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Solid-State Chemistry of Organic Polyvalent Iodine Compounds. I. The Crystal Structures of Two Polymorphs of 1-(2′-iodobenzoyloxy)-1,2-benziodoxolin-3-one

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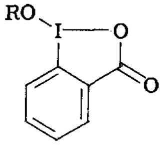
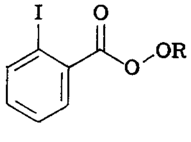
Solid-state reactions involving organic polyvalent iodine compounds frequently result in the formation of preferentially oriented single-crystal product phases (topotaxy). Geometrical comparisons of the mutually oriented reactant and product crystal structures may define the extent of molecular motions, and suggest geometrical mechanisms of transformation. The crystal structures of two monoclinic polymorphs (α and β) of 1-(2′-iodobenzoyloxy)-1,2-benziodoxolin-3-one are reported in this first in a series of papers describing the crystallography of the transformations. The α crystal structure is formed directly in the three-dimensionally ordered topotactic transformation of the isomeric bis-(orthoiodobenzoyl) peroxide crystal structure, and further is hydrolytically transformed to the single crystal phase of 2-iodobenzoic acid.

The asymmetric unit of the acicular α form ($a = 4.21$, $b = 30.86$, $c = 22.52$ Å, $\beta = 93.3°$, Cc, $Z = 8$) consists of two independent molecules which are mutually associated through two strong I–O *inter*molecular coordination bonds across a pseudo inversion center. In both molecules, the monovalent 2′-iodo substituent and the carbonyl oxygen atom of the adjacent carboxyl group are oriented in an unusual *transoid* relationship as a consequence of the mutual coordination bonds. By contrast, the configuration of these atoms is *cisoid* in the prismatic β crystal structure ($a = 8.03$, $b = 12.58$, $c = 13.74$ Å, $\beta = 92.6°$, $P2_1/c$, $Z = 4$), which moreover does not contain the common I–O coordination bonds. However, closely analogous coordination bonds are indicated between the monovalent and trivalent iodine atoms in the β form. A sluggish polymorphic transformation (single crystal → polycrystal) of the α structure to the β structure occurs at ~110°C.

Introduction

Many examples of the seemingly rare phenomenon of topotaxy[1] in transformations of organic molecular crystals have been discovered during X-ray crystallographic studies (*1*, *2*) of solid-state chemical reactions of 2-iododibenzoyl peroxide derivatives, II. Single crystals of several of the reactant peroxides are smoothly transformed at room temperature to single crystal pseudomorphs of the corresponding isomeric benziodoxolinone structures, I.


(I)


(II)

R
(a) H
(b) acetyl
(c) 2′-iodobenzoyl
(d) 2′-bromobenzoyl

R
(e) 2′-chlorobenzoyl
(f) 3′-chlorobenzoyl
(g) benzoyl
(h) 2′fluorobenzoyl

Competing and/or consecutive hydrolyses of crystalline I and II, by atmospheric moisture, further produce single crystal phases of *o*-iodosobenzoic acid, Ia, and/or the corresponding substituted benzoic acids. The crystal structures of the reactant and product phases of each transformation were determined in order to study the extent of solid-state molecular migration. The mutually oriented and simultaneously present *product* phases usually could be identified through comparisons of their single crystal diffraction spectra with those from authentic phases which had been synthesized

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[1] Topotaxy denotes a reticular crystallographic correspondence which is *established* between two different crystal structures (the "reactant" and "product") during the course of a chemical or physical transformation.

independently and crystallized from one or several solvents. The product crystal structures I therefore were analyzed using the structurally equivalent phases from solution crystallizations rather than the transformed phases. In this way, complications from unusual lattice twinning modes (*3*) and difficulties in estimating the intensities of the rather elongated reflections of the transformed phases were circumvented.

Polymorphism is common in structures I and the crystal structure of each modification obtained from solution crystallizations was investigated even if the phase was not also produced in the solid-state process. A comparison of the benziodoxolinone crystal structures revealed an *inter*molecular I–O coordination mode of essentially constant geometry about the polyvalent iodine atom in at least one of the phases of each structure, I (*4*). All benziodoxolinone phases, which have been found to result directly from these solid-state reactions, contain this coordination mode.

We report here the crystal structures of two polymorphs (α and β) of Ic, the chemical product from the solid-state rearrangement of IIc.[2] The polymorphism is particularly interesting in this case since Ic adopts markedly different molecular conformations in the two phases. The conformational change appears to be a direct consequence of the I–O coordination mode which, moreover, is present only in the sole polymorph (α) which results directly from the solid-state rearrangement of IIc.

Generated in this manner, the α phase is slowly hydrolytically transformed by atmospheric moisture to a second pseudomorph, which displays only the single crystal spectrum of *o*-iodobenzoic acid.[3] By contrast, crystals of the α phase grown from a variety of solvents are less defective and not hydrolyzed at any appreciable rate under similar conditions.

Characterization of the α and β Forms of Ic

Ic was synthesized by a modification of Leffler's procedure (*7*). Crystallization from warm benzene, toluene, nitromethane, chloroform or acetonitrile usually gives a mixture of the α and β forms, the relative amounts obtained depending upon the specific concentration, rate of cooling, etc.[4] The crystals can be easily identified and separated under a microscope since the β form (mp 190°C) is prismatic with many well-defined crystal faces while the α form is acicular. The melting behavior of the latter is complicated by an $\alpha \rightarrow \beta$ polymorphic transformation; with rapid heating (~25°/min), melting occurs more or less sharply at 180°. DTA and photographic X-ray diffraction studies demonstrate that several hours are necessary for complete $\alpha \rightarrow \beta$ transformation at ~110°C. Unlike the chemical transformation IIc $\rightarrow \alpha$, the polymorphic change is of the single crystal → polycrystal type. The separate forms give identical solution ir spectra but different spectra in the solid phase (KBr) (Fig. 1). Recrystallization of either form again gives a mixture of both.

X-Ray Diffraction Studies of Ic-β

The monoclinic crystals have unit cell parameters $a = 8.03 \pm 0.01$, $b = 12.58 \pm 0.01$, $c = 13.74 \pm 0.01$ Å, $\beta = 91.6 \pm 0.2°$, space group $P2_1/c$ (from systematic absences), $Z = 4$ and facile cleavage parallel to (101). Diffraction intensities from reciprocal lattice levels $h0l - h6l$, $0kl$, $1kl$, $hk0$, and $hk1$ were measured on a Supper-Pace diffractometer at 22°C using Cu$K\alpha$ radiation. Several crystals (typically $0.12 \times 0.06 \times 0.06$ mm) were needed to obtain the data since the crystals decomposed appreciably (monitored by check reflections) in the X-ray beam.[5] The data were corrected for absorption, converted to $|F|^2$ and correlated to produce the 1053 independent reflections used in the analysis. All twenty atomic positions excluding hydrogen atoms were clearly revealed through conventional Patterson and Fourier methods and refined by least squares analysis assuming anisotropic thermal parameters for the two iodines and isotropic parameters for the other atoms. The refinements (100 total parameters) rapidly converged to $R = 0.09$ where the analysis was terminated. The fractional atomic coordinates and thermal parameters are given in Tables I and II, respectively; the observed and calculated structure factors are available.[6]

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[2] Abstracted from the Ph.D. thesis of J.C.C. (*5*) which also describes the published crystal structure (*6*) of the reactant peroxide.

[3] A description of this crystal structure and the topotactic transformation will be presented in a separate report in this series.

[4] Only one form was obtained in previous preparations (*8*) of Ic (*9*).

[5] No X-ray reflections from a newly formed product phase were evident on photographs of decomposed crystals.

[6] 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, NY 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.

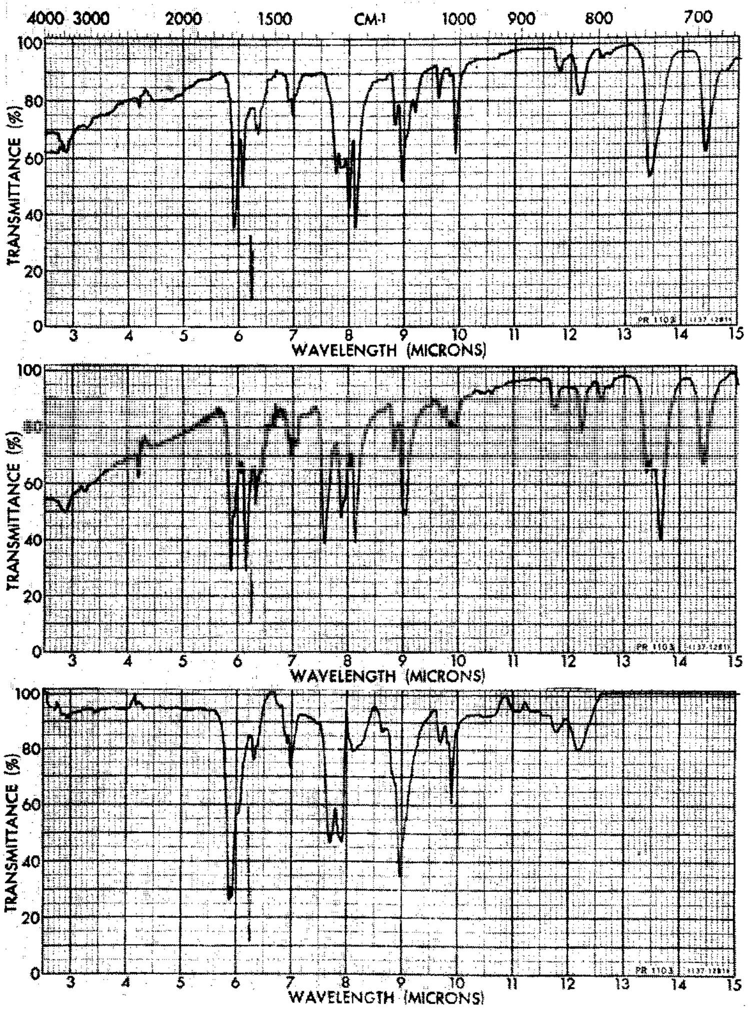

FIG. 1. (Top) The ir spectrum of the prismatic Ic-β crystals in the solid phase (KBr). (Center) The ir spectrum of the acicular Ic-α crystals in the solid phase (KBr). (Bottom) The ir spectrum of Ic in chloroform solutions. The calibration band is the 1603 cm^{-1} absorption of polystyrene.

The molecular conformation including the calculated bond distances, angles, and the least squares estimated errors is shown in Fig. 2. Averages and rms deviations from the averages of the twelve aromatic C–C bonds and internal angles are 1.39 ± 0.06 Å and 120 ± 5° while rms deviations from the least squares planes, *P*1 and *P*2 (Table III) through the two phenyl rings are 0.03 and 0.02 Å, respectively. The geometry of the 1-oxy-benziodoxolin nucleus, atoms 1–8, 10, 20, is identical within experimental error to that found for Ib (*4*), though less precisely determined. Of these atoms, only the displacement (0.18 Å) of O(20) from *P*2 is appreciably larger than the corresponding rms deviation. (The analogous displacement in Ib is 0.20 Å). The apparent displacement of the cyclic carbonyl oxygen atom O(9) from *P*2 (0.11 Å) will be considered below with reference to the crystal packing.

The orientation of the nonfused substituted phenyl ring (*P*1) merits further description since it is this molecular variable which accounts for the markedly different conformation of Ic in the polymorphs. As in other reported crystal structures containing the *ortho*-halo benzoate group, the monovalent halogen, I(11), and O(19) have adopted the more stable *cisoid* relationship (*10*) in this polymorph. The dihedral angle between the least squares plane (*P*3) through atoms 17–20 and *P*1 is 8° and the I(11)–O(19) distance is 3.05 ± 0.04 Å [the corresponding values for *o*-bromobenzoic acid are 18° and 3.004 Å (*11*).] The dihedral angle between *P*3 and *P*2 is 9° with a resultant I(1)–O(19) distance of 2.75 ± 0.04 Å (the

TABLE I

FRACTIONAL ATOMIC COORDINATES FOR THE β FORM OF Ic (esd's × 10^3 are given in parentheses)

Atom	X	Y	Z
I(1)	−0.1993(0.4)	0.6711(0.3)	0.4755(0.3)
I(11)	0.0693(0.3)	0.9979(0.4)	0.2261(0.3)
C(2)	−0.329(3)	0.671(3)	0.605(2)
C(3)	−0.367(4)	0.753(3)	0.656(2)
C(4)	−0.459(3)	0.741(4)	0.743(3)
C(5)	−0.497(5)	0.641(2)	0.773(2)
C(6)	−0.465(5)	0.546(4)	0.717(3)
C(7)	−0.369(3)	0.562(3)	0.630(3)
C(8)	−0.312(4)	0.467(3)	0.566(2)
O(9)	−0.364(4)	0.381(3)	0.578(2)
O(10)	−0.232(3)	0.504(4)	0.492(2)
C(12)	−0.081(5)	1.068(4)	0.338(2)
C(13)	−0.106(4)	1.181(2)	0.332(3)
C(14)	−0.206(5)	1.220(4)	0.406(2)
C(15)	−0.281(4)	1.156(3)	0.470(3)
C(16)	−0.245(5)	1.056(3)	0.476(3)
C(17)	−0.152(4)	1.001(3)	0.411(2)
C(18)	−0.142(3)	0.880(3)	0.412(2)
O(19)	−0.075(5)	0.826(2)	0.356(3)
O(20)	−0.211(3)	0.836(2)	0.487(2)

corresponding values for Ib are 24° and 2.86 Å) and an I(11)–O(19)–I(1) angle of 178 ± 2°. The entire structure thus is only slightly nonplanar with a 14 ± 5° dihedral angle obtaining between $P1$ and the least squares plane, $P4$, through the nine atoms of the fused heterocyclic nucleus.

An essentially covalent molecular structure with localized bonds to the mono and trivalent iodine atoms is indicated both by the above *intra*molecular geometry and also by the *inter*molecular crystal packing described below.

Molecular Packing in the β Form of Ic

The molecules lie in polar close-packed layers which essentially contain the (404) and ($\bar{4}0\bar{4}$) planes. Dihedral angles between these planes and $P1$ and $P4$ are 10 and 6°, respectively. The layers are stacked with inversion symmetry (Fig. 3) with an approximate interlayer spacing $d_{202} = 3.42$ Å.[7] Two direct contacts involving the π systems of sp^2 hybridized carbon atoms [C(5)–C(18) and C(4)–C(14)] represent the shortest distances (~3.4 Å) between the layers. All other interlayer contacts are greater than 3.5 Å and, in particular, the three contacts less than 4 Å involving the monovalent iodine are greater than 3.75 Å. Of the two interlayer distances less than 4 Å to the trivalent iodine atom, 3.85 and 3.62 Å, the shorter involves the carbonyl oxygen atom O(9)

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[7] $|F(202)|$ is at least 1.7 times greater than any other amplitude.

TABLE II

ATOMIC THERMAL PARAMETERS FOR Ic

A. Anisotropic parameters of the form $\exp(-\Sigma\Sigma h_i h_j \beta_{ij})$. The esd's × 10^4 are given in parentheses.

Atom	Structure	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	β	0.0142(3)	0.0043(2)	0.0035(4)	−0.0000(3)	0.0035(5)	0.0001(2)
I(11)	β	0.0153(2)	0.0067(4)	0.0052(3)	−0.0006(2)	0.0051(5)	0.0002(3)
I(1)	α	0.010(60)	0.0008(1)	0.0017(1)	−0.0009(4)	−0.0015(5)	−0.0000(1)
I(11)	α	0.018(70)	0.0013(1)	0.0020(1)	0.0002(4)	−0.0020(5)	−0.0006(1)
I(21)	α	0.032(80)	0.0008(1)	0.0015(1)	−0.0009(5)	0.0030(4)	−0.0001(1)
I(31)	α	0.037(60)	0.0014(1)	0.0020(1)	−0.0006(4)	0.0016(5)	−0.0004(1)

B. Isotropic parameters, B, of the form $\exp[-B(\sin\theta/\lambda)^2]$. The esd's × 10 are given in parentheses.[a]

Atom	β-form	α-form(1)	α-form(2)[b]	Atom	β-form	α-form(1)	α-form(2)[b]
C(2)	2.2(5)	2.6	1.6	C(12)	3.6(7)	2.5	2.7
C(3)	3.7(7)	4.2	1.5	C(13)	2.3(5)	4.7	3.1
C(4)	4.1(8)	2.6	5.6	C(14)	3.8(7)	5.0	5.9
C(5)	5.0(9)	4.8	1.9	C(15)	3.6(7)	7.2	2.7
C(6)	5.4(9)	2.9	2.8	C(16)	3.0(7)	1.8	2.7
C(7)	3.3(7)	2.7	2.3	C(17)	2.8(7)	5.4	4.8
C(8)	4.0(5)	3.2	4.4	C(18)	4.5(5)	2.8	2.2
O(9)	3.4(4)	4.1	3.3	O(19)	3.1(7)	4.6	4.1
O(10)	2.6(6)	5.0	3.6	O(20)	2.3(3)	1.8	4.5

[a] The esd's for the α-form are uniformly ~1.0.

[b] Numbers (1) and (2) refer to the two molecules in the asymmetric unit. The atom numbers for (2) are 20 + [atom number of the corresponding atom in molecule (1).]

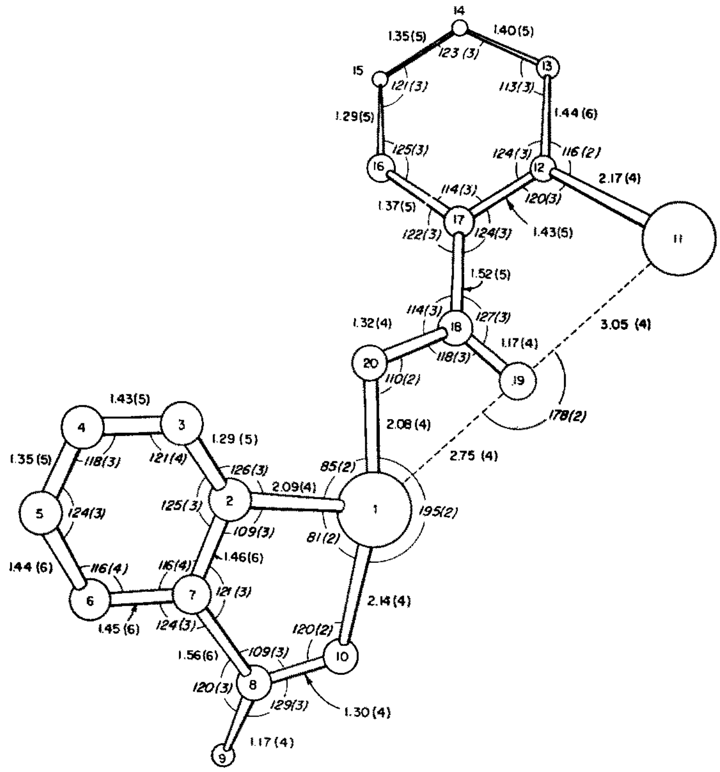

FIG. 2. The molecular conformation, bond distances and angles of Ic in the β crystal structure. Least squares estimated errors in the final significant figures are given in parentheses.

which appears to be displaced from $P2$ toward I(1) of the neighboring molecule.[8] (See Table III.) No strong coordination of the trivalent iodine atom is indicated by these interlayer distances.

The common I–O coordination mode (average I–O distance (*4*) = 3.0 Å) also is not present *within* the layers. The only short intermolecular distance to I(1) (3.70 Å) implies its less than van der Waals' contact with the monovalent iodine, I′(11), of a screw-axis related molecule (Fig. 4). Further, the angles between the I′(11)–I(1) vector and the three covalent bonds from I(1) to C(2), O(10) and O(20), 143, 62, 142°, respectively, are reminiscent of the analogous angles in the common I–O coordination mode (average values (*4*) are 158, 78, and 118°, respectively), and it appears that normally unshared electrons of monovalent iodine I′(11) also may participate in intermolecular coordination bonding to trivalent iodine atoms of this type. Moreover, there appears to be some interaction of I′(11) with O(10) [I′(11)–O(10) distance = 3.3 Å] which is consistent with the implied electron deficiency of I′(11), and it is perhaps for this reason that the above described angular orientation of the I′(11)–I(1) interaction is distorted from the remarkably constant orientation of the commonly observed trivalent iodine–oxygen coordination bond. The difference in the trivalent iodine coordination distances to monovalent iodine and oxygen is essentially equal to the difference in the van der Waals' radii of the latter atoms; these and similar contacts in related crystal structures suggest a minimum radius of ~1.6 Å for coordinated trivalent iodine atoms.

In contrast to this polymorph, the α form displays the I–O coordination mode in a striking manner which can obtain only after a major change in the molecular conformation.

X-Ray Diffraction Studies of Ic-α[9]

Unless otherwise noted, the following experiments were carried out with crystals obtained by conventional crystallization from solvents. Their structural

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[8] Although the opposite displacements of O(9) and O(10) from $P2$ suggest that the carbonyl group is rotated slightly about the C(7)–C(8) bond, the apparent displacement of C(8) seems anamolous and the determination is not considered to be sufficiently accurate to establish this conformational detail.

[9] Any incorrect data in previous reports (*5*) are revised in this paper.

TABLE III

LEAST SQUARES PLANES IN THE α AND β FORMS OF Ic

Plane *P*1

$0.784X + 0.148Y + 0.603Z = 4.20$[a]

	Deviation		Deviation
C(12)[b]	−0.01 Å	C(16)[b]	0.04 Å
C(13)[b]	−0.00	C(17)[b]	0.00
C(14)[b]	0.03	C(18)	−0.15
C(15)[b]	−0.05	I(11)	−0.09

Plane *P*2

$0.849X - 0.085Y + 0.521Z = 1.17$[a]

	Deviation		Deviation
I(1)	0.00 Å	C(8)	0.07 Å
C(2)[b]	−0.00	O(10)	0.07
C(3)[b]	0.00	O(9)	−0.11
C(4)[b]	−0.02	O(19)	−0.13
C(5)[b]	0.03	O(20)	−0.18
C(6)[b]	−0.03	I(1)[c]	−3.29
C(7)[b]	0.01		

Plane *P*3

$0.846X + 0.064Y + 0.529Z = 2.61$[a]

	Deviation		Deviation
C(17)[b]	0.00 Å	O(19)[b]	0.01 Å
C(18)[b]	−0.01	O(20)[b]	0.00

Plane *P*4

$0.847X - 0.070Y + 0.526Z = 1.35$[a]

	Deviation		Deviation
I(1)[b]	−0.02 Å	C(7)[b]	−0.01 Å
C(2)[b]	−0.01	C(8)[b]	0.02
C(3)[b]	0.01	O(10)[b]	0.02
C(4)[b]	0.00	O(9)	−0.17
C(5)[b]	0.03	O(19)	−0.14
C(6)[b]	−0.05	O(20)	−0.17

Plane *P*5

$-0.90X + 0.420Y + 0.128Z = 4.54$[a]

	Deviation		Deviation
I(1)[b]	−0.10 Å	C(8)[b]	0.11 Å
C(2)[b]	0.22	O(9)[b]	−0.05
C(3)[b]	−0.01	O(10)[b]	−0.07
C(4)[b]	0.01	C(18)	−0.49
C(5)[b]	−0.19	O(19)	−0.73
C(6)[b]	0.07	O(20)	−0.10

Plane *P*6

$0.92X - 0.251Y + 0.313Z = 2.23$[a]

	Deviation		Deviation
I(11)	0.07 Å	C(15)[b]	0.03 Å
C(12)[b]	−0.03	C(16)[b]	−0.10
C(13)[b]	−0.04	C(17)[b]	0.11
C(14)[b]	0.04	C(18)	0.00

TABLE III—*continued*

Plane *P*7

$-0.81X + 0.418Y + 0.405Z = 7.12$[a]

	Deviation		Deviation
I(1)	−0.08 Å	C(18)[b]	−0.02 Å
I(11)	−2.02	O(19)[b]	0.01
C(17)[b]	0.00	O(20)[b]	0.01

Plane *P*8

$-0.84X + 0.360Y + 0.409Z = 7.21$[a]

	Deviation		Deviation
I(21)[b]	−0.12 Å	C(28)[b]	−0.18 Å
C(22)[b]	0.08	O(29)[b]	0.09
C(23)[b]	0.09	O(30)[b]	0.06
C(24)[b]	−0.05	O(40)	−0.24
C(25)[b]	−0.01	C(38)	−0.04
C(26)	−0.11	O(39)	−0.07
C(27)	0.16		

Plane *P*9

$0.93X - 0.100Y + 0.345Z = 5.43$[a]

	Deviation		Deviation
I(31)	0.13 Å	C(35)[b]	−0.05 Å
C(32)[b]	0.23	C(36)[b]	0.17
C(33)[b]	−0.04	C(37)[b]	−0.26
C(34)[b]	−0.04	C(38)	0.04

Plane *P*10

$-0.82X + 0.192Y + 0.541Z = 6.47$[a]

	Deviation		Deviation
I(21)	0.52 Å	C(38)[b]	−0.02 Å
I(31)	2.00	O(39)[b]	0.01
C(37)[b]	0.01	O(40)[b]	0.00

[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] Related to the molecule by the symmetry operation $-1 - x, 1 - y, 1 - z$.

identity with rearranged pseudomorphs of IIc will be demonstrated in a separate report.

Several crystal segments for survey and intensity measurements were sliced from the needles which were nearly rhomboidal in cross section with [010] directed along the shorter diagonal and [100] parallel to the needle axis. Eight molecules per unit cell ($16 \times C_7H_4IO_2$) were indicated by the observed lattice constants $a = 4.21 \pm 0.01$, $b = 30.86 \pm 0.04$, $c = 22.52 \pm 0.03$, $\beta = 93.3 \pm 0.5°$ which define a unit cell volume (2920 Å^3) approximately twice that of

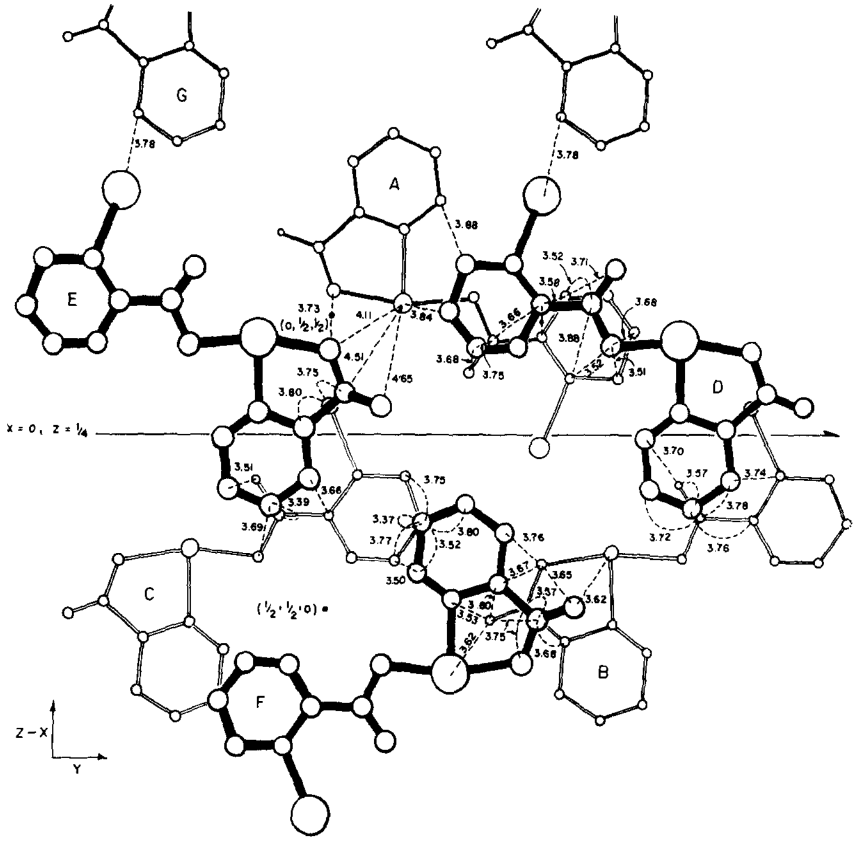

FIG. 3. The molecular packing in Ic-β. The lettered molecules are related as: $A(x,y,z)$; $B(-x,1/2+y,1/2-z)$; $C(-x,-1/2+y,1/2-z)$; $D(-x,2-y,1-z)$; $E(-x,1-y,1-z)$; $F(1+x,3/2-y,-1/2+z)$; $G(-1-x,-1/2+y,3/2-z)$.

the β-form (1390 Å^3). Systematically absent spectra (all classes, $h+k=2n+1$; $h0l$, $l=2n+1$) were consistent with space group Cc and $C2/c$, with $Z=8$ required for Ic.

Since a pronounced group of pseudo-extinctions [$0k0$ absent unless $k=4n$ ($k \leqslant 38$)] was indicated on normally exposed photographs,[10] many crystals were surveyed in order to examine the authenticity of the apparent crystal symmetry. However, the diffraction from the more than 50 crystals, grown under a variety of conditions, confirmed the above assignments of lattice dimensions and symmetry. One of the needles in fact was found to be twinned on (001) of the above monoclinic structure, as evidenced by its pseudo-orthorhombic diffraction pattern. The two twin members, present in unequal proportions, could be separated by cleavage at the twin boundary. In contrast to this very infrequent twinning of solution grown crystals of Ic-α, transformed pseudomorphs of IIc invariably were found to be *repeatedly* twinned on (001) and the equally present members could not be separated by repeated cleavage.

Intensities were estimated visually from multiple-film equi-inclination Weissenberg photographs (Cu$K\alpha$) of levels $0kl-2kl$, $h0l$ and $hk0$, and corrected for absorption. Different crystal segments (typically 0.06 × 0.03 × 0.03 mm) were used for each exposure since the originally discrete high angle reflections (out to $2\theta \sim 160°$) became quite diffuse during the approximately week-long period of continual recording required to obtain suitable intensities. Unlike pseudomorphs of transformed IIc, the slowly disappearing reflections from these crystals were not replaced by any other reflections from newlyformed product phases. The decomposition is probably attributable to thermal or photochemical rather than hydrolysis reactions of Ic.

A decision between the two possible space groups was first made on the basis of the projection Patterson synthesis computed from the 414 $0kl$

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[10] Only (0,18,0) was observed and later calculated to be significantly above the background level of strongly exposed photographs.

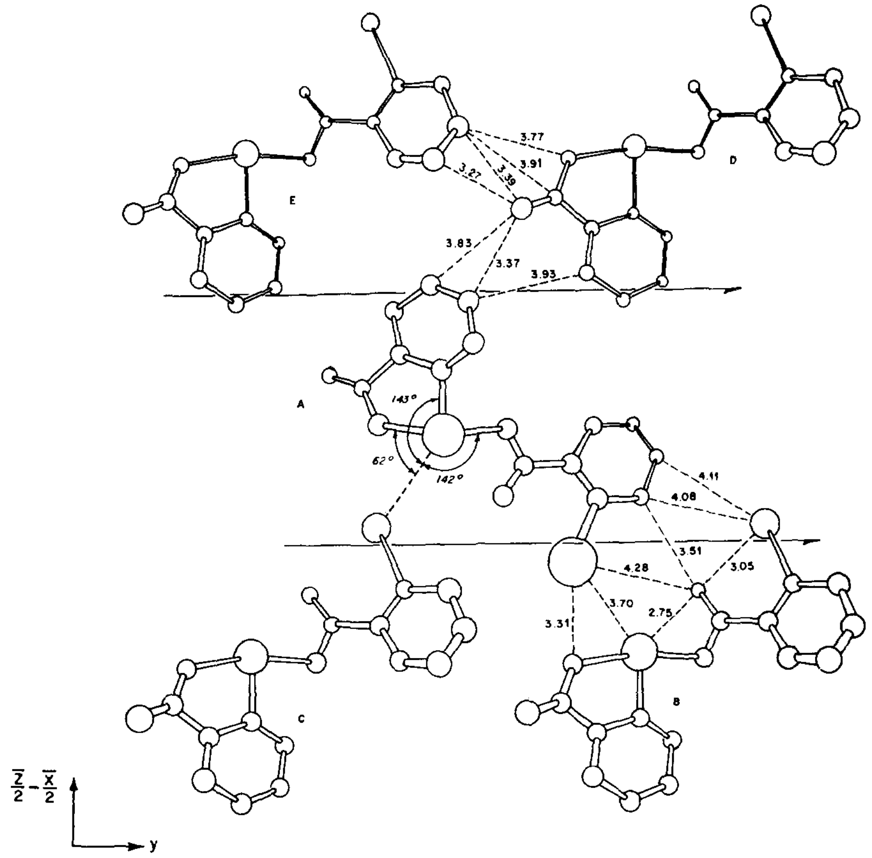

FIG. 4. The molecular packing of Ic-β in the (404) and $(\bar{4}0\bar{4})$ layers. The lettered molecules are related as: A(x,y,z); B($-x,1/2+y,1/2-z$); C($-x,-1/2+y,1/2-z$); D($-1-x,1/2+y,3/2-z$); E($-1-x,-1/2+y,3/2-z$).

reflections. Space group *C*2/*c* was excluded by the absence of iodine interactions required for a twofold axis along *b*. However, all of the iodine–iodine peaks were consistent with space group *Cc* with two molecules (four iodine atoms) in the asymmetric unit. Two-dimensional Fourier synthesis revealed the two molecules in what appeared to be a centrosymmetric arrangement with the pseudo-center midway between the crystallographic glide planes. The projected crystal structure was refined by least-squares methods to $R_{0kl} = 0.14$.

Three-dimensional Patterson and Fourier calculations using all data confirmed the above results. The coordinates of all nonhydrogen atoms in both molecules of the asymmetric unit were thus obtained and subsequently refined by least squares analysis together with anisotropic thermal parameters for the four iodines and isotropic parameters for the lighter atoms. The final R factor was 0.13 for the entire data set of 1547 independent reflections. (The four independent iodine atoms alone gave $R = 0.19$.)

The observed and calculated structure factors are available[11] and the fractional coordinates and temperature factors are listed in Tables IV and II, respectively.

The Molecular Structure in the α-Form of Ic

The centrosymmetric arrangement of the two molecules in the asymmetric unit of the accepted space group *Cc* is evident in the refined atomic coordinates listed in Table IV. Relative to the *c*-glide plane perpendicular to *b* at $y = 0$, the pseudocenter appears at (3/4, 3/8, 1/2) and approximately relates

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[11] 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, NY 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.

TABLE IV

FRACTIONAL ATOMIC COORDINATES FOR THE α FORM OF Ic (esd's × 10^3 are given in parentheses)

Atom	*X*	*Y*	*Z*
I(1)	0.512(2)	0.3678(0.2)	0.3984(0.3)
I(11)	0.436(2)	0.2094(0.2)	0.3834(0.3)
I(21)	0.940(2)	0.3802(0.2)	0.6030(0.3)
I(31)	0.823(2)	0.5389(0.2)	0.6128(0.3)
C(2)	0.28(20)	0.353(2)	0.308(2)
C(3)	0.19(20)	0.312(2)	0.299(3)
C(4)	0.10(20)	0.307(2)	0.237(3)
C(5)	0.20(20)	0.332(2)	0.200(3)
C(6)	0.30(20)	0.377(2)	0.214(3)
C(7)	0.39(20)	0.380(2)	0.275(3)
C(8)	0.51(20)	0.417(2)	0.292(3)
O(9)	0.62(10)	0.447(1)	0.259(2)
O(10)	0.64(10)	0.423(1)	0.350(2)
C(12)	0.30(20)	0.218(2)	0.466(3)
C(13)	0.18(20)	0.177(2)	0.489(3)
C(14)	0.10(20)	0.179(2)	0.559(3)
C(15)	0.13(20)	0.221(2)	0.593(3)
C(16)	0.21(20)	0.257(2)	0.565(3)
C(17)	0.35(20)	0.251(2)	0.501(3)
C(18)	0.46(20)	0.299(2)	0.474(3)
O(19)	0.65(10)	0.326(1)	0.507(2)
O(20)	0.33(10)	0.308(2)	0.422(2)
C(22)	1.17(20)	0.401(2)	0.679(3)
C(23)	1.33(20)	0.437(2)	0.696(3)
C(24)	1.54(20)	0.444(2)	0.747(3)
C(25)	1.56(20)	0.410(2)	0.795(3)
C(26)	1.41(20)	0.373(2)	0.773(3)
C(27)	1.15(20)	0.361(2)	0.723(3)
C(28)	1.04(20)	0.314(2)	0.703(3)
O(29)	0.99(10)	0.290(1)	0.738(2)
O(30)	0.86(10)	0.322(1)	0.656(2)
C(32)	0.99(20)	0.528(2)	0.522(3)
C(33)	1.00(20)	0.572(2)	0.496(3)
C(34)	1.08(20)	0.569(2)	0.446(3)
C(35)	1.11(20)	0.528(2)	0.407(3)
C(36)	1.09(20)	0.495(2)	0.438(3)
C(37)	0.88(20)	0.495(2)	0.497(3)
C(38)	0.89(20)	0.451(2)	0.517(3)
O(39)	0.74(10)	0.423(1)	0.493(2)
O(40)	1.09(10)	0.443(1)	0.575(2)

the x-coordinates but closely relates the y and z coordinates of the corresponding atoms of the two molecules. All differences between the corresponding bond distances and valence angles in the two molecules are within the relatively large estimated errors of this analysis. The average values (Fig. 5) are in reasonable agreement with the distances and angles observed in the β crystal form.

Least squares planes through the fused heterocyclic nucleus (*P*5), the nonfused phenyl ring (*P*6), and the noncyclic carboxyl group (*P*7) of one molecule, and the corresponding planes (*P*8, *P*9, *P*10) in the other molecule are given in Table III. Although the calculated dihedral angles between these planes (Table V) suggest two slightly different molecular conformations, the quantitative differences are of questionable statistical significance and, in any case, immaterial to the striking aspect of molecular structure which characterizes this polymorph: *In both molecules, the monovalent iodine atom* [*I*(*11*) *and I*(*31*)] *and the noncyclic carbonyl oxygen atom* [*O*(*19*) *and O*(*39*)] *are in the* transoid *relationship* (see Fig. 5). Relative to the essentially flat *cisoid* molecular conformation of Ic in the β-form, the nonfused phenyl rings are rotated about the C–C bonds to the carboxyl groups through ~130° resulting in an average dihedral angle of 143° between the two phenyl planes in each molecule (14° in Ic-β). Further rotation toward a completely flat *transoid* conformation is precluded by the intramolecular nonbonded contact (3.3 Å) between the monovalent iodine atoms and the hydrogen atoms *ortho* to the trivalent iodine atom in the fused phenyl rings. (These experimentally unobserved hydrogen atoms were placed in the planes of the fused rings at a C–H bonded distance of 1.08 Å in order to calculate the contact distance.)

Two intermolecular coordination bonds [I(1)–O(39) and I(21)–O(19)] are indicated between the crystallographically independent molecules. The length and angular orientation of each coordination bond relative to the covalent bonds to the trivalent iodine atoms are very similar to those observed in the crystal structure of Ib (*4*). The coordination here is particularly noteworthy since, unlike the bonding in Ib and also in Ic-β, the centrosymmetric molecular arrangement allows for the cooperative formation of two apparently identical coordination bonds between the molecules. Further, the unusual *transoid* molecular conformation appears to be directly related to this novel coordination mode, since a close mutual approach of the four coordinated atoms is sterically obstructed when the molecules have the *cisoid* conformation [i.e., I(11) and I(31) bonded to C(16) and C(36), respectively, in Fig. 5.]

The mutually coordinated unit gives rise to two well separated and equally intense carbonyl absorption bands at 1700 and 1627 cm^{-1} in the solid phase ir spectrum of Ic-α (see Fig. 1). The carbonyl absorption in the solid phase spectrum of the β-crystal structure is markedly different since none of the carbonyl groups are coordinated with trivalent

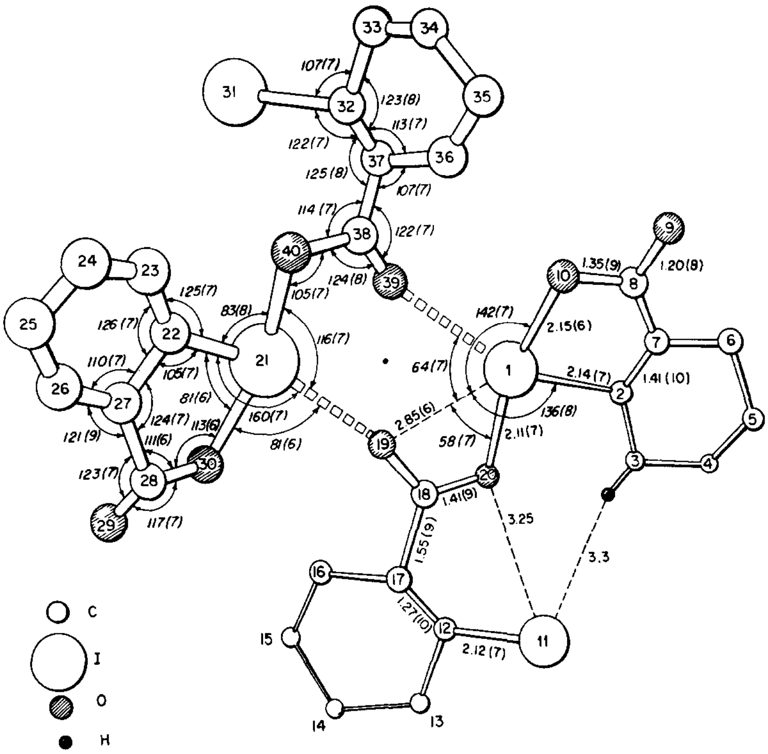

FIG. 5. The molecular conformation and structure of the two doubly coordinated molecules which comprise the asymmetric unit of the Ic-α crystal structure. The average bond distances and angles of the two independent molecules are shown together with least squares estimated uncertainties in the final significant figures.

iodine. Since the carbonyl absorption of a chloroform solution of Ic more nearly resembles the latter absorption spectrum, it appears that the coordinated "dimeric" units are not present to any appreciable extent in a dispersed phase.

Molecular Packing in the α-Form of Ic

We have been unable to discern any convincing reason why the two coordinated molecules might not be strictly centrosymmetrically related[12] or further, why a potential inversion center of this type was not incorporated in another, centrosymmetric space group as a group symmetry operation of the entire lattice. Indeed, the different crystal structures of Id–Ig consist of entirely analogous bimolecular units which are doubly coordinated in this manner across crystallographically required inversion centers.[13]

Considered alone, the $0kl$ data and the derived molecular arrangement in (100) projection (see Fig. 6) are consistent with a (100) pgg projection of a $P2_1/c$ crystal structure having a b cell length equal to half of the b repeat of the proposed Cc structure.

TABLE V

DIHEDRAL ANGLES BETWEEN LEAST SQUARES PLANES IN Ic-α

Planes	Angle	Planes	Angle
6, 7	136°	7, 10	15°
9, 10	127	5, 11	26
5, 6	27	8, 11	33
8, 9	47	6, 11	24
5,7	17	9, 11	21
8, 10	12	7, 11	36
5, 8	17	10, 11	35
6, 9	9		

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[12] The reactant peroxide (IIc) crystal structure is centrosymmetric except for the asymmetric arrangement of oxygen atoms which arises from the chemically preferred geometry of the peroxide linkage (*6*).

[13] The crystallographically isostructural Id and Ie derivatives also adopt *transoid* molecular conformations in the solid state (*12*). If and Ig also are isostructural; although the *meta*-chloro substituent in If appears in the *cisoid* orientation, it is far removed from the coordinated iodine and oxygen atoms, and therefore does not interfere with their centrosymmetric mutual coordination bonding (*13*).

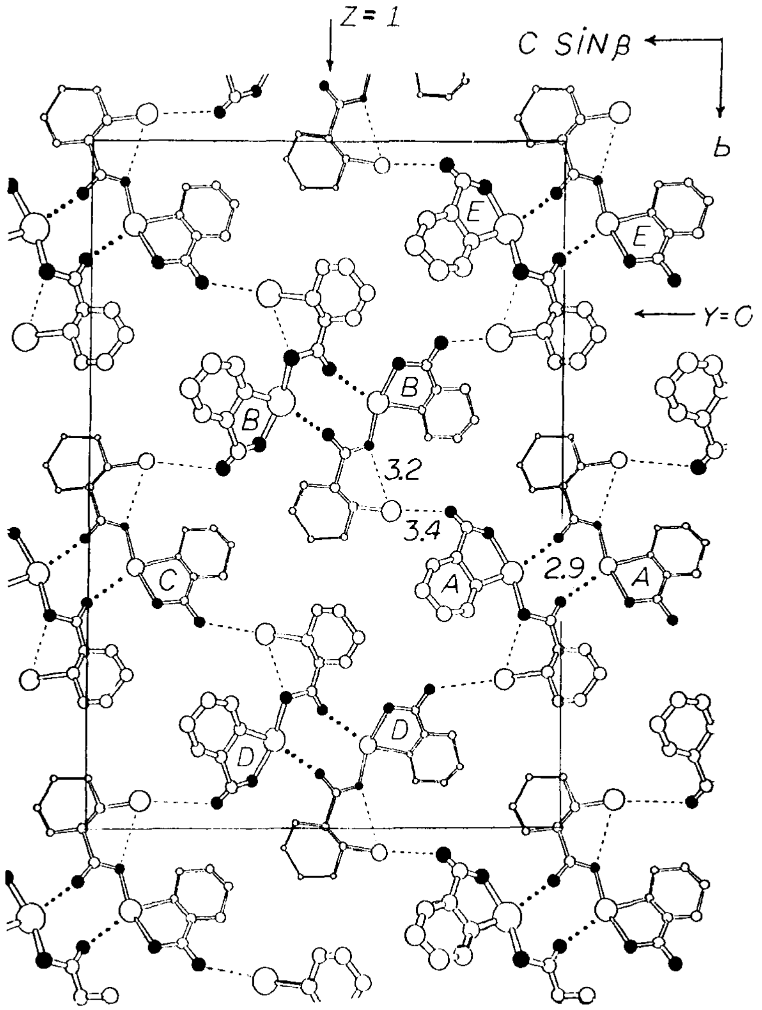

FIG. 6. The molecular packing in Ic-α, shown in projection down the short *a* lattice repeat. The lettered molecules are related as: A(x,y,z); B($1/2 + x, 1/2 - y, 1/2 + z$); C($x,y,1 + z$); D($x,-y,1/2 + z$); E($1/2 + x,-1/2 + y,z$).

The three-dimensional reciprocal lattice, however, is consistent with a *C* centered rather than a primitive crystal lattice. Although unrecognized twinning, pseudosymmetric (e.g., see Ref. *14*) and order–disorder structures (*15*) have been considered as possible causes of the apparent diffraction symmetry of Ic-α, we have found no experimental evidence in support of these more subtle interpretations of this crystal structure. The recognized twinning on (001) which occasionally complicates the interpretation of $h \neq 0$ reciprocal lattice levels does not affect the $0kl$ data and the derived molecular arrangement in (100) projection.

The short *a* lattice repeat of the layered *Cc* crystal structure corresponds to twice the van der Waals' radius of monovalent iodine and no unusual *inter*molecular contacts are indicated between the layers. The *intra*layer proximity of the monovalent iodine atoms and the heterocyclic carbonyl oxygen atoms (~3.4 Å) (Fig. 6) may reflect additional weak *inter*molecular I–O bonding which, together with possible *intra*molecular interactions between the monovalent iodine atoms and O(20) and O(40) (average I–O distance = 3.2 Å), may act to distribute any polarization of the covalent and coordination bonds to the trivalent iodine atoms.

An extension of these considerations leads to the interesting possibility that the reconstructive Icα → Icβ polymorphic phase transformation occurs through an *inter*molecular bond delocalization process having a kinetic barrier consistent with the observed sluggish rate of conversion. Thus, collapse of the existing covalent I–O bonds and formation of new covalent bonds between the monovalent iodine

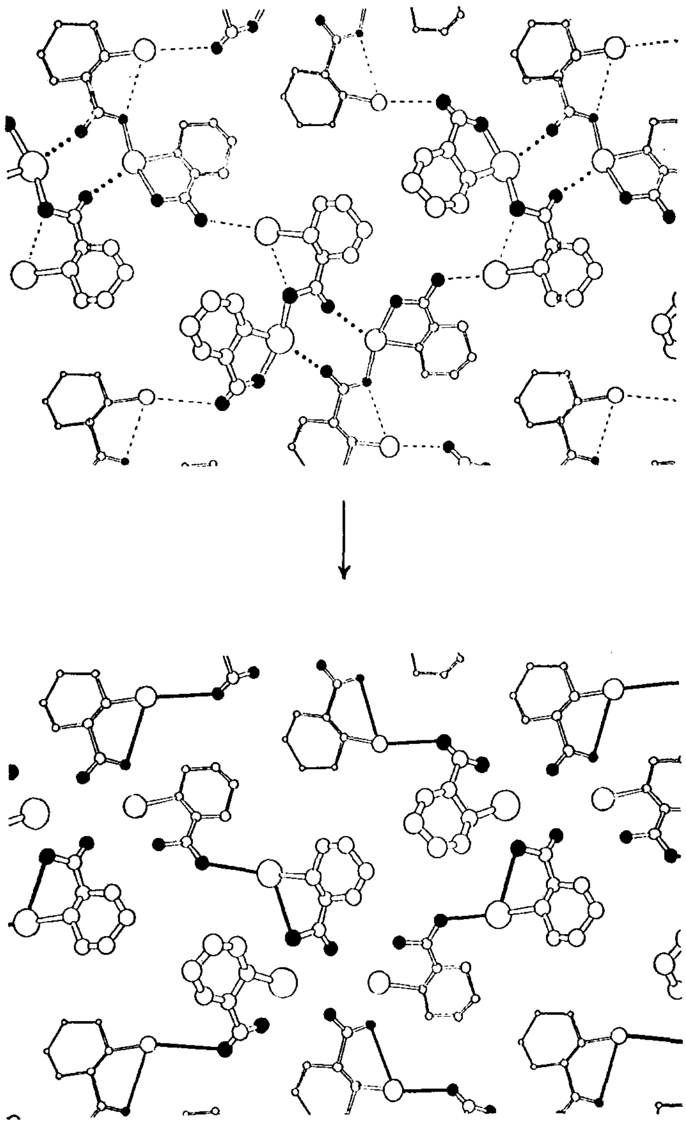

FIG. 7. A schematic representation of a bond delocalization process which could eventually result in the transformation of the *transoid* conformers in Ic-α (Top) to the *cisoid* conformers found in Ic-β. New covalent I–O bonds are shown by heavy lines in the lower half of the drawing.

atoms and their two oxygen neighbors [I(11) bonds to O(20) and O(29) and I(31) bonds to O(40) and O(9)] could effect the *transoid* → *cisoid* conformational change after only relatively small motions[14] of the individual iodobenzoate groups *within* the layers (Fig. 7).

The validity of this essentially two-dimensional molecular transformation mechanism *vs.* other *intra*molecular processes requiring ~120–130° rotations of the bulky iodophenyl rings [i.e., "flipping" about the C(17)–C(18) and C(37)–C(38) bonds]

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[14] The T-shaped bonding about the incipient trivalent iodine atoms derivable from such a simple static bond redistribution would differ from that in all known benziodoxolinone structures, which consistently have apical oxygen substituents and the phenyl carbon atom in an equatorial position of the presumed trigonal bipyramid. While geometrical isomerism of this general type and pseudorotational isomer interconversion processes are well recognized in the structural chemistry of phosphorus, they apparently have not been observed in these structures. Slight rotations and displacements of the iodobenzoate groups within the layers therefore would be required in order to form the *cisoid* molecular conformation actually observed in the β crystal structure.

within the inadequate space *between* the (100) layers is difficult to assess in the absence of isotopic labeling experiments. However, it is clear that whatever the mechanism of molecular transformation, major solid-state reorganization of the iodobenzoate groups, either individually, or chemically combined in the initial *transoid* or the final *cisoid* molecular conformation, is required in order to duplicate the symmetry and molecular packing in the β crystal structure.

Although the specific mechanism of this non-topotactic polymorphic transformation is only of peripheral interest in our studies of topotaxy in these systems, the problem of assessing the relative ease of motions *within vs.* flipping *between* such layers is fundamental to an understanding of the molecular motions during the topotactic formation of Ic-α from IIc. The reticular relationships and possible geometric mechanisms of the latter chemical transformation will be presented in a separate report in this series.

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