JOURNAL OF SOLID STATE CHEMISTRY 9, 155–164 (1974)

Solid State Chemistry of Organic Polyvalent Iodine Compounds. III. The Crystal Structures of 3-Oxo-3*H*-2,1-benzoxiodol-1-yl *m*-chlorobenzoate (Two Polymorphs) and its Isostructural Derivative, 3-Oxo-3*H*-2,1-benzoxiodol-1-yl benzoate

J. ZANOS GOUGOUTAS AND L. LESSINGER*

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

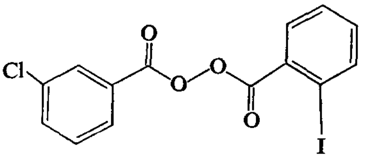
Received January 26, 1973

Two polymorphic modifications (IIα and IIβ) of 3-oxo-3*H*-2,1-benzoxiodol-1-yl *m*-chlorobenzoate ($C_{14}H_8O_4ClI$) have been obtained through crystallizations from a variety of solvents but neither crystal structure is formed at room temperature during the various topotactic transformations of the isomeric 2-iodo-3′-chlorodibenzoyl peroxide crystal structure (the crystalline peroxide topotactically isomerizes to IIα at $\sim$65°C). Single-crystal X-ray diffraction analyses have shown that the fundamental structural motif of the acicular (α) crystal structure ($a = 6.376$, $b = 10.547$, $c = 20.066$ Å, $\beta = 92.0°$, $z = 4$, $P2_1/n$) consists of two molecules mutually associated through two strong intermolecular I···O coordination bonds; the other polymorph ($a = 5.057$, $b = 13.035$, $c = 10.339$ Å, $\beta = 99.5°$, $z = 2$, Pc) was investigated only in (100) projection where it appears that a chlorine rather than an oxygen atom is *inter*molecularly coordinated to the trivalent iodine. Although these coordination modes suggest a structural analogy of IIα and IIβ with the two known crystal structures of 3-oxo-3*H*-2,1-benzoxiodol-1-yl *o*-iodobenzoate [one of which is formed in the facile topotactic isomerization of bis-(*o*-iodobenzoyl)peroxide at $\sim$22°C], several differences are evident in their molecular conformations and packing modes.

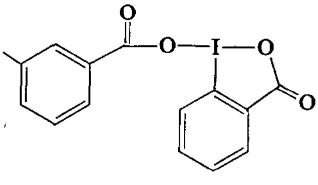
The only crystalline modification of 3-oxo-3*H*-2,1-benzoxiodol-1-yl benzoate, obtained from solvent crystallizations, is isostructural with IIα.

Introduction

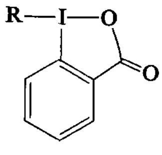
2-Iodo-3′-chlorodibenzoyl peroxide, I, readily isomerizes to the heterocyclic structure 3-oxo-3*H*-2,1-benzoxiodol-1-yl *m*-chlorobenzoate, II, in aprotic solvents at room temperature, but neither of the two known crystalline phases of II (α and β) appears to be present among the several topotactically formed products of solid state transformations of I at $\sim$22°C.[1]



I



II



III

(a) R = Cl; (b) R = acetoxy; (c) R = *o*-iodobenzoyloxy; (d) R = benzoyloxy.

In view of the facile topotactic phase isomerizations of several closely related peroxide crystal structures *at room temperature* (*1*), we have determined the crystal structure of I (*2*) and both IIα and IIβ in order to discern structural features which may inhibit the corresponding topotactic phase isomerization I → II. The crystal structures of IIα and IIβ are reported here and compared to the crystal structures of the two polymorphic forms of IIIc, one of which is formed directly in the topotactic phase isomerization of bis-(*o*-iodobenzoyl)peroxide (hereafter BIP).

---

* Present address: Department of Physics, University of York, Heslington, York, YO1 5DD, U.K.

[1] Dr. Douglas Naae in this laboratory has recently found that I is topotactically transformed to IIα upon heating at $\sim$62°C for several hours in the absence of x-radiation. A complete account of the topotactic transformations of I will be published in a future report.

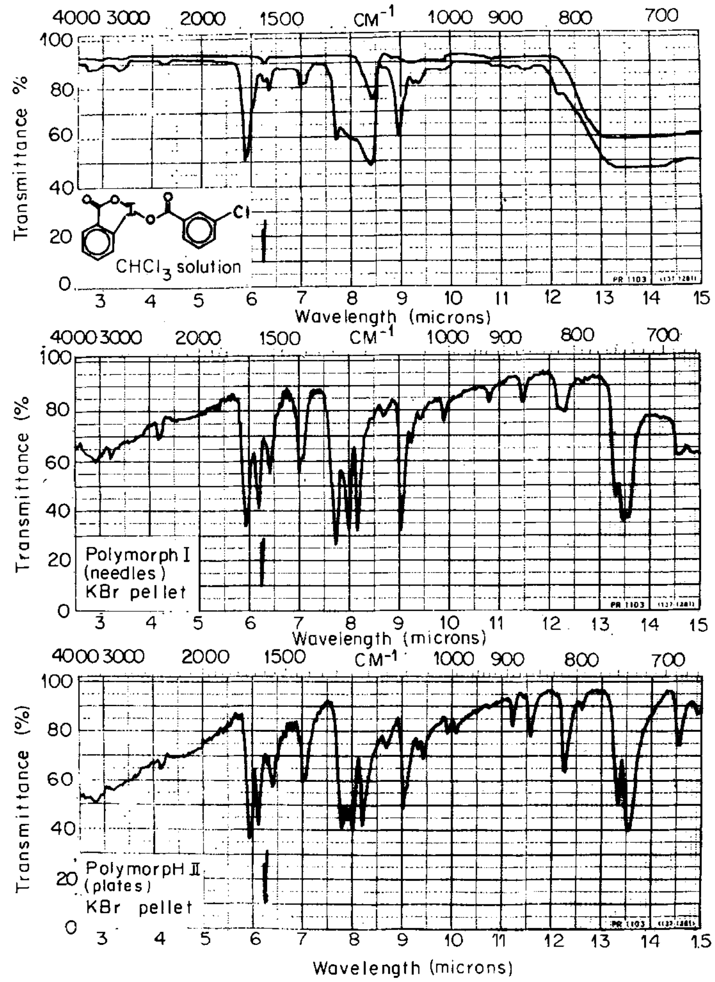


FIG. 1. (Top) The infrared spectrum of 3-oxo-3*H*-2,1-benzoxiodol-1-yl *m*-chlorobenzoate in chloroform solution. The base line compares the sample and reference cells when each contains only chloroform. (Center) The infrared spectrum of the acicular IIα polymorph in a KBr pellet. (Bottom) The infrared spectrum of the IIβ polymorph in a KBr pellet. The calibration band in each spectrum is the 6.24-μ absorption of polystyrene.

Experimental[2]

3-Oxo-3*H*-2,1-benzoxiodol-1-yl *m*-chlorobenzoate was synthesized through a modified version of the Honsberg and Leffler procedure (*4*). The bright-yellow crystals of the intermediate *o*-(dichloroiodo)benzoic acid, prepared by bubbling chlorine gas through a chloroform solution of *o*-iodobenzoic acid, readily lose HCl upon warming and are transformed to a solid phase of the heterocyclic monochloro structure 1-chloro-3-oxo-3*H*-2,1-benzoxiodole, IIIa. In previous syntheses of this type, IIIa was not manipulated further but treated directly with the appropriate silver benzoate salt to form structures of the type II. However, it is quite stable and can be alternatively prepared by stirring briefly a suspension of the dichloride in methanol; the bright yellow crystals of the dichloride very quickly are transformed to tiny straw colored prisms of the monochloride. 1-Chloro-3-oxo-3*H*-2,1-benzoxiodole can be recrystallized from warm methanol without appreciable methanolysis.

A stirred suspension of crystalline IIIa in dichloromethane was treated with excess dry silver *m*-chlorobenzoate and the mixture extracted with a large quantity of hot dichloromethane. The extracts, after concentration *in vacuo* and cooling, deposit a mixture of two

---

[2] Abstracted from the Ph.D. thesis of L. L. (*3*).

TABLE I

CRYSTAL DATA

Structure	a (Å)	b (Å)	c (Å)	β (degrees)	Z	D_m (g/cm^{-3})	m.p. (°C)	V (Å^3)	Space group
I	22.28 (1)[a]	4.057 (2)	15.38 (1)	94.5 (1)	4	1.90	—	1386	$P2_1/c$
IIα[b]	6.376 (1)	10.547 (1)	20.066 (2)	92.0 (1)	4	1.984	223–225 (d)	1348	$P2_1/n$
IIβ	5.057 (2)	13.035 (2)	10.339 (3)	99.5 (1)	2	2.009	209–210 (d)	672	Pc
IIId	6.56	9.94	20.61	94.1	4	—	—	1340	$P2_1/n$

[a] The least-squares estimated uncertainty in the last significant figure is given in parentheses.

[b] The crystallographic a axis is directed along the needle axis.

polymorphic crystal forms of II. They are only slightly soluble in common organic solvents, but recrystallization can be effected by rapidly dissolving the mixture in a large volume of hot nitromethane and allowing the solution to cool to room temperature. Although both forms crystallize together, the acicular IIα form usually predominates; recrystallizations of the separate forms again give mixtures of both. They have different ir spectra in KBr pellets but identical ir absorption in chloroform solution (Fig. 1).

The crystal data (Table I) for both forms were obtained from least-squares analyses of aluminum-calibrated Weissenberg photographs. Crystal densities were measured by flotation in mixtures of 1,3-dibromopropane and bromoform. The diffraction intensities were recorded by the multiple-film equi-inclination Weissenberg method (~22°C; $\lambda = 1.542$ Å for Cu$K\alpha$) and visually estimated by comparison with standardized intensity scales prepared from reflections of representative spot shape. Absorption corrections were applied using a Gaussian quadrature numerical integration method (*5*).

The Acicular IIα Polymorph

Since the crystals slowly decompose in the X-ray beam, a fresh specimen (average dimensions 0.13 × 0.05 × 0.04 mm) was used for the collection of each of the recorded levels, $0kl$–$3kl$ and $h0l$. Standard deviations in intensities, $\sigma(\mathrm{I})$, were assigned in terms of the minimum observable intensity, I', according to: $\sigma(\mathrm{I}) = 0.3$ I for $\mathrm{I} > 53\ I'$; $\sigma(\mathrm{I}) = 0.2$ I for $3.5\ I' < I \leqslant 53\ I'$; $\sigma(\mathrm{I}) = 0.83\ \mathrm{I}'$ for $\mathrm{I} \leqslant 3.5\,I'$. Unobserved reflections were assigned an intensity $= 0.5\ I'$ with $\sigma = 0.8\ I'$. Of the 3081 independent and nonextinct reflections within the Cu sphere, 1876 (61%) were recorded and estimated. Of these, 1583 (84%) were observed and 293 unobserved. After correction for absorption, the data were converted to F^2 and correlated by a least-squares procedure (*6*).

Solution of the structure by Patterson and Fourier methods was straightforward; the conventional agreement index, R, was 0.38 for a trial structure consisting of iodine only, and 0.27 for one based on all atoms but hydrogen. Least-squares refinements[3] of all coordinates and temperature factors in which only the halogen vibrations were assumed to be anisotropic reduced the value of R to 0.15. Refinement of a totally anisotropic model resulted in $R = 0.14$ for the 1876 reflections.[4] Parameter shifts during the final cycle of refinement were uniformly less than 1/5 the standard deviations estimated from the least-squares inverse matrix. A difference Fourier showed no significant features, and therefore no attempt was made to locate the hydrogen atoms.

The final fractional atomic coordinates and temperature factors are given in Tables II and III, respectively.

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

[4] A table of observed and calculated structure factor amplitudes from this analysis has been deposited. See NAPS document No. 02143 for 41 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, NY 10017. 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 II

ATOMIC COORDINATES FOR IIα[a]

Atom	x	y	z
I	0.7490 (3)	0.1611 (1)	0.02221 (6)
C(1)	0.948 (5)	0.303 (2)	0.055 (1)
C(2)	0.911 (5)	0.379 (3)	0.111 (1)
C(3)	1.071 (5)	0.478 (3)	0.127 (1)
C(4)	1.250 (6)	0.495 (3)	0.093 (1)
C(5)	1.274 (4)	0.422 (2)	0.031 (1)
C(6)	1.114 (5)	0.329 (3)	0.017 (1)
C(7)	1.127 (5)	0.238 (2)	−0.045 (1)
O(1)	1.263 (4)	0.248 (2)	−0.085 (1)
O(2)	0.968 (3)	0.162 (2)	−0.054 (1)
O(3)	0.579 (3)	0.202 (2)	0.109 (1)
O(4)	0.378 (3)	0.050 (2)	0.068 (1)
C(8)	0.425 (6)	0.130 (3)	0.111 (1)
C(9)	0.279 (5)	0.140 (2)	0.173 (1)
C(10)	0.108 (4)	0.064 (2)	0.173 (1)
C(11)	−0.023 (4)	0.081 (2)	0.227 (1)
C(12)	0.008 (5)	0.174 (3)	0.275 (1)
C(13)	0.193 (5)	0.250 (2)	0.271 (1)
C(14)	0.331 (5)	0.237 (2)	0.220 (1)
Cl	−0.244 (1)	−0.0136 (7)	0.2288 (3)

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

The Crystal and Molecular Structure of IIα

All of the calculated molecular bond lengths and valence angles in IIα (Fig. 2) are within 2 estimated standard deviations of accepted values. The average bond lengths and internal angles with root-mean-square deviations from the means are 1.42 ± .05 Å and 120 ± 4°, respectively, for the fused benzene ring and 1.40 ± .03 Å and 120 ± 4°, respectively, for the chloro-substituted benzene ring. The molecular geometry clearly suggests three covalent *intra*molecular bonds to iodine arranged in accord with the expected trigonal bypyramidal geometry. Distortions from the idealized T-shape are such that angle C(1)-I-O(2) is reduced from 90° to 79° and the angle C(1)-I-O(3) from 90° to 85°. The short nonbonded *intra*molecular distance of 2.82 Å between the trivalent iodine atom and the oxygen atom, O(4), of the acyclic carbonyl group is similar to that observed between the corresponding iodine and oxygen atoms in the crystal structures of 1-acetoxy-3-oxo-3*H*-2,1-benzoxiodole, IIIb (2.86 Å) (*8*), and in the acicular (2.85 Å) as well as prismatic (2.75 Å) polymorphs of the closely analogous

TABLE III

ANISOTROPIC TEMPERATURE FACTOR PARAMETERS FOR IIα[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	0.0293 (6)	0.0150 (1)	0.00301 (3)	−0.0049 (5)	0.0069 (2)	−0.0012 (1)
C(1)	0.03 (1)	0.013 (2)	0.0035 (6)	−0.016 (7)	0.008 (4)	−0.001 (2)
C(2)	0.05 (1)	0.017 (3)	0.0038 (7)	0.004 (10)	0.002 (4)	0.002 (2)
C(3)	0.05 (2)	0.016 (3)	0.0043 (9)	−0.009 (11)	0.002 (5)	0.001 (3)
C(4)	0.09 (2)	0.021 (4)	0.0026 (6)	0.006 (13)	−0.002 (5)	−0.001 (3)
C(5)	0.02 (1)	0.014 (2)	0.0057 (10)	−0.019 (8)	0.004 (5)	−0.004 (2)
C(6)	0.04 (1)	0.018 (3)	0.0032 (6)	0.033 (10)	0.003 (4)	0.002 (2)
C(7)	0.04 (1)	0.015 (3)	0.0037 (7)	0.009 (10)	−0.002 (5)	−0.001 (2)
O(1)	0.046 (9)	0.025 (3)	0.0045 (6)	0.006 (8)	0.016 (4)	−0.002 (2)
O(2)	0.048 (9)	0.015 (2)	0.0038 (4)	−0.025 (6)	0.016 (3)	−0.005 (2)
O(3)	0.029 (6)	0.018 (2)	0.0037 (4)	−0.016 (7)	0.010 (3)	−0.003 (2)
O(4)	0.040 (8)	0.020 (2)	0.0048 (6)	−0.015 (7)	0.004 (3)	−0.005 (2)
C(8)	0.04 (1)	0.015 (3)	0.0042 (8)	−0.007 (10)	0.008 (5)	−0.002 (2)
C(9)	0.04 (1)	0.017 (3)	0.0034 (6)	0.014 (10)	0.009 (4)	0.003 (2)
C(10)	0.03 (1)	0.015 (3)	0.0037 (6)	−0.015 (9)	0.014 (4)	−0.000 (2)
C(11)	0.03 (1)	0.020 (3)	0.0021 (5)	0.004 (9)	0.006 (3)	0.005 (2)
C(12)	0.05 (1)	0.016 (3)	0.0031 (6)	0.004 (10)	0.008 (4)	−0.000 (2)
C(13)	0.05 (2)	0.014 (3)	0.0040 (8)	0.005 (9)	0.011 (5)	0.002 (2)
C(14)	0.05 (1)	0.016 (3)	0.0038 (7)	−0.003 (9)	0.005 (5)	−0.002 (2)
Cl	0.041 (3)	0.0228 (9)	0.0046 (2)	0.000 (3)	0.012 (1)	0.0049 (7)

[a] The temperature factor is of the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. Least-squares estimated uncertainty in the final significant figure is given in parentheses.

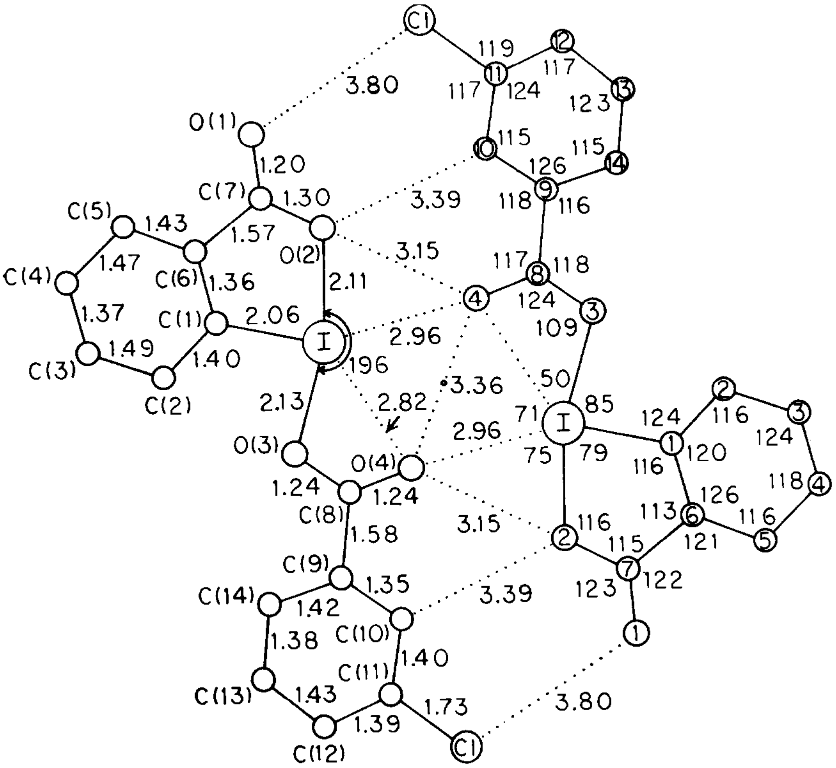


FIG. 2. Calculated bond lengths, valence angles, and the *inter*molecular coordination within the bimolecular unit of IIα. E.s.d.s for C–C and C–O bond lengths fall in the range .03–.05 while the values for I–C, I–O, and Cl–C bond lengths are .02, .02 and .03, respectively. E.s.d.s for the valence angles fall in the range 1–3°.

structure 3-oxo-3*H*-2,1-benzoxiodol-1-yl *o*-iodobenzoate, IIIc (*9*).

Like the acicular polymorph of IIIc, the fundamental structural motif of the acicular IIα crystal structure consists of two molecules bonded together by two mutually established intermolecular coordination bonds between the trivalent iodine atoms and the acyclic carbonyl oxygen atoms, O(4) (see Fig. 2 for the structure of this "bimolecular unit"). Although the geometries of coordination to the trivalent iodine atoms [in IIα, the O′(4)···I distance is 2.96 Å; O′(4)···I–O(2) angle is 75°; O′(4)···I–C(1) angle is 154°; O′(4)···I–O(3) angle is 121°] are remarkably similar (*8*) within the bimolecular units of II and IIIc, several interesting differences in the overall

TABLE IV

DISPLACEMENTS FROM THE LEAST-SQUARES PLANE[a] OF THE BIMOLECULAR UNIT IN IIα

Atom[b]	d (Å)	Atom[b]	d (Å)	Atom[b]	d (Å)	Atom[b]	d (Å)
I	−0.04	C(5)	0.03	O(3)	0.00	C(11)	0.01
C(1)	−0.00	C(6)	−0.02	O(4)	−0.06	C(12)	−0.03
C(2)	−0.08	C(7)	0.01	C(8)	−0.01	C(13)	0.03
C(3)	−0.05	O(1)	0.00	C(9)	0.07	C(14)	0.06
C(4)	0.08	O(2)	−0.09	C(10)	0.01	Cl	−0.07

[a] The equation of the plane is $0.533X' - 0.656Y + 0.534Z' = 1.70$, where X', Y, and Z' are referred to the orthogonal axes $\bar{a}$, $\bar{b}$, $\bar{c}^*$ and are expressed in Å.

[b] Corresponding atoms in the centrosymmetrically related molecule are displaced to the opposite side of the plane.

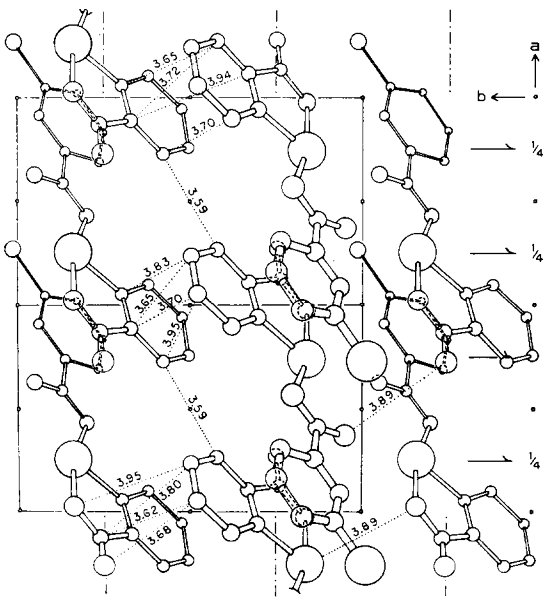


FIG. 3. A perspective drawing of the molecular packing of bimolecular units in the acicular IIα polymorph, viewed normal to the (001) plane.

structures of the two units are apparent. The coordinated molecules in IIIc are crystallographically independent (space group *Cc*, $Z = 8$) though pseudocentrosymmetrically arranged; in IIα, the bimolecular unit is strictly centrosymmetric about a crystallographic inversion center. The halobenzoate group attached to the trivalent iodine atom of IIIc adopts an abnormal conformation in order to permit the close intermolecular approach necessary for the formation of its bimolecular unit: the bulky *ortho*-monovalent iodine substituent and the carbonyl oxygen atom occur in a *transoid* arrangement about the carbon–carbon bond from the phenyl ring to the carboxyl group, in contrast to the more common *cisoid* arrangement found in BIP, the solid state precursor of IIIc [with reference to Fig. 2, the monovalent iodine atom in the bimolecular unit of IIIc would be bonded to C(14) rather than C(10)]. The dihedral angle between the two phenyl rings of IIIc in that conformation was found to be 37°. By comparison, the molecular structure in IIα is essentially flat and, moreover, all 40 observed atoms of the entire bimolecular unit are planar to within 0.09 Å. The least-squares plane of the unit centered at (1/2, 0, 0) closely approximates the $(2\bar{4}6)$ crystallographic plane; atomic displacements from the plane are given in Table IV. The observed *cisoid* relationship of O(4) with the chlorine atom [rather than the alternative *transoid* conformation in which Cl would be bonded to C(13) in Fig. 2] suggests that *meta* substituents of this size do not interfere with the formation of the doubly coordinated unit. A similarly *cisoid* relationship between Cl and the carbonyl oxygen atom obtains in the crystal structure of I (*2*) while *m*-chlorobenzoic acid appears to have the *transoid* conformation (*3*).

No other unusual *inter*molecular contacts are indicated in the crystal structure of IIα. Figure 3

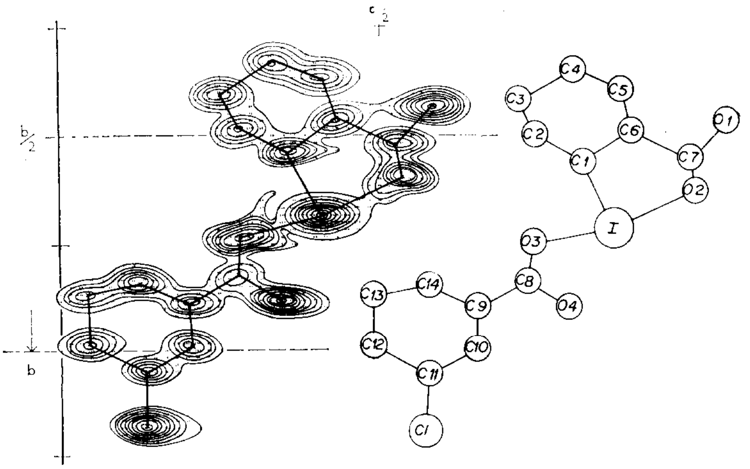


FIG. 4. (Left) Fourier synthesis of the crystal structure of IIβ based on the observed 0*kl* data. The linear dimensions are not to scale. The contour lines are at arbitrary intervals of *n* electrons/Å^3 for the carbon and oxygen atoms, 2*n* electrons/Å^3 for the chlorine atom, and 10*n* electrons/Å^3 for the iodine atom. (Right) The atomic numbering scheme for IIβ.

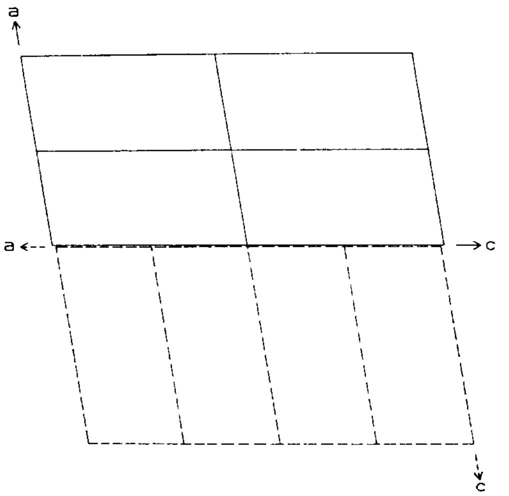


FIG. 5. The observed twinning mode in the IIβ polymorph (plates). Four unit cells of one twin member are shown with unbroken lines and four unit cells of the other twin individual are shown by dashed lines. The b axes of both individuals are normal to the drawing.

illustrates the packing of bimolecular units throughout the crystal structure.

TABLE V

ATOMIC PARAMETERS FOR IIβ

Atom	y	z	B[a]
I	0.6833 (2)[b]	0.413 (—)	3.92 (5)
Cl	1.179 (1)	0.137 (2)	4.7 (4)
C(1)	0.538 (5)	0.359 (7)	—
C(2)	0.482 (6)	0.282 (7)	—
C(3)	0.406 (5)	0.253 (6)	—
C(4)	0.327 (5)	0.337 (7)	—
C(5)	0.371 (4)	0.413 (11)	—
C(6)	0.460 (5)	0.436 (6)	—
C(7)	0.519 (6)	0.527 (7)	—
O(1)	0.432 (3)	0.584 (5)	—
O(2)	0.595 (4)	0.537 (5)	—
O(3)	0.734 (4)	0.285 (5)	—
O(4)	0.883 (4)	0.349 (4)	—
C(8)	0.822 (4)	0.282 (7)	—
C(9)	0.889 (5)	0.206 (6)	—
C(10)	0.990 (6)	0.211 (7)	—
C(11)	1.051 (5)	0.140 (6)	—
C(12)	0.983 (5)	0.048 (7)	—
C(13)	0.868 (5)	0.046 (7)	—
C(14)	0.842 (5)	0.129 (6)	—

[a] The isotropic temperature factor is of the form $T = \exp(-B\sin^2\theta/\lambda^2)$ with B having dimensions Å^2. B for the light atoms is 3.57 (6).

[b] Least-squares estimated uncertainties in the final significant figures are given in parentheses.

The Second (IIβ) Crystal Structure of II

This crystal structure analysis was undertaken primarily to examine qualitatively the structural relationship between IIα and IIβ and to investigate its possible correspondence with that between the two polymorphic forms of IIIc. A two-dimensional analysis in which all atoms proved to be clearly resolved in projection along the short a axis (Fig. 4) was sufficient to establish the salient features of the molecular conformation and probable *inter*molecular coordination modes; the three-dimensional crystal structure, therefore, was not determined.

Crystals of this form are easily identified in mixtures of the two polymorphs by virtue of their unusual growth characteristics. The thin plates extend parallel to (010), and frequently their peripheral edges are multiply indented with large notches or steps of varying complexity.[5] This unmistakable growth habit undoubtedly is closely related to the frequently observed twinning in which the a and c axes of one twin individual are closely aligned with the c and a axes, respectively, of the other twin member (note $c \simeq 2a$ in Table I) (Fig. 5). The twinning, however, is not intimate and single crystal regions can be identified under the polarizing microscope and removed with a razor blade (a segment measuring 0.28 × 0.03 × 0.13 mm was used for data collection). Although the diffraction symmetry ($2/m$) and systematically absent reflections ($h0l$, $l = 2n + 1$) are consistent with either space group Pc or $P2/c$, the presence of only two molecules per unit cell and the absence of either a twofold axis or an inversion center in any conformation of II exclude the latter.

Errors in the intensity measurements were estimated according to the scheme described for the analysis of the IIα structure. Of the 185 independent nonextinct $0kl$ reflections within the Cu$K\alpha$ sphere, 179, of which 17 were unobserved, were recorded and estimated. A two-dimensional Patterson synthesis clearly revealed both halogen atoms, which alone gave $R = 0.24$. A Fourier synthesis based on these atoms revealed the remainder of the structure excluding hydrogen

---

[5] Some have been found to contain large irregular cavities extending through the entire thickness of the plates.

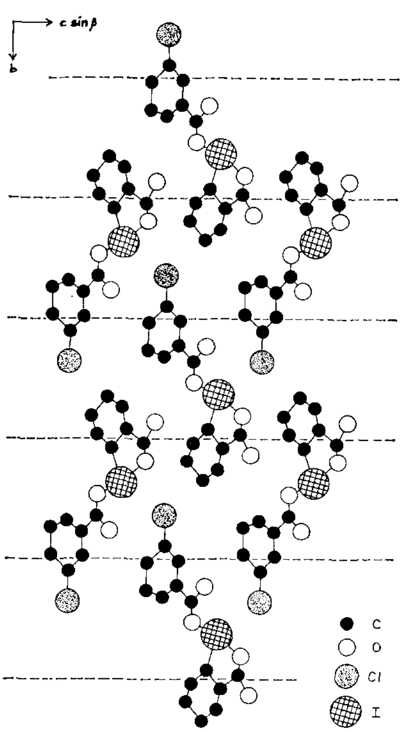


FIG. 6. The molecular packing in the IIβ polymorph, shown in projection along [100].

atoms. The discrepancy index at this stage, $R = 0.15$, was reduced to its final value of 0.10 through least-squares refinements[3, 4] of all y and z coordinates and independent isotropic temperature factors for the halogen atoms.[6] The final coordinates and temperature factors are presented in Table V (the atomic numbering scheme is given in Fig. 4).

Considerations of the molecular geometry in projection and the assumption of flat, regular phenyl rings suggest essentially equal, ~55°, dihedral angles between the plane of projection and each of the two phenyl rings. By analogy with the structures of several related derivatives, it seems likely that the rings, therefore, are approximately parallel, rather than inclined, to each other by an angle of $180° - 110° = 70°$ in the three-dimensional molecular structure.

The bimolecular unit of IIα clearly is not present in this crystal structure (Fig. 6), nor does any oxygen atom appear to coordinate *inter*molecularly with the trivalent iodine atom. Rather, the apparent *inter*molecular proximity and angular disposition of the chlorine atom about the trivalent iodine atom of a glide related molecule (projected I···Cl distance = 2.9 Å) suggest an *inter*molecular Cl···I coordination bond similar to that observed between the mono- and trivalent iodine atoms in the three-dimensional structure of the prismatic polymorph of IIIc (I···I distance = 3.70 Å). A structural correspondence thus is indicated between the various crystal structures of II and IIIc: the acicular polymorphs of both derivatives are comprised of closely analogous bimolecular units arising from the favorable I···O coordination mode, while the second polymorph, in each case, probably contains comparable intermolecular coordination bonds between the electron-rich monovalent halogen atoms and the relatively electropositive trivalent iodine atoms.

The Crystal Structure of 3-Oxo-3H-2,1-benzoxiodol-1-yl benzoate, IIId

Crystals of IIId were examined during a study of the solid state behavior of its peroxide isomer, 2-iododibenzoyl peroxide (*1*). The latter peroxide is crystallographically isostructural with I, and has not been observed to isomerize topotactically to IIId at any temperature. However, unlike II, only one crystalline form of IIId has been obtained during crystallizations from a variety of solvents. The unit-cell parameters and space group[7] (Table I), together with the very close similarity of the X-ray diffraction intensities of IIId with those of IIα suggested closely analogous crystal structures, and therefore we did not undertake an independent structure analysis. The crystal structure of IIId accordingly also contains analogous bimolecular units with the favorable I···O *inter*molecular coordination bonding. The apparent absence of a second polymorphic form of IIId analogous to IIβ is consistent with the lack of a monovalent halogen atom on the phenyl ring to coordinate in the alternative (I···halogen) *inter*molecular coordination mode.

---

[6] Since the specification of origin in the c direction is arbitrary for this space group, the z coordinate of iodine was kept constant during the refinements. When the light atom temperature factors were refined individually, they varied more or less randomly within 1 standard deviation from the value of 3.57 Å^2 obtained from statistical methods and the value of R was not significantly reduced.

[7] We are grateful to Mr. Art Reis for the preliminary survey of this crystal structure.

Discussion

The apparent failure of I to undergo topotactic phase isomerization to II at room temperature may be attributable to the specific molecular packing arrangement in the reactant structure I (*2*). Nevertheless, since preliminary studies (*10*) indicate that 2-iodo-2′-fluorodibenzoyl peroxide, which has a crystal structure very similar to that of I, does undergo topotactic phase isomerization at $\sim$22°C, it is necessary to examine other structural aspects of these transformations and, in particular, to draw comparisons not only between the various reactant crystal structures but also between the molecular conformations and total crystal structures of the various actual and potential benzoxiodole products.

It has been noted above that dimorphism in the case of II and IIIc is a manifestation of two different types of *inter*molecular coordination bonding to the trivalent iodine atom. In each case, both dimorphs usually crystallize together from a variety of solvents, but only the acicular structure, with its apparently more stable $I \cdots O$ coordination mode, has been observed to form during topotactic isomerization of the corresponding peroxide crystal structure. Thus, crystalline BIP yields only the acicular structure of IIIc, and crystalline I similarly yields IIα but not IIβ. However, despite the correspondence of *inter*molecular coordination modes in the respective dimorphs of II and IIIc, the structural analogy is incomplete, particularly with regard to the molecular conformations in the two acicular phases. A *cisoid* relationship between the chlorine atom and O(4) obtains in the molecular conformations of *both* IIα and IIβ, while only the prismatic polymorph of IIIc contains an analogous *cisoid* molecular conformation. The acicular form of IIIc, which is readily formed in crystalline BIP at $\sim$22°C, contains a *transoid* arrangement of the monovalent iodine and O(4) type oxygen atoms.[8]

This difference in the preferred molecular conformations of II and IIIc implies definite differences in the types of molecular motions necessary for their formation within the single crystal structures of I and BIP, respectively. The molecular conformations of these peroxides are qualitatively similar and they may be regarded as approximately flat in view of the small dihedral angle between the planes of the phenyl rings [5° in I and $\sim$0° in BIP (*11*)], which also contain the halogen and carboxyl carbon atoms. Their monoclinic crystal structures have short unique axes, $b \sim 4$ Å, which correspond to a translational stacking of the "flat" molecules on top of one another. In crystals of BIP, the formation of each molecule of IIIc in the *transoid* conformation, at some stage, necessitates a "flip" of *one* of the *o*-iodobenzoate groups out of, and approximately back into, the peroxide molecular plane, and total phase isomerization eventually requires that half of the *o*-iodobenzoate groups

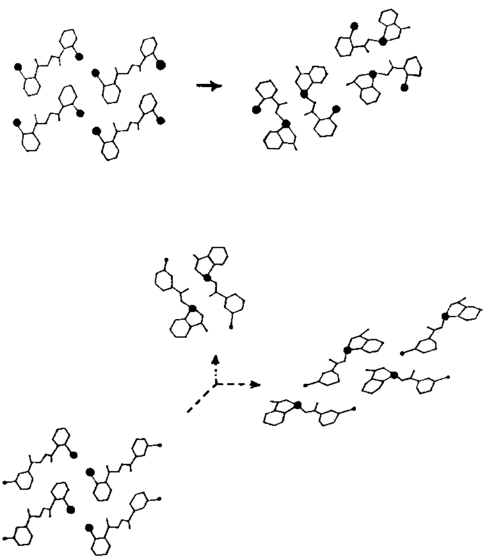


FIG. 7. (Top) Molecular transformations in the topotactic phase isomerization of BIP (left) to the acicular polymorph of IIIc (right). The structures are aligned in accord with the observed topotaxy and shown in projection down their parallel 4 Å axes (*1*). Half of the *o*-iodobenzoate groups of BIP have flipped over in forming the *transoid* conformation of IIIc. (Lower left) A part of the crystal structure of I projected down its unique monoclinic 4 Å axis. (Center) An exemplary bimolecular unit of IIα projected onto its $(2\bar{4}6)$ plane. (Lower right) IIβ in (100) projection. Both IIα and IIβ are shown in arbitrary orientations relative to I. At least half of the iodobenzoate and chlorobenzoate groups of I would be required to flip in order to form IIβ. Although the bimolecular unit of IIα formally may be formed through motions of I in the plane of the drawing, the formation of additional bimolecular units of IIα also requires "flips" of both types of halobenzoate groups of I.

---

[8] The *ortho*-bromo analogue of IIIc, 3-oxo-3*H*-2,1-benzoxiodol-1-yl *o*-bromobenzoate is also dimorphic, but the molecular conformation is *transoid* in both forms, and *both* exhibit the $I \cdots O$ *inter*molecular coordination mode. Further, both are topotactically formed during the room-temperature isomerization of their crystalline peroxide isomer, 2-iodo-2′-bromodibenzoyl peroxide (*1*).

of BIP flip over. By contrast, isomerization within crystalline I to yield *molecules* of *cisoid* II may be realized in principle through movements of halobenzoate groups *within* the peroxide molecular plane; however, formation of the complete crystal structure of IIα (or IIβ) requires the production of an equal number of molecules in which *both* halobenzoate groups have "flipped" from their original orientation in the crystal structure of I (Fig. 7).

These distinctions may be expected to be particularly significant if the flipping motion of halobenzoate groups in some way plays a decisive role in the chemical mechanism of molecular rearrangement. In any case, the minimum "flips" and displacements of halobenzoate groups which are required for the topotactic transformation I → IIα, whether during chemical reaction or subsequent solid state recrystallization, appear to be substantially greater than those suggested by the relatively simple correspondence between the positions and orientations of iodobenzoate groups in crystalline BIP and (acicular) IIIc. The approximate molecular planes of the latter reactant and product structures are roughly perpendicular to their ~4 Å crystal axes, which maintain a strictly parallel alignment during the topotactic transformation, but no comparable correspondence of molecular packing modes or unit-cell lengths exists between I and IIα (or IIβ).[9] Initially, the apparent absence of a good reticular "fit" or "match" between the crystal lattices of I and either IIα or IIβ was considered as one possible explanation for the seeming absence of topotactic isomerization of I (*2*). However, in light of the recently discovered topotaxy at elevated temperatures,[1] it appears that the qualitative difference in the solid state behavior of BIP and I, in part,[10] is attributable to (kinetic) differences in the ease and extent of molecular migrations necessary to form the aligned benzoxiodole crystal structures.

Acknowledgments

A NIH predoctoral fellowship to L.L. and financial support by the United States Air Force Office of Scientific Research (Grant Nos. AFOSR-68-1509, -69-1769, and -69-1769A) are gratefully acknowledged. The experimental and computational aspects of this work were performed while both authors were members of the Department of Chemistry, Harvard University. More recently, the research has been funded through a grant from the University of Minnesota.

References

1. J. Z. Gougoutas, *Pure Appl. Chem.* **27**, 305 (1971).
2. J. Z. Gougoutas and L. Lessinger, *J. Solid State Chem.* **7**, 175 (1973).
3. L. Lessinger, Ph. D. Thesis, Harvard University, 1971.
4. W. Honsberg and J. E. Leffler, *J. Org. Chem.* **26**, 733 (1961).
5. C. W. Burnham, *Amer. Mineral.* **51**, 159 (1966).
6. A. D. Rae, *Acta Crystallogr.* **19**, 683 (1965).
7. "International Tables for X-Ray Crystallography" (C. H. MacGillavry and G. D. Rieck, Eds.), Vol. III, pp. 202, 203, 211, 214, 215, The Kynoch Press, Birmingham (1962).
8. J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.* **4**, 226 (1971).
9. J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.* **4**, 230 (1971) (Paper I in this series).
10. J. Z. Gougoutas and K. H. Chang, unpublished.
11. J. Z. Gougoutas and J. C. Clardy, *Acta Crystallogr.* **B26**, 1999 (1970).
12. J. Z. Gougoutas, *Israel J. Chem.* **10**, 305 (1972).

---

[9] In these respects, the solid state behavior of the above mentioned 2-iodo-2′-fluorodibenzoyl peroxide is in accord with that of BIP even though its crystal structure is closely analogous with that of I (*2*); its isomeric benzoxiodole crystal structure, whether produced by independent crystallization from solvents or though topotactic solid state peroxide isomerization, contains a *transoid* arrangement of the fluorine and O(4)-type atoms and, moreover, has a 4 Å unit-cell repeat which aligns with the 4 Å repeat of the fluoroperoxide structure (*10*).

[10] At room temperature, both peroxides undergo other topotactic transformations which are competitive with phase isomerization (*12*).