycles of full matrix least-squares refinement[1] of all coordinates and anisotropic temperature parameters reduced R to 0.107. Further refinements based on all 2085 "observed" intensities gave $R = 0.07$, at which point all eight hydrogen atoms were located in a difference synthesis. Further refinements of the complete structure converged to $R = 0.059$[2] and the analysis was terminated. Fractional atomic coordinates for Ib are given in Table II, while Table III contains the anisotropic thermal parameters for the non-hydrogen atoms.

The bond distances and angles of the 1-substituted-benzoxiodolin-3-one moiety in Ib are similar to those in the previously reported structures, Ic (*6*), Id (*4*), If (*5*), *o*-iodosobenzoic acid (*2*), and its acetate (*3*), though more precisely determined. This analysis also provides a precise description of the mutual intermolecular $I^{III}\cdots O$ coordination bonding (*3*) which gives rise to the characteristic "dimers" (Fig. 3) of Type 1 polymorphs. A comparison of the conformations of the individual molecules and "dimers" of Ia–f (Ie is isostructural with If), in terms of several planes (Table IV) and torsional angles is given in Table V. The angle of twist of the carboxyl group about the C16–C11 bond, ψ_{23}, and the displacements of C16 and Cl to opposite sides of the phenyl plane in Ib are similar to those found in *o*-chlorobenzoic acid ($\psi_{23} = 13.7°$; displacements $= -0.058$ and $+0.036$ Å (*8*)) but the Cl and carbonyl oxygen atoms of the acid adopt an *s-cis* or *cisoid* arrangement about the exocyclic (C16–C11) bond. The unusual *s-trans* or *transoid* disposition of these atoms in Ib, and in the Type 1 crystal structures of all of the other 2′-halo derivatives, has been adopted in order to permit the close *inter*molecular approach necessary for "dimer" formation (*6*).

TABLE II

Atomic Coordinates for Ib[a]

Atom	X	Y	Z
I	0.46419(10)	0.38469(4)	−0.13681(5)
Cl	0.6361(4)	0.0942(2)	0.734(2)
C-1	0.4194(13)	0.2644(6)	−0.2363(7)
C-2	0.4493(14)	0.1688(7)	−0.2036(7)
C-3	0.4107(14)	0.0992(7)	−0.2811(7)
C-4	0.3407(14)	0.1221(8)	−0.3836(7)
C-5	0.3110(15)	0.2189(7)	−0.4136(8)
C-6	0.3523(13)	0.2907(7)	−0.3379(7)
C-7	0.3171(13)	0.3935(8)	−0.3647(7)
O-8	0.2610(11)	0.4244(5)	−0.4511(5)
O-9	0.3541(9)	0.4519(5)	−0.2815(5)
C-10	0.7450(13)	0.1724(7)	0.1709(7)
C-11	0.7380(13)	0.2728(6)	0.1593(7)
C-12	0.8260(15)	0.3289(7)	0.2443(7)
C-13	0.9237(14)	0.2861(7)	0.3347(8)
C-14	0.9333(16)	0.1856(7)	0.3427(7)
C-15	0.8439(13)	0.1307(7)	0.2603(7)
C-16	0.6432(13)	0.3292(7)	0.0679(7)
O-17	0.6182(9)	0.4175(5)	0.0722(5)
O-18	0.5799(11)	0.2826(5)	−0.0196(5)
H-2[b]	0.476(16)	0.148(8)	−0.135(9)
H-3	0.427(16)	0.023(9)	−0.263(8)
H-4	0.334(16)	0.078(8)	−0.436(9)
H-5	0.252(16)	0.236(9)	−0.484(9)
H-12	0.831(16)	0.396(9)	0.236(8)
H-13	0.982(16)	0.333(8)	0.390(8)
H-14	0.984(15)	0.159(8)	0.411(8)
H-15	0.859(16)	0.058(8)	0.253(9)

[a] Least-squares estimated uncertainty in the final significant figure is given in parentheses.

[b] Hydrogen atoms are given the same number as the carbon to which they are bonded.

The dimers are packed in chains parallel to *b*, through van der Waals–London dispersion interactions between the 2′-chlorine (bromine in Ia-β) atoms of adjacent dimers (Fig. 4). The alternate **a**-glide stacking of chains of dimers is shown in Figs. 5 and 6.

The Acicular Polymorph Ia-α

All of the (~10) crystals of this polymorph which were examined for unit cell and intensity data displayed orthorhombic diffraction symmetry and systematic extinctions (*h*0*l*, *l*-odd) consistent with a **c**-glide element

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[1] The function minimized was $\Sigma w(|F_{\mathrm{obs}}|^2 - |F_{\mathrm{calc}}|^2)^2$, where the weight $w = 1/[\sigma(|F_{\mathrm{obs}}|^2)]^2$. Atomic scattering factors including $\Delta f'$ and $\Delta f''$ for I and Cl were taken from the International Tables for X-ray Crystallography (*7*).

TABLE III

ANISOTROPIC TEMPERATURE FACTOR PARAMETERS FOR Ib[a]

Atom[b]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	0.0138(1)	0.00218(2)	0.00293(3)	0.00015(9)	0.00013(4)	−0.00012(4)
Cl	0.0235(7)	0.0025(1)	0.0043(2)	−0.0001(2)	−0.0001(3)	−0.0003(1)
C-1	0.010(2)	0.0022(4)	0.0030(6)	−0.0006(8)	−0.0000(9)	−0.0006(4)
C-2	0.014(2)	0.0028(5)	0.0034(6)	0.0006(9)	0.001(1)	−0.0003(4)
C-3	0.014(2)	0.0031(6)	0.0055(6)	−0.001(1)	0.004(1)	−0.0011(5)
C-4	0.019(2)	0.0038(5)	0.0042(6)	−0.000(1)	0.0011(9)	−0.0015(6)
C-5	0.014(2)	0.0038(6)	0.0035(6)	0.000(1)	0.000(1)	−0.0009(5)
C-6	0.010(2)	0.0031(5)	0.0034(6)	0.000(1)	0.0005(9)	−0.0000(4)
C-7	0.012(2)	0.0036(5)	0.0039(6)	0.001(1)	0.0006(9)	−0.0001(5)
O-8	0.027(2)	0.0046(4)	0.0034(4)	0.0010(8)	−0.0004(8)	0.0010(4)
O-9	0.015(2)	0.0026(4)	0.0038(4)	0.0007(6)	0.0003(6)	0.0003(3)
C-10	0.010(2)	0.0030(5)	0.0030(6)	−0.0007(9)	0.0018(9)	−0.0001(4)
C-11	0.010(2)	0.0026(4)	0.0032(5)	−0.0004(8)	0.0012(8)	−0.0005(4)
C-12	0.014(2)	0.0032(5)	0.0032(6)	0.0004(9)	0.0009(9)	−0.0004(4)
C-13	0.013(2)	0.0034(5)	0.0048(7)	−0.001(1)	0.003(1)	−0.0008(5)
C-14	0.017(3)	0.0036(5)	0 0041(7)	0.000(1)	0.001(1)	−0.0010(5)
C-15	0.012(2)	0.0035(6)	0.0038(6)	0.000(1)	0.0002(8)	−0.0008(5)
C-16	0.011(2)	0.0032(5)	0.0029(6)	0.0005(9)	−0.0001(9)	0.0002(4)
O-17	0.014(2)	0.0031(4)	0.0048(5)	0.0011(7)	0.0013(7)	−0.0004(3)
O-18	0.024(2)	0.0042(4)	0.0035(4)	0.0007(8)	0.0002(8)	0.0007(4)

[a] The temperature factor is of the form $\exp(-\sum_{i,j} h_i h_j \beta_{ij})$. Least-squares estimated uncertainty in the final significant figure is given in parentheses.

[b] The isotropic temperature factor of 2.18 Å^2 assigned to the hydrogen atoms was not varied.

perpendicular to **b**. Although a **b**-glide symmetry operation perpendicular to **a** was suggested by the presence of both k-even and k-odd rows on upper levels $1kl$ and $2kl$ ($\mathbf{b} = 26.553$ Å; only k-even rows in $0kl$), appreciable faulting disorder of this symmetry was evident: reflections of the type ($h \neq 0$, k-odd, l) were elongated in the direction of $\mathbf{c}^*$ to the extent that continuous streaks of intensity were present along the entire festoons. The degree of disorder was somewhat variable; for most crystals, the streaks peaked only to rather diffuse maxima at reciprocal lattice points, but one needle gave rise to relatively discrete reflections and only faint streaking. The other reflections which have been observed are discrete and show no intensity variation from crystal to crystal. Either space group $Pbc2_1$ or $Pbcm$ with eight molecules per unit cell is indicated for a unit cell (Table I) chosen so as to include the "streaked" k-odd reciprocal lattice rows; however, under this interpretation, the $0k0$ reflections show pseudoextinctions with intensities observable only for $k = 4n$.

The derivative structural relationship (*9*) between the two polymorphs of Ia which was suggested by the correspondence of their unit cell axes: $\vec{a}_\alpha \simeq \vec{a}_\beta/2$, $\vec{b}_\alpha \simeq 2\vec{b}_\beta$, $\vec{c}_\alpha \simeq 2\vec{c}_\beta - \vec{a}_\beta$, was especially evident in comparisons of their $0kl$ intensities. To a very close approximation, the intensities of $0KL$ reflections of Ia-β were contained as a subset in the $0kl$ reflections of Ia-α, according to: $\mathrm{I}(0kl)_\alpha \simeq \mathrm{I}(0KL)_\beta$ when $k = 2K$ and $l = 2L$ (the l-odd reflections of Ia-α have no counterpart in $(0KL)_\beta$, while the k-odd reflections of Ia-α are absent in $(0kl)_\alpha$). In light of these observations, it seemed probable that the molecular structure and packing of Ia-α in (100) projection closely approximated that of the $(20\bar{1})$ molecular layers of Ia-β (Fig. 4). However, the short **a**-axis of 3.99 Å requires a *translational* stacking of these layers in Ia-α, while in

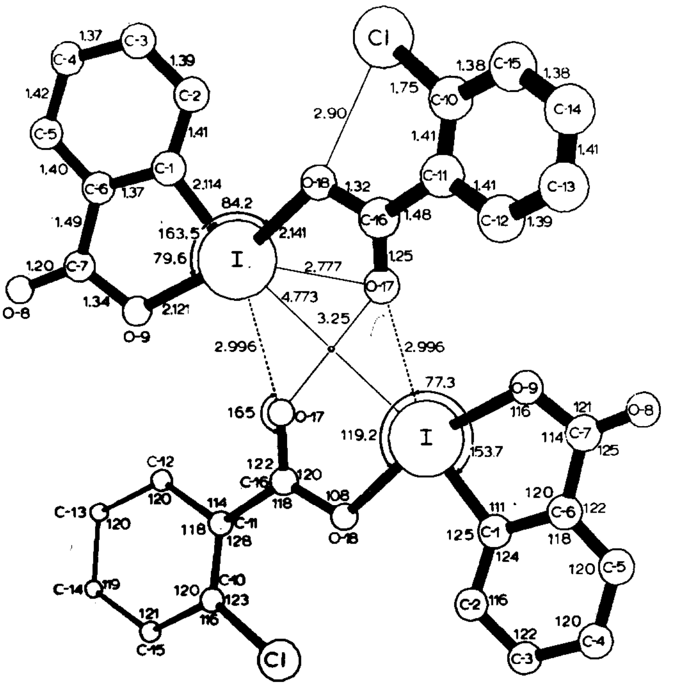

FIG. 3. Calculated bond lengths, angles, and the geometry of the intermolecular coordination bonding in the "dimer" of Ib, viewed down the crystallographic *a* axis. The experimentally observed hydrogen atoms have been omitted. E.s.d.s for C–Cl, C–C, and C–O bond lengths fall in the range 0.01–0.02 Å, while the values for I–C and I–O are 0.009 and 0.006 Å, respectively. E.s.d.s for valence angles about C and O are ~1° while those about I are 0.2–0.3°.

Ia-β, the layers are *alternately* stacked by the glide element of translational component $\mathbf{a}/2 = 3.737$ Å.

Since our primary objective of identifying the *type* of intermolecular coordination and molecular packing in this polymorph could be realized through a two-dimensional analysis, the crystal structure was examined only in projection down the short **a** repeat. The $0kl$ reflections were indexed relative to a cell having the same **c**-axis as above, but with $\mathbf{b}' = b/2 = 13.277$ Å, in which case the axial pseudoextinctions assumed the form ($0k'0$ absent for k'-odd) characteristic of a screw axis or glide line along $\mathbf{b}'$. A Patterson synthesis, based on 156 observable intensities (~22°C, $2\theta_{max} = 100°$; CuK_α, $\lambda = 1.5418$ Å) which had been visually estimated from a multiple-film $(0kl)_\alpha$ Weissenberg photograph and corrected for absorption, contained halogen–halogen vectors consistent with two-dimensional space group *pgg* for this reduced cell, and a Fourier synthesis with phases from the I and Br atoms revealed the presence of Type 1 "dimers" in the anticipated molecular arrangement of Fig. 4. Least-squares refinements of this structure, assuming strict *pgg* symmetry and, therefore, crystallographically centrosymmetric "dimers," converged to $R = 0.08$ for the 156 observed structure factors.[1,2] The refined fractional y and z

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[2] A table of observed and calculated structure factor amplitudes from this analysis has been deposited. See NAPS document No. 02629 for 30 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Ave. South, New York, NY 10016. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications.

TABLE IV

LEAST-SQUARES PLANES IN Ib

Plane $P1$, $0.982x + 0.102y - 0.160z = 4.573$[a]

	Deviation (Å)		Deviation (Å)		Deviation (Å)
I[b]	−0.00	C-2	0.10	O-17	−0.17
C-1[b]	0.02	C-3	0.11	O-17[c]	−0.62
C-6[b]	−0.01	C-4	0.10	O-18	−0.14
C-7[b]	−0.02	C-5	0.03	i[d]	0.23
O-9[b]	0.02	O-8	−0.07		

Plane $P2$, $0.950x + 0.154y - 0.272z = 4.809$[a]

	Deviation (Å)		Deviation (Å)
C-11[b]	0.00	I	−0.12
C-16[b]	−0.01	I[c]	0.55
O-17[b]	0.00	Cl	0.58
O-18[b]	0.00	i[d]	0.21

Plane $P3$, $0.926x - 0.003y - 0.376z = 3.859$[a]

	Deviation (Å)		Deviation (Å)
C-10[b]	0.02	C-15[b]	−0.00
C-11[b]	−0.02	Cl	0.04
C-12[b]	0.01	C-16	−0.04
C-13[b]	0.00	i[d]	0.45
C-14[b]	−0.01		

Plane $P4$, $0.909x + 0.333y - 0.249z = 5.698$[a]

	Deviation (Å)		Deviation (Å)
I[b]	—	C-1	0.30
I[b,c]	—	O-9	−0.40
O-17[b]	—	O-18	0.36
O-17[b,c]	—		

Plane $P5$, $0.987x + 0.058y - 0.151z = 4.376$[a]

	Deviation (Å)		Deviation (Å)
C-1[b]	−0.00	C-6[b]	−0.00
C-2[b]	0.01	I	0.04
C-3[b]	−0.01	C-7	0.04
C-4[b]	0.00	O-9	0.11
C-5[b]	0.00	i[d]	0.32

[a] Planes are defined in terms of the orthonormal axes, x, y, and z which are directed along the crystallographic axes, **a**, **b**, and **c***, respectively.

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

[c] The corresponding atoms in the other member of the "dimer."

[d] The inversion center between the dimers at $\frac{1}{2}$, $\frac{1}{2}$, 0.

TABLE V

CONFORMATIONAL PARAMETERS[a] IN Ib, (Ia-β), Ic, Id, AND If

(A) Molecular Conformational Parameters

Structure	ϕ_1	ϕ_2	ϕ_3	ψ_{12}	ψ_{13}	ψ_{23}
Ib	177	4	167	7	14	169
Ia-β[b]	−176	−2	168	11	18	163
Ic[c]	167	8	−158	12	38	132
Id	172	19	167	5	5	173
If	180	2	−3	3	2	4

(B) Dimer Conformational Parameters

Structure	ψ_{14}	ψ_{24}	ψ_{34}
Ib	15	11	21
Ia-β[b]	12	5	22
Ic	15	17	37
Id	4	4	10
If	3	5	2

[a] All values given in degrees. ϕ is the torsional angle for a group of atoms A–B–C–D. In sighting down the B–C bond from A toward D, a positive value of ϕ requires a clockwise rotation of the A–B bond, about the B–C bond, in order to eclipse the B–D bond. ϕ_1 = C1–I–O18–C16; ϕ_2 = I–O18–C16–O17; ϕ_3 = O17–C16–C11–C10. Angle ψ_{ij} is the dihedral angles between planes i and j (Table IV).

[b] Structure refinement incomplete.

[c] Averaged over the two molecules in the asymmetric unit.

coordinates relative to the reduced cell correspond to a structure which qualitatively is very similar to that shown in Fig. 4. (See Table VI; no attempt was made to locate the hydrogen atoms. The thermal parameters—anisotropic for I and Br, isotropic for C and O—have been deposited.[2,3])

In extrapolating the results from this analysis to the three-dimensional structure of

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[3] We have not attempted to refine any acentric arrangement of the structure in (100) projection. While small deviations from the assumed two-dimensionally centric structure may account for the misbehavior of isotropic temperature factors of some of the light atoms during refinements, it was felt that further refinements with double the number of variables were not warranted in two dimensions.

Ia-α, it is clear that space group *Pbcm* may be excluded. For the alternative, acentric orthorhombic space group $Pbc2_1$ consistent with the apparent systematic extinctions, the measured crystal density would require two molecules in the asymmetric unit, in which

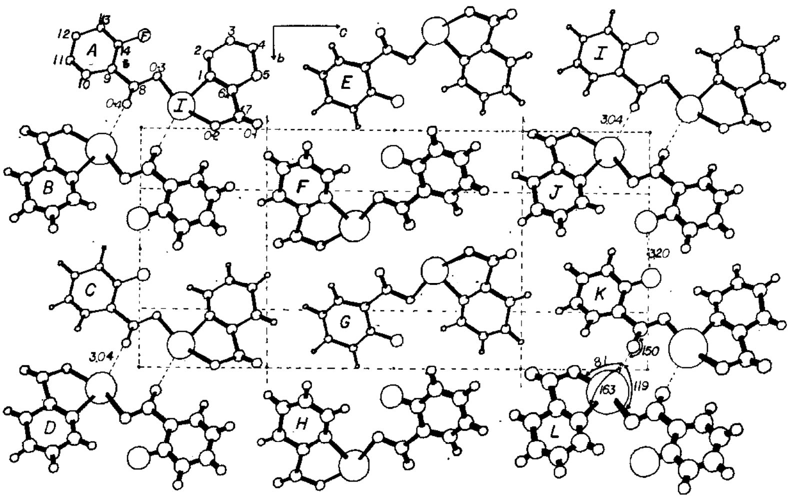

FIG. 4. The molecular arrangement of Ib (and Ia-β) in layers parallel to $(20\bar{1})$. The lettered molecules are related as: A(x, y, z); B($1-x, 1-y, \bar{z}$); C($x, 1+y, z$); D($1-x, 2-y, \bar{z}$); E($\frac{1}{2}+x, \frac{1}{2}-y, 1+z$); F($\frac{3}{2}-x, \frac{1}{2}+y, 1-z$); G($\frac{1}{2}+x, \frac{3}{2}-y, 1+z$); H($\frac{3}{2}-x, \frac{3}{2}+y, 1-z$); I($1+x, y, 2+z$); J($2-x, 1-y, 2-z$); K($1+x, 1+y, 2+z$); L($2-x, 2-y, 2-z$). The broken lines indicate the reduced unit cell (**b**′ vertical, **c** horizontal) of Ia-α, which has a very similar packing arrangement. The infinite chains of "dimers" which are commonly found in these structures are parallel to **b** (e.g., molecules A, B, C, D).

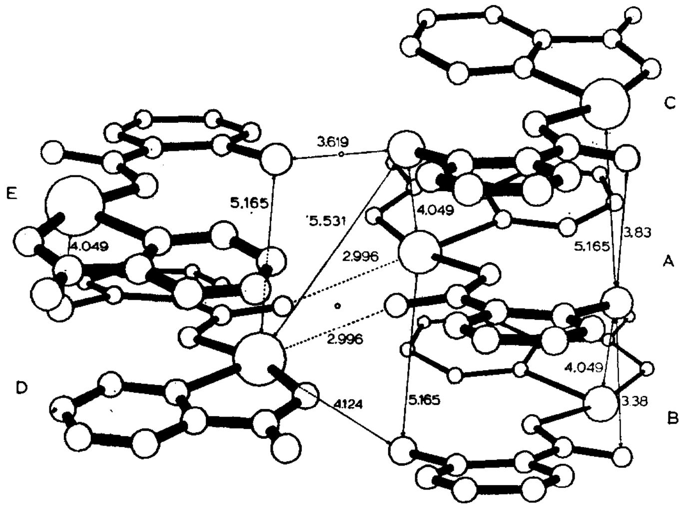

FIG. 5. Selected *inter*dimer contacts resulting from the **a**-glide stacking of the $(20\bar{1})$ layers of Ib (see Fig. 4). The lettered molecules are related as A(x, y, z); B($x-\frac{1}{2}, \frac{1}{2}-y, z$); C($x+\frac{1}{2}, \frac{1}{2}-y, z$); D($1-x, 1-y, \bar{z}$), and E($\frac{3}{2}+x, y-\frac{1}{2}, \bar{z}$). Molecules A and D form a centrosymmetric "dimer."

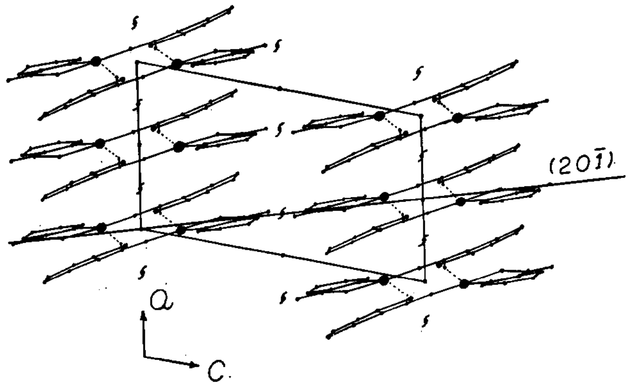

FIG. 6. The layered arrangement of chains of dimers in the crystal structures of Ia-β and Ib, viewed in projection down the chain axes, which are parallel to **b**.

case, each "dimer" could consist of two symmetry independent molecules related by a noncrystallographic pseudoinversion center or pseudotwofold axis.[3] A somewhat parallel situation was encountered in the Type 1 polymorph of Ic (apparent space group *Cc* with $Z = 8$), but the Type 1 "dimers" of Ia-β and Ib, Id, Ic, and If have strict centrosymmetry about space group inversion centers.

TABLE VI

ATOMIC COORDINATES FOR Ia-α

Atom[a]	y^b	z
I	0.1134(4)	−0.0687(2)
Br	0.4165(7)	0.0370(4)
C-1	0.222(6)	−0.124(3)
C-2	0.322(6)	−0.106(3)
C-3	0.379(5)	−0.143(3)
C-4	0.356(6)	−0.200(3)
C-5	0.265(6)	−0.209(3)
C-6	0.206(6)	−0.176(3)
C-7	0.109(6)	−0.174(3)
O-8	0.075(3)	−0.218(2)
O-9	0.057(4)	−0.136(2)
C-10	0.313(6)	0.087(3)
C-11	0.211(6)	0.084(3)
C-12	0.154(6)	0.116(3)
C-13	0.196(6)	0.161(3)
C-14	0.299(6)	0.166(3)
C-15	0.359(5)	0.130(3)
C-16	0.167(6)	0.036(3)
O-17	0.076(3)	0.043(2)
O-18	0.209(4)	−0.006(2)

[a] The numbering scheme is the same as for Ib.

[b] Fractional coordinates relative to $\mathbf{b} = 13.276$ (half the value of **b** quoted in Table I).

Discussion

In the series of 2′-halobenzoate derivatives, Ia–Id, only Ia-β and Ib are isostructural; nevertheless, several similarities as well as subtle differences in their crystal structures are evident through the series: (a) The *intra*-dimer O—I^{III} coordination bond length and O—I^{III}-Y angles (Y is a carbon or oxygen atom covalently bonded to I^{III}) are remarkably constant; consequently, the conformations of the various dimers qualitatively differ only through the extent to which the planes of the nonfused phenyl and heterocyclic rings are nonparallel. Although all molecules adopt a *transoid* conformation (*vide supra*), the dihedral angle between the planes of these rings, ψ_{13} (see Table V) ranges from 38° in Ic with its bulky 2′-iodo substituent, to 5° in Id (*4*) which has minimal steric repulsion between the small fluorine atom and the hydrogen atom *ortho* to I^{III}. The value of ψ_{13} for Ia presumably lies between 14° (in Ib) and 38° and it is possible that the atypical crystal structures of Ia-α and Ic reflect unusual packing requirements of their distinctly nonplanar "dimers;" (b) with the exception of Ic, the various "dimers" pack in chains of similar structures, through van der Waals interaction between the 2′-halogen atoms of adjacent dimers. Molecules A, B, C, and D of Fig. 4 are part of a chain which is directed along [010] in Ia-β (and Ia-α?) and Ib. Since the chains are parallel to b, chain-packing by screw axes results in a parallel arrangement of chains in relatively flat layers containing (20$\bar{1}$) (Figs. 4 and 6). A comparable layered structure is not present in Id for the screw-related chains (directed along [110] and [$\bar{1}$10]) are inclined by ~40° to one another.

Although the angle between the chains and screw axes is not known for Ia-α, its structure in (100) projection is very similar to that of the monoclinic structure of Id. In the exceptional packing of Ic, the *mono*valent iodine atoms appear to interact weakly with carbonyl oxygen rather than iodine atoms of adjacent dimers; (c) no especially favorable *inter*chain contacts are evident and it seems likely that the frequent twinning of Ia-β and Ib across (001) is a consequence of an initial packing fault *between* the chains. This twinning appears to be related to the disorder in Ia-α, for the "streaking" of intensities on k-odd festoons in the direction of $\mathbf{c}$ is consistent with the presence of stacking faults of $\mathbf{b}/2$ between ordered layers of chains parallel to (001).

All of these chain structures are readily assembled during the topotactic isomerization of the corresponding peroxides, and in this connection the complex behavior of single crystals of the isostructural peroxides, IIa and IIb, is particularly noteworthy. The former peroxide yields Ia-α and Ia-β, the latter yields Ib, but both also yield *novel* single-crystal phases X_{Ia} and X_{Ib}, which are isostructural with one another. Our recently completed analysis of the single crystal diffraction intensities of X_{Ib} provides strong evidence that these phases, which apparently cannot be obtained from solvent crystallizations, are new polymorphs of Ia and Ib consisting of the above-described chains of dimers packed in *triclinic* crystal structures.

Details of this analysis and the topotactic formation of the benzoxiodole crystal structures will be presented in a future paper in this series.

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