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Solid-State Chemistry of Organic Polyvalent Iodine Compounds. 8. Solid-State Chemistry and Molecular and Crystal Structures of Two Polymorphs of 1-Methoxy-1,2-benziodoxolin-3-one[1a]

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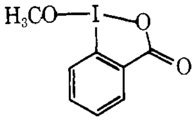
Abstract: 1-Methoxy-1,2-benziodoxolin-3-one crystallizes in two polymorphic forms: I-α, orthorhombic diamond-shaped crystals, space group $Pbca$, $a = 15.440$ (15) Å, $b = 8.097$ (2) Å, $c = 13.532$ (12) Å, $\rho_m = 2.17$ g/cm^3, $Z = 8$; and I-β, monoclinic acicular crystals which are metastable in solution relative to I-α, space group $P2_1/a$, $a = 7.73$ (1) Å, $b = 10.06$ (1) Å, $c = 12.60$ (1) Å, $\beta = 118.3$ (1)°, $\rho_m = 2.16$ g/cm^3, $Z = 4$. The molecular structures are the same for both polymorphs and they both exhibit a stereospecific intermolecular coordination interaction between trivalent iodine and the carbonyl oxygen of a neighboring screw-related molecule. The geometry of the chains of coordinated molecules are different, resulting in unique molecular packing properties. Single crystals of both polymorphs can be hydrolyzed quantitatively to give *o*-iodosobenzoic acid and reduced quantitatively by x-ray radiation to give *o*-iodobenzoic acid. The reaction products formed are in both an amorphous and a preferentially oriented crystalline phase. The chemistry of these transformations is presented in this paper and the topotactic relationships between crystalline reactant and product lattices are discussed in the following paper in this series.

Introduction

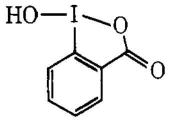
1-Methoxy-1,2-benziodoxolin-3-one (I) crystallizes in two polymorphic modifications (orthorhombic I-α and monoclinic I-β), both of which are readily hydrolyzed and reduced in the solid state. The two polymorphs, which crystallize with the same molecular structures and conformations, undergo the same chemical reactions but at different rates. The most striking aspect of these reactions is the growth of preferentially oriented crystalline product phases, a phenomenon commonly observed in single-crystal transformations of organic polyvalent iodine compounds.[2] In order to understand the significance of molecular packing modes, intermolecular coordination interactions, and geometrical lattice parameters of the reactant matrix on nucleating and directing the growth of a product lattice, the molecular and crystal structures of the two polymorphs have been determined. In addition, the chemical aspects of the reactions of I have been investigated in both solution and solid-state samples, leading to the discovery of a novel photolytic reaction of benziodoxole compounds.

Experimental Section

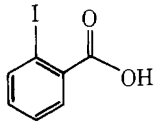
Compound Preparation. I was prepared according to a procedure of Baker[3] by methanolysis of 1-acetoxy-1,2-benziodoxolin-3-one (IV). An alternative esterification procedure was also developed which gave comparable yields of I by refluxing a solution of 1 g of *o*-iodosobenzoic acid (II), 0.12 ml of acetic acid, and 10 ml of methanol for 24 h. After filtration, the filtrate was allowed to sit for about 4 h until crystallization was complete. A 60% yield of I, in the form of diamonds and



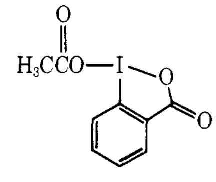
I



II



III



IV

Table I. Fractional Atomic Coordinates and Temperature Factors for I-α[c]

Atom[b]	x	y	z	β[a]
I(1)	0.3977 (2)	0.5873 (4)	0.1930 (3)	
C(2)	0.370 (4)	0.468 (8)	0.049 (6)	4.5
C(3)	0.314 (4)	0.552 (8)	−0.024 (4)	1.9
C(4)	0.306 (3)	0.482 (7)	−0.113 (4)	1.6
C(5)	0.348 (3)	0.339 (8)	−0.133 (4)	2.7
C(6)	0.410 (3)	0.25 (1)	−0.056 (4)	2.8
C(7)	0.422 (3)	0.340 (8)	0.032 (5)	2.3
C(8)	0.480 (3)	0.282 (7)	0.104 (4)	1.2
O(9)	0.526 (3)	0.166 (5)	0.101 (4)	3.2
O(10)	0.485 (3)	0.370 (5)	0.186 (3)	4.6
O(11)	0.313 (2)	0.765 (5)	0.164 (3)	3.6
C(12)	0.360 (5)	0.927 (6)	0.125 (6)	5.4

[a] The isotropic temperature factor is of the form $T = \exp(-B \sin^2 \theta/\lambda^2)$ with B having dimensions Å^2. For iodine, the anisotropic temperature factor parameters calculated in the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ are, for $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{12}, \beta_{13}$, and β_{23}, respectively: 0.00205, 0.00834, 0.00260, −0.00058, −0.00047, −0.00004. [b] The atom identifiers refer to Figure 1, which appears immediately following this article in the microfilm edition of the journal. [c] Least-squares estimated uncertainties in the last significant figure are in parentheses.

needles, was obtained. After several recrystallizations from methanol, the diamond form (I-α) melted at ~171 °C, the needle form (I-β) at ~173 °C (see discussion of thermal degradations for details of melting behavior). The infrared spectra of these polymorphs, which have been previously reported,[4] differ mainly in their different solid-state carbonyl stretching frequencies: I-α, 1635 cm^{-1}, and I-β, 1648 cm^{-1}.

The ethyl ester of II was also prepared by this esterification procedure (mp 127-128 °C), but other alkyl derivatives were not successfully synthesized due to oxidation of the reagent alcohols by II.

Attempts to prepare I by diazomethane esterification of single crystals of II were unsuccessful. Both powdered samples and large single crystals of II were suspended in ethereal solution of CH_2N_2 for 5 days (fresh CH_2N_2 was added daily). There was no sign of gas evolution or of crystal or powder decomposition. Single-crystal diffraction patterns of the exposed crystals of II matched those of reference patterns of unreacted II.[5]

Crystal and Molecular Structure Determinations. I-α Polymorph. This polymorph is readily obtainable as flat diamonds or diamond-based bipyrimidal-shaped crystals (av vol = 0.1 mm^3) from a slowly cooled methanol solution or from polymorphic transformation of I-β in a methanol solution saturated with I. The crystals of I-α cleave readily parallel to (100), the largest face of the flat diamond-shaped crystals. The space group is *Pbca* as determined by the systematic extinctions ($h0l$, l odd; $hk0$, h odd; and $0kl$, k odd). The unit cell parameters, determined from calibrated Weissenberg photographs, are a = 15.440 (15) Å, b = 8.097 (2) Å, c = 13.532 (12) Å, V = 1691 cm^3. The measured density (CH_2I_2/CCl_4) is 2.17 g/cm^3, indicating Z = 8 (ρ_{calcd} = 2.18; mol wt 266).

Seven crystals were used for obtaining diffraction intensities from levels $h0l - h5l$, $hk0 - hk8$, and $0kl - 6kl$ on a PAILRED automatic diffractometer (22 °C, Cu Kα radiation). The data were converted to $|F|^2$ and correlated to produce 1637 independent reflections (99% of the independent nonextinct reflections within the Cu Kα sphere). Crystal decomposition had caused considerable loss in intensity for high angle reflections from crystals with longest exposure times (48 h maximum), so the data set was reduced to 1214 reflections from crystals with the least exposure. Of these reflections, 585 were observed ($I > 3\sigma(I)$, where $\sigma(I)$ is the square root of the sum of the background plus the peak counts), and used in further analysis. The application of absorption corrections was considered unnecessary due to the poor quality of the data obtained from these decomposing crystals.

Conventional Patterson and Fourier methods revealed all the nonhydrogen atomic positions. Structure factors phased with these positions gave an R value of 0.26, which rapidly converged through least-squares refinements of these positional parameters, anisotropic thermal parameters for iodine, and isotropic parameters for the other atoms to R = 0.13.[6] The analysis was terminated here, since a difference map showed no significant features. The fractional atomic coordinates and thermal parameters are given in Table I; the observed and calculated structure factors are available in the microfilm edition of this journal.

I-β Polymorph. This form is obtained as needle-like crystals by rapid cooling of a concentrated solution of I in methanol.[8] If these crystals are left in contact with the mother liquor, they are transformed overnight into the I-α polymorph. Exclusively I-β crystals are most easily obtained after several recrystallizations of crude I-β using dust-free glassware and solvent. I-β is indefinitely stable in the undisturbed mother liquor if it is meticulously free of seed particles or crystals of I-α. Introduction of a seed crystal I-α into such a solution induces a rapid transformation of I-β to I-α. Isolated crystals of solvent-free I-β do not transform to I-α.

I-β crystallizes in space group $P2_1/a$ (from systematic extinctions) and has cell parameters (from calibrated Weissenberg photographs) of a = 7.73 (1) Å, b = 10.06 (1) Å, c = 12.60 (1) Å, β = 118.3 (1)°, V = 862.7 cm^3. A measured density of 2.16 g/cm^3 indicates Z = 4 (ρ_{calcd} = 2.14; mol wt 266). The crystals have no particularly good cleavage plane; they grow with the long morphological axis parallel to **a**.

From eight freshly recrystallized crystals of I-β (exposed to the atmosphere no more than 30 min, and to x rays no more than 15 min prior to data collection), 581 reflections ($2\theta_{max}$ = 70°) were collected using a multifilm equiinclination Weissenberg method (Cu Kα radiation), from levels $h0l$, $h1l$, and $0kl$–$3kl$. Single-crystal exposures were limited to 5 h, but the diffraction patterns obtained were extremely poor due to crystal decomposition, with an average ω spread of ~4° (low angle reflections often were spread 8-10°). Several standard scales were prepared corresponding to different spot shapes, and were used to visually estimate the intensities. Cross-level correlations were made and the data were converted to $|F|^2$ and the 314 observable reflections were used in the following analyses.

The positions of all the nonhydrogen atoms except the lactone carbonyl group were clearly revealed by conventional Patterson and Fourier techniques. Structure factors phased with these positions gave R = 0.20. A difference map using both observed and unobserved reflections revealed the carbonyl oxygen atom position. The approximate carbonyl carbon atom position was calculated from the structures of other known benziodoxole compounds. Least-squares refinements of the positional parameters of all atoms, the anisotropic thermal parameters for iodine, and isotropic thermal parameters for the other atoms led to a final R value of 0.16.[6] The fractional atomic coordinates and temperature factors are given in Table II; the observed and calculated structure factors are available. Because of the limited accuracy of these analyses, the differences in isotropic temperature factors are probably not significant and atomic parameters should be used mainly as a guide to the molecular packing modes rather than as a precise determination of the molecular geometry.

X-Ray Decomposition of I. Methanol solutions of I, powder samples of mixed I-α and I-β, and single crystals of I-α and I-β are completely decomposed (under ambient atmospheric conditions, or in specially dried evacuated vials) by x-ray radiation (Cu or Mo, filtered or unfiltered). The solution samples are completely reacted in about 4 days when exposed to unfiltered Cu radiation, the powder samples require about 7 days, and the single crystals about 10 days for I-α and 4 days for I-β (these times are somewhat variable depending on crystal size, but I-β is significantly more reactive than I-α under all reaction conditions). The crystals develop a reddish-brown color during irra-

Table II. Fractional Atomic Coordinates and Temperature Factors for I-β[c]

Atom[b]	x	y	z	β[a]
I(1)	−0.202 (2)	0.450 (1)	0.1281 (7)	
C(2)	−0.15 (2)	0.34 (2)	0.29 (1)	3.5
C(3)	−0.15 (2)	0.40 (1)	0.38 (1)	4.7
C(4)	−0.14 (2)	0.32 (1)	0.49 (1)	5.3
C(5)	−0.15 (3)	0.17 (1)	0.46 (1)	5.3
C(6)	−0.15 (2)	0.09 (1)	0.35 (1)	3.7
C(7)	−0.18 (2)	0.18 (2)	0.26 (1)	8.9
C(8)	−0.21 (3)	0.15 (2)	0.14 (1)	
O(9)	−0.19 (2)	0.02 (1)	0.111 (8)	6.4
O(10)	−0.21 (1)	0.24 (1)	0.069 (8)	1.6
O(11)	−0.14 (2)	0.61 (1)	0.243 (7)	4.2
C(12)	−0.37 (3)	0.69 (1)	0.19 (1)	2.7

[a] The isotropic temperature factor is of the form $T = \exp(-B \sin^2 \theta/\lambda^2)$ with B having dimensions Å^2. For iodine, the anisotropic temperature factor parameters calculated in the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ are, for β_{11}, β_{22}, β_{33}, β_{12}, β_{13}, and β_{23}, respectively: 0.01800, 0.01188, 0.00565, 0.00253, 0.00261, 0.00 258. T for atom C(8) was indeterminate (see text). [b] The atom identifiers refer to Figure 1, which appears immediately following this article in the microfilm edition of the journal. [c] Least-squares estimated uncertainties in the last significant figure are in parentheses.

diation and become opaque. Infrared analysis of the decomposed samples showed *o*-iodobenzoic acid (III) to be the exclusive detectable nonvolatile reaction product. The single-crystal reactions are pseudomorphic and for I-α the formation of III is topotactic. The melting points of the decomposed crystals were variable, but generally fell 10–20° lower than the melting point of pure III.

The chemical nature of the reaction by-product has not been unambiguously established. It was shown that the by-product was a volatile product which was escaping from the crystal by running the reaction in a vial with a miniature side-arm manometer. The height of the mercury column after 48 h of exposure of I-α to Mo x-ray radiation corresponded to evolution of 60% of the theoretical volume of gas (presumed to be CH_2O) expected from complete decomposition. Five independent samples were collected and gave virtually identical mass spectra (see Table III for characteristics[9]). The spectrum of the unknown does not match that of formaldehyde or methanol, but has some characteristics similar to the spectrum of methyl formate. Ir and NMR analysis of x-ray decomposed perdeuteriomethanol solutions of I show the presence of significant amounts of methanol, but no detectable aldehydes.

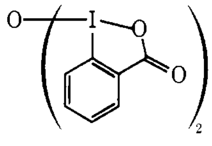
Hydrolysis of I. Single crystals of I-α decompose slowly on the shelf, showing loss of transparency and a generally speckled appearance after several months. I-β crystals likewise decompose, often in only a week or two under ambient conditions. X-ray diffraction analyses of the pseudomorphic product crystals[12] of each polymorph showed the presence of preferentially-oriented crystalline II. II is also the reaction product observed from hydrolysis of crystals of I in a saturated aqueous atmosphere at 50 °C (under these conditions, I-α is completely hydrolyzed in 1–2 weeks, and I-β in ~24 h). I can be hydrolyzed in a few minutes by suspending crystals of I in water. This transformation is not pseudomorphic, however, and long whisker-like crystals (presumably crystals of II) can be seen forming around the decomposing reactant crystal.

Infrared spectra of completely hydrolyzed crystals of I matched reference spectra of II and showed no evidence for methanol, the expected hydrolysis by-product. By running the hydrolysis in a sealed vial in which the crystals of I were suspended above water, we were able to trap evolved methanol in the aqueous layer. Gas chromatographic analysis (using a Porapak Q column and a thermal conductivity detector) of aqueous layers from several samples showed up to 100% yield of methanol.

Table III. Mass Spectral Data of Samples

m/e	Unknown	CH_2O[10]	CH_3OH[11]	$CH_3O\overset{O}{\overset{\|}{C}}H$[11]
60	50			28
32	60		72	34
31	100	2	100	100
30	3	89	8	7
29	16	100	42	63

Thermal Degradation of I. Owing to their rapid solid-state hydrolysis, crystals of I-α and I-β exhibit anomalous melting point behavior, depending on heating rate and humidity conditions. Under dry conditions, I-α begins to sublime at 145 °C (the sublimate at this temperature is unchanged I, as determined by ir), becomes somewhat molten at 170 °C, resolidifies at 180 °C, and melts again at 200+ °C, with irreversible decomposition. Infrared analysis of the resolidified sample formed at ~185 °C shows exclusively the spectrum of di(*o*-iodosobenzoic acid) anhydride (V). I-β, which also sublimes at ~145 °C, is converted slowly in a pseudomorphic transformation to V. Under especially dry conditions, I-β melts at 173 °C and then abruptly resolidifies at 180 °C.



V

The results of these experiments imply that I is hydrolyzing during heating to give II, which is dehydrated to give V.[13] When crystalline samples of I were maintained at 80 °C for 4 days in a carefully dried vessel containing P_2O_5, they were still converted to V, although in much lower yield (there was no evidence from ir spectra for the presence of any II). The crystals had become opaque and covered with a dense coat of very fine transparent whiskers. Attempts to obtain a diffraction pattern or an ir spectrum of the whiskers alone were unsuccessful.

Differential thermal analysis measurements (Perkin-Elmer Model DC-1) on I-α showed a reproducible well-defined endotherm at 171.0 °C. On cooling and reheating the sample, the endotherm reproducibly occurred at 173.0 °C, the melting point of I-β, indicating that rapid cooling of the melt of I gives the metastable I-β polymorph.

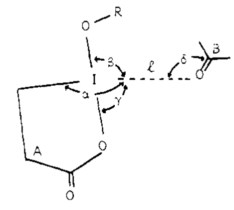
Semiquantitative measurements of ΔH_f for I-α gave 6.3 kcal/mol, and for I-β, 5.7 kcal/mol. There was no indication of solid-state polymorphic transformations from these DTA spectra. Continued heating of both polymorphs gave an irreversible endotherm at 233 °C.

Ultraviolet Radiation of I and II. Single crystals of I were irradiated with a xenon lamp filtered to give a window from 190 to 350 nm (λ_{max} 235 nm for methylcyclohexane solutions of I). After 30 h, the faint yellow-colored translucent crystals were shown by ir and x-ray diffraction to be unreacted starting material. When the crystals were cut, the interior surfaces were still transparent, indicating that the ultraviolet light was being completely absorbed at the exterior surfaces.

Methanol solutions of I were exposed to unfiltered ultraviolet radiation from a medium-pressure mercury arc lamp and surprisingly were reduced quantitatively in less than 1 h into III, the same product as observed from x-ray decomposition. To test the generality of this reduction process for benziodoxole compounds, II was similarly irradiated in $CHCl_3$ solution. It also was rapidly reduced to III, even though single crystals of II are apparently indefinitely stable to x-ray radiation. Photolysis of solutions of several benzoyloxy-substituted benziodoxole compounds also led to rapid decomposition, giving mixtures of reaction products containing carboxylic acids.

Results and Discussion

Molecular and Crystal Structures. Molecular Structures. The molecular structure and geometry of the benziodoxole fused ring systems for I-α and I-β are essentially the same as that found for IV.[14] A perspective drawing of the molecular conformation of I-α in the crystal lattice including the calculated bond distances and angles is shown in Figure 1 in the microfilm edition of this journal (the molecular conformation and bond lengths and angles for I-β are the same as those of I-α within the limited accuracy of these determinations). The benziodoxole ring system is planar, with an atomic root-



	I-α	I-β
α	163(2)°	163(4)°
β	106(1)	113(3)
γ	88(1)	86(3)
δ	112(1)	119(2)
$\vec{\ell}$	3.09(5)Å	2.8(1)Å

Figure 2.

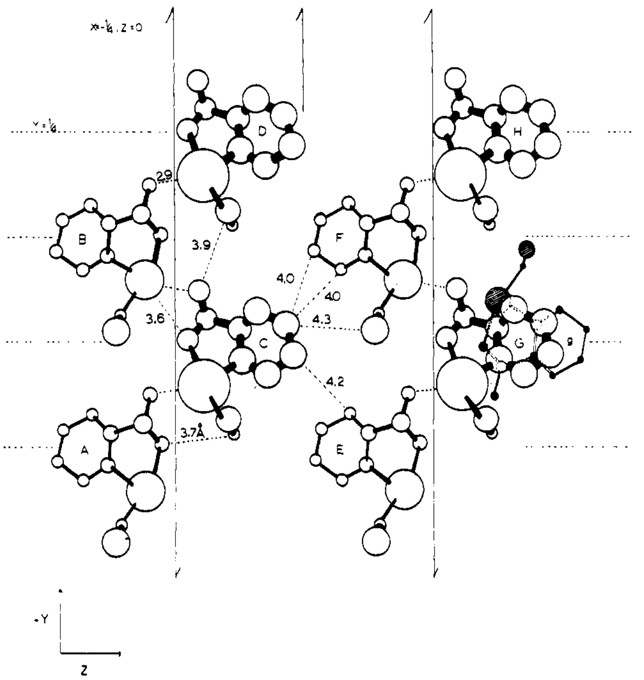


Figure 3. The molecular packing of I-β, shown in a perspective drawing viewed along [100]. Molecules A-B-C-D along the screw axis are coordinated by intermolecular trivalent iodine to oxygen interactions. The lettered molecules are related as: A ($-\frac{1}{2} - x, \frac{3}{2} + y, \bar{z}$); B ($-\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$); C ($x, 1 + y, z$); D ($x, y, z$); E ($-\frac{1}{2} - x, \frac{3}{2} + y, 1 - z$); F ($-\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$); G ($x, 1 + y, 1 + z$); H ($x, y, 1 + z$); g ($-\frac{1}{2} + x, \frac{3}{2} - y, 1 + z$).

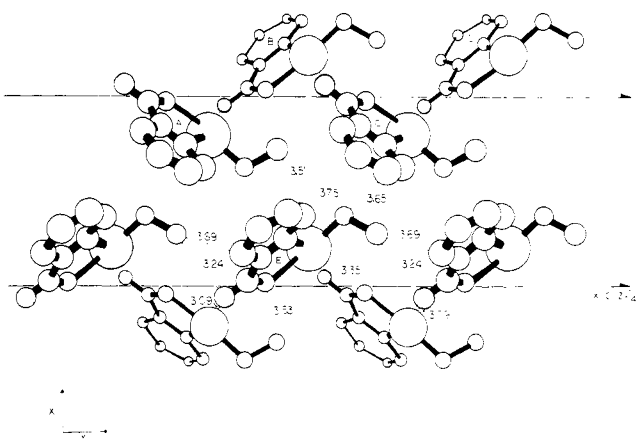


Figure 4. The molecular packing of screw-related molecules involved in intermolecular I ··· O coordination interactions (the coordinating oxygen atoms are shaded) in I-α, viewed along [001]. The lettered molecules are related as: A (x, y, z); B ($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$); C ($x, 1 + y, z$); D ($1 - x, \frac{3}{2} + y, \frac{1}{2} - z$); E ($\frac{1}{2} - x, \frac{1}{2} + y, z$).

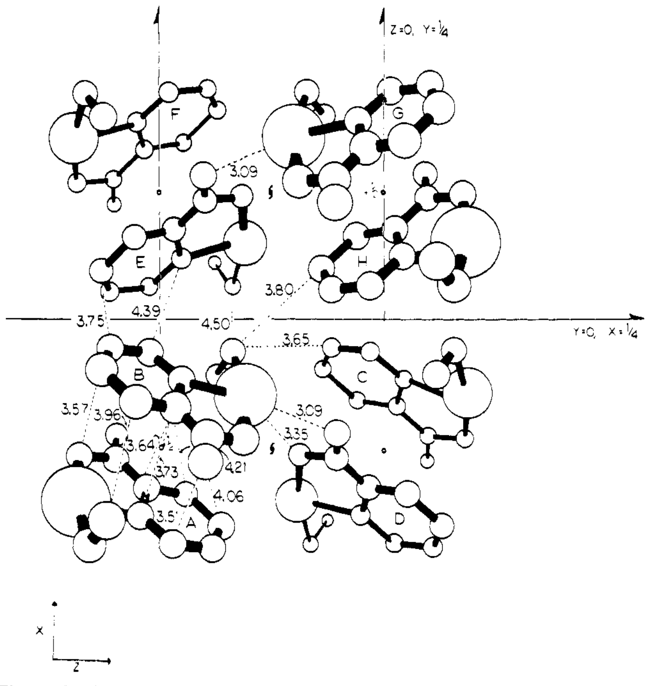


Figure 5. The molecular packing and intermolecular contact distances in I-α, viewed along [010]. Molecules which are coordinated by an I ··· O interaction are B-D, and E-G. The lettered molecules are related as: A ($-\frac{1}{2} + x, y, -\frac{1}{2} - z$); B ($\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$); C ($\frac{1}{2} - x, -\frac{1}{2} + y, z$); D ($-\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$); E ($x, \frac{1}{2} - y, -\frac{1}{2} + z$); F ($1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z$); G ($1 - x, 1 - y, \bar{z}$); H ($x, y, z$).

mean-square deviation from the least-squares plane of 0.04 Å,[15] and is parallel to the crystallographic plane (411) for I-α and (100) for I-β. The major structural difference between I-α (or I-β) and IV is the angle of rotation of the O(11) substituent relative to the molecular plane. For I-α, in which this substituent is a methyl group, the dihedral angle defined by C(2)-I(1)-O(11)-C(12) is 96 ± 2°, and for I-β it is 106 ± 10°. For compounds which have a carbonyl group bonded to O(11), the comparable dihedral angles range from 156 to 180°, so the O(11) substituent is nearly in the benziodoxole molecular plane and is in position to establish a close intramolecular contact between its carbonyl oxygen and trivalent iodine.

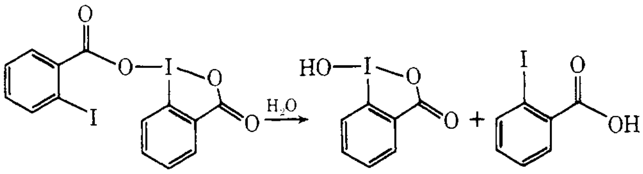
Molecular Packing. The molecular packings of I-α and I-β are significantly different even though they both exhibit an intermolecular coordination interaction between trivalent iodine and the carbonyl oxygen of a neighboring screw-related molecule. Trivalent iodine has been found to coordinate with a stereospecific intermolecular interaction in all previously determined benziodoxole structures.[2a-d,14] The interaction is a chemically stabilizing interaction[4] involving an unusually short intermolecular contact between trivalent iodine and an electronegative atom. For I-α, the distance was calculated to be 3.09 ± 0.05 Å, and for I-β, 2.9 ± 0.1 Å. Both polymorphs have nearly the same coordination stereochemistry about trivalent iodine, consistent with the coordination geometry observed for other benziodoxole structures (Figure 2). The geometry of the molecular packing about the screw axes is not completely fixed by this coordination mode, since the coordinating molecule (B) (Figure 2) is still free to rotate about its carbonyl bond or to precess about the vector parallel to $\vec{l}$ without changing the geometry of the bonds to trivalent iodine. These rotational parameters can be represented by the dihedral angle between the molecular planes of the coordinated molecules (117° for I-α, nearly 0° for I-β). Perspective drawings of these coordinated molecular chains are shown in Figures 3 and 4.

A possible secondary interaction may be occurring between overlapping parallel benziodoxole rings. For I-α, the overlapping rings are inversion related (molecules A and B in Figure 5) with the benzene ring directly overlapping the neighboring five-membered ring. This intermolecular separation is ~3.6 Å. Since the glide plane in the structure of I-β bisects the molecules, neighboring glide-related benziodoxole rings in this polymorph also overlap and have an interplanar spacing of 3.6 Å (molecules G and g in Figure 3). We have no independent chemical evidence that either of these modes involves significant chemical stabilization, but similar intermolecular packing effects frequently occur for other benziodoxole molecules.

From structural considerations it is not obvious why I-β is metastable relative to I-α. I-α is a slightly denser crystal form with a molecular volume of 211.3 Å^3, as compared to 215.7 Å^3 for I-β. I-α is also of higher symmetry, but no additional stabilizing interactions appear to exist in this structure. From Figure 5 one can see that molecules ABCD as a subgroup are a monoclinic $P2_1/c$ structure containing both the coordinated screw chain units and the overlapping ring interactions. The (200) plane between molecules B and C of this subgroup and molecules E and H of the other monoclinic subgroup is bounded by contiguous methoxyl groups, which would be expected to give rise to nonstabilizing interactions (consistent with the (h00) planes being the natural cleavage planes).

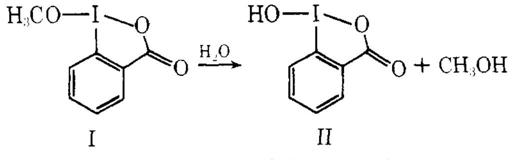
The polymorphic transformation which occurs in solution (I-$\beta \rightarrow$ I-α) is most likely a dissolution-recrystallizaton process rather than a single-crystal solid-state transformation, since crystals of I-β do not transform to I-α in the absence of solvent. Although there are no obvious structural relationships between I-α and I-β which are suggestive of possible solid-state transformational modes, in a few crystallizations we have observed allotriomorphic crystals[16] which have both needle and diamond morphology (). An x-ray Weissenberg photograph of such a crystal distinctly shows the superimposed diffraction patterns of ($0kl$) of I-β and ($hk0$) of I-α with their [010] directions 47° apart. The isolated needle portion of the crystal gave only the diffraction pattern of the I-β form, so these unusual crystals may result from an epitaxial growth.

Solid State Chemistry. The short shelf life of single crystals of I-α or I-β is due to their facile hydrolysis by atmospheric moisture. Water penetrates the crystals and causes homogeneous pseudomorphic transformations to II rather than just reaction at the crystal faces.[18] The hydrolyses are chemically quantitative and some of the reaction product grows as an oriented crystalline phase. Other benzoyloxy-substituted benziodoxole compounds, such as VI, can also be hydrolyzed



VI II III

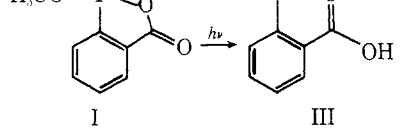
in the solid state, but these reactions are very slow and often need to be run at elevated temperatures and pressure in a saturated aqueous atmosphere. Both hydrolysis products formed from VI remain in the pseudomorphic product crystal. The hydrolysis of I gives only a single component pseudomorph,



I II

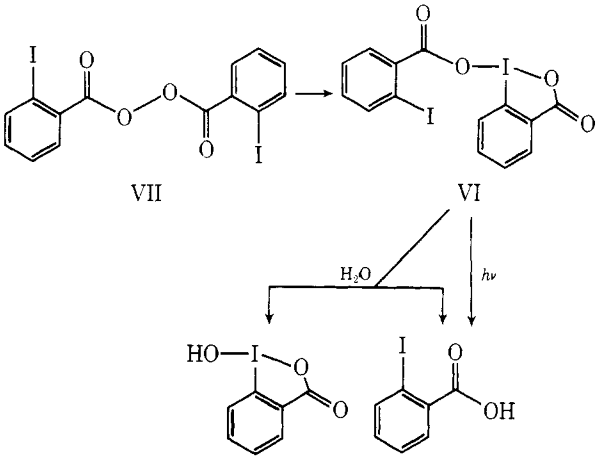
since methanol vaporizes out of the crystal.

The radiation-induced transformation of I to III, both in the solid state and in solution, is the first unambiguous example of photolytic reduction of trivalent iodine in a benziodoxole ring.[19]



I III

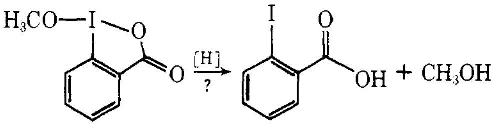
III has also appeared as a reaction product in the single-crystal thermal isomerization of bis(o-iodobenzoyl) peroxide (VII) to give VI. It was formerly thought that III was formed in this transformation by competing hydrolysis reactions, but it is now apparent that III may also be formed as a photolytic reduction product of VI. In the photolytic decompositions of single crystals of I-α with x rays, III is formed in quantitative yield in both an amorphous phase and a highly twinned oriented crystalline phase. For I-β the pseudomorphic transformation is also chemically quantitative, but gives amorphous III. The latter reaction is much more rapid than the photolysis of I-α.



VII VI

II III

The stoichiometry of photolytic benziodoxole reductions is still unclear. Formaldehyde is a chemically reasonable by-product of the reduction of I, but we have not been able to confirm its presence. If methanol is the by-product, then an additional and unknown source of hydrogen atoms is necessary. The fact that compounds such as VI, with no alkyl or hydroxyl hydrogen atoms available for abstraction, also can be reduced to III suggests that an external hydrogen source such as H_2O is necessary. Hopefully these ambiguities can be clarified by the study of photolytic reduction of higher alkyl derivatives, such as butoxy-substituted benziodoxoles in which the by-products may be liquids, which would be more easily isolated and analyzed than the gaseous by-products of I.



The hydrolysis and photolysis reactions of I discussed above occur in solution as well as in the solid state, and no chemical differences are found between reactions of I-α and I-β, so the crystal lattices do not effect topochemical control over product formation.[21] Both polymorphs do, however, exert stereospecific control over the nucleation and growth of crystalline product phases, a property common to many organic trivalent iodine compounds. The structural, chemical, and geometrical significance of orientational effects in the reactions of I-α and I-β will be discussed in the following paper in this series.

Acknowledgment. The financial support of the National Science Foundation and Minnesota Mining and Manufacturing is greatly appreciated. I am indebted to Professor Jack Gougoutas for his stimulating guidance of this work.

Supplementary Material Available: Observed and calculated structure factors for I-α and I-β crystal structures and Figure 1, calculated bond distances and angles in I-α (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Partially based on a Ph.D. thesis by M. C. Etter, University of Minnesota, Dec 1974; (b) National Science Foundation Predoctoral Fellow, 1970–1973, Minnesota Mining and Manufacturing Predoctoral Fellow, 1973–1974.

(2) (a) J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.*, **4,** 230 (1972); (b) J. Z. Gougoutas and L. Lessinger, *ibid.*, **9,** 155 (1974); (c) J. Z. Gougoutas, K. H. Chang, and M. C. Etter, *ibid.*, **15,** 283 (1976); (d) J. Z. Gougoutas and D. Naae, *ibid.*, **16,** 271 (1976); (e) J. Z. Gougoutas, *Pure Appl. Chem.*, **27,** 305–325 (1971).

(3) G. P. Baker, F. G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 3721 (1965).

(4) M. C. Etter, *J. Solid State Chem.*, **16,** 399 (1976).

(5) E. Shefter and W. Wolf, *Nature* (*London*), **203,** 512 (1964).

(6) $R = \Sigma\ //F_o| - |F_c||/\Sigma|F_0|$; the function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where the weight $w = 1/[\sigma(|F_0|^2)]$.[2] Atomic scattering factors were taken from the "*International Tables for X-ray Crystallography*".[7]

(7) "International Tables for X-ray Crystallography", Vol. III, C. H. MacGillavry and G. D. Riech, Ed., Kynoch Press, Birmingham, England, 1962.

(8) After multiple recrystallizations one occasionally obtains a batch of large (~1 mm long) hollow acicular crystals. These unusual crystals have a channel about 0.1 mm in diameter extending the length of the crystal (as evidenced by "stringing" several crystals on a glass fiber). The channels are not cylindrical; they exhibit distinct trigonal, square, pentagonal, or hexagonal symmetry. X-ray photographs of these crystals showed that they were untwinned single crystals of I-β.

(9) I am grateful to Roger Upham for his assistance in preparing special inlet systems and appropriate samples, and for running the mass spectral analyses. The samples were run on an AEI MS-30 mass spectrometer at 1000 resolution, 70 eV. Sample inlet temperature was room temperature, and source temperature 110–200 °C.

(10) Reference samples of formaldehyde (prepared by heating paraformaldehyde) were run and the mass spectra agreed with the data given in the "Atlas of Mass Spectral Data".[11]

(11) S. Abrahamson, E. Stenhagen, and R. W. McLafferty, "Atlas of Mass Spectral Data", Wiley, New York, N.Y., 1969.

(12) A pseudomorphic transformation is one in which the morphology of the reactant crystal does not change during reaction. In a single crystal to single crystal pseudomorphic transformation, the diffraction pattern of the reacting crystal changes but the dimensions and shape of the crystal itself does not (color and density changes often occur also).

(13) M. C. Etter, Ph.D. Thesis (Appendix), University of Minnesota, 1974.

(14) J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.*, **4,** 226–229 (1972).

(15) The least-squares plane of the molecule was calculated using all the atomic positions except for C(12). Defined in terms of orthonormal axes *x*, *y*, and *z* which are directed along crystallographic axes *a*, *b*, and *c**, respectively, this plane calculates to be $0.743x + 0.558y - 0.387z = 6.16$.

(16) A term used to describe crystals of unusual or distorted morphology resulting from intercrystal contacts during growth.[17]

(17) J. S. Evans, *Discuss. Faraday Soc.*, **No. 5,** 77 (1949).

(18) Many single crystal–gas reactions are known in which the gaseous reagent actually penetrates the crystal lattice. A review of these reactons and other organic crystal–gas reactions has appeared recently: I. C. Paul and D. Y. Curtin, *Science*, **187,** 19 (1975).

(19) The only other known example of photolytic reduction of organic trivalent iodine is the photolysis of iodobenzene dichloride to give iodobenzene and chlorine.[20]

(20) D. F. Banks, *Chem. Rev.*, **66,** 249 (1966).

(21) There is a topochemical effect[22] on the kinetics of these reactions, since the I-β polymorph is much more reactive than I-α. It is difficult to relate this effect to specific structural differences between the two polymorphs, especially since there are no observable reactant–product boundaries indicative of directional product growth.

(22) G. M. J. Schmidt and M. D. Cohen, "Reactivity of Solids", T. J. deBoer, Ed., Elsevier, Amsterdam, 1961, p 556.

Solid-State Chemistry of Organic Polyvalent Iodine Compounds. 9. Topotactic Reactions of Two Polymorphs of 1-Methoxy-1,2-benziodoxolin-3-one[1a]

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Abstract: From the topotactic relationships established between chemically identical, but crystallographically unique polymorphs of 1-methoxy-1,2-benziodoxolin-3-one (I) and their reaction products, *o*-iodosobenzoic acid (II) and *o*-iodobenzoic acid (III), we have been able to evaluate the significance of specific molecular and geometric lattice properties on the nucleation and directed crystallization of product molecules. Irradiation of the orthorhombic polymorph, I-α, leads to formation of four conservatively twinned crystalline phases of III which are ordered such that iodine-containing planes of the reactant and each of the four product lattices are mutually parallel and have the same ~4 Å interplanar spacing. Irradiation of monoclinic I-β gives only a powdered phase of III. Hydrolysis of I-α gives twinned crystalline phases of II, with $(100)_{II}$ and $(100)_{I\text{-}\alpha}$ parallel and rotated relative to one another such that several lattice site coincidences occur. I-β orients II such that several different symmetry independent twin phases are formed. For one twin, the glide direction of I-β is parallel to the unique symmetry axis of product, two other twins have $(001)_{I\text{-}\beta}$ aligned parallel to $(100)_{II}$, and four of the twins have their (010) planes parallel to $(010)_{I\text{-}\beta}$. Since none of the reactant and product lattices are isomorphous, these single-crystal transformations involve large-scale molecular reorganization prior to product nucleation. The topotactic relationships established, nonetheless, are reproducible and highly stereospecific.

Introduction

Chemical reactions in single crystals are fundamentally different from mobile phase reactions in two respects: (1) the ordering of reactant molecules into a lattice can result in topochemical control over reaction pathways,[2] and (2) the reactant lattice can control the nucleation and preferential orientation of crystalline product phases. Topochemistry has been the subject of intensive research in recent years,[3] but most often these solid-state reactions have not been topotactic; i.e., no crystalline product phases were formed, which had a unique orientation relative to the reactant lattice. Our studies have focused on the single-crystal reactions of organic polyvalent iodine compounds, which generally do give oriented crystalline product phases.[4] Because of the wide variety of reactions observed and the facility with which these single-crystal transformations occur, we have been able to study the effects of molecular packing, intermolecular coordination interactions, geometrical lattice parameters, and space group symmetry on the nature of the interlattice relationships established during reaction. Some of the significant observations concerning topotaxy in polyvalent iodine transformations are summarized here as a basis for understanding the results of the current investigation: