

Solid-State Chemistry of Organic Polyvalent Iodine Compounds. VI. The Crystal Structure and Topotactic Hydrolysis of 3-oxo-3H-2,1-benzoxiodol-1-yl *o*-Fluorobenzoate

J. ZANOS GOUGOUTAS, KUO H. CHANG, AND M. C. ETTER

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

Received March 10, 1975; in revised form June 19, 1975

3-Oxo-3H-2,1-benzoxiodol-1-yl *o*-fluorobenzoate (IIIc) is formed as a topotactically aligned crystal structure when single crystals of its dibenzoyl peroxide isomer thermally decompose at room temperature. Independently, it has been found that single crystals of IIIc grown from solvents are hydrolyzed to *o*-iodosobenzoic acid, II, and *o*-fluorobenzoic acid after ~4 weeks in a moist atmosphere at ~45°C. II is formed topotactically in a conservatively twinned arrangement in which the (100) planes of the equally present twin members are parallel to (001) of IIIc. In addition, the 4 Å *b* axes of the twin members align with the 4 Å *a* axis of IIIc. Other examples of topotactic hydrolyses resulting in twinned arrangements of II are cited in reference to the novel possibility that the favored mode of alignment (the specific topotaxy between the reactant and *one* twin member) is one which, when augmented by conservative twinning, results in a favorable interphase between the conservatively twinned members.

The transformation IIIc → II and more than 20 other corroborating examples of topotaxy in our studies lead us to expect the alignment of 4 Å axes whenever they are present in both the reactant and product of topotactic transformations involving comparable aromatic molecules.

The crystal structure of IIIc (C₁₄H₈IFO₄), *a* = 4.08, *b* = 12.00, *c* = 26.25 Å, β = 90.5°, *Z* = 4, *P*2₁/*c* (refined to *R* = 0.10 for 453 photographically recorded intensities) consists of chains of *transoid* "dimers" similar to those previously observed in structures of closely related derivatives.

Introduction

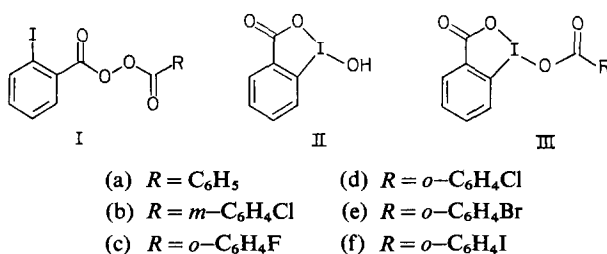
2-Iododibenzoyl peroxide and its 3'-chloro- and 2'-fluoro-derivatives, Ia-c, have very similar crystal structures (1) which readily undergo hydrolytic topotactic transformations to *o*-iodosobenzoic acid, II, upon exposure to moisture at room temperature. For the most part, the other product of hydrolysis (benzoic acid or its *m*-Cl or *o*-F derivatives) is formed as an amorphous phase within the pseudomorph.

Molecular isomerization of peroxides Ia-c to the corresponding benzoxiodole structures, IIIa-c, also occurs in the solid state. However, despite the similarities in the parent crystal structures, I, the extent and nature of the

topotaxy established during their isomerization is quite variable,¹ apparently because of major differences between the crystal structures and unit cell dimensions of the products, III (3).

The crystal structure of IIIc, which is formed in a conservatively twinned (4) arrangement during topotactic peroxide isomerization, can be obtained as a pure single-crystal phase, devoid of any twinning, by independent synthesis and crystallization of IIIc from solvents. In a separate solid-state

¹ The complex behavior of Ib is described in a previous paper in this series (2). The topotactic isomerization of Ic to IIIc will be described in a future report.



reaction, these single crystals can be hydrolyzed to II and *o*-fluorobenzoic acid. Although the latter is formed as an amorphous phase, II is topotactically aligned relative to the crystal structure of IIIc.

Unlike many of the benzoxiodole derivatives in our studies, only one crystalline modification of IIIc has been obtained under a variety of conditions. Its crystal structure and topotactic hydrolysis are described in this report.

Crystal Structure of IIIc

IIIc was synthesized according to the previously described procedure used for the synthesis of IIIb (3) and crystallized from hot benzene or dichloromethane. The unit cell data for the fine colorless needles (mp, 194–6°C) are given in Table I. Diffraction intensities from reciprocal lattice levels $0kl$ – $2kl$ and $h0l$ ($\text{CuK}\alpha$, $\lambda = 1.5418 \text{ \AA}$) were recorded by the equi-inclination Weissenberg method and estimated by visual comparisons with a standardized intensity scale. The solution of the structure was straightforward.

Least-squares refinements² resulted in $R = 0.10$ for the 453 "observed" intensities.³ The fractional atomic coordinates are given in Table II.

Two strong *intermolecular* coordination bonds involving the exocyclic carbonyl oxygen, O (4), and trivalent iodine atom (I—O distance = 3 Å) occur between pairs of molecules related by crystallographic inver-

² The function minimized was $\sum w(|F_{\text{obs}}|^2 - |F_{\text{calc}}|^2)^2$. Anisotropic thermal parameters for I and F, isotropic parameters for C and O, and all coordinates were refined. Extensive refinements were not attempted in view of the limited and rather low-quality intensity data. The unobserved hydrogen atoms were introduced at expected positions but their parameters were not refined.

³ Tables of observed and calculated structure factors, least-squares planes, and thermal parameters from this analysis have been deposited. See NAPS document No. 02629 for 30 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications.

TABLE I

Structure	a (Å)	b (Å)	c (Å)	β (deg)	Z	D_{calc} (g/cm ³)	V (Å ³)	Space group
Ic	21.41	4.20	15.46	93.7	4	1.85	1387	$P2_1/c$
II	12.89	4.10	14.05	96.7	4	2.38	737	$P2_1/c$
IIIc	4.08(1)	12.00(3)	26.25(10)	90.5(1)	4	2.00	1283	$P2_1/c$
G ^a	6.553	3.813	24.754	100.71	4	1.53	608	$P2_1/c$

^a G = *o*-fluorobenzoic acid.

TABLE II
FRACTIONAL ATOMIC COORDINATES FOR IIIc

Atom	X	Y	Z
I	0.144(1)	0.0919(3)	-0.0790(2)
F	0.69(1)	0.384(3)	-0.005(1)
C(1)	0.33(1)	0.214(5)	-0.136(2)
C(2)	0.48(2)	0.302(6)	-0.132(3)
C(3)	0.57(2)	0.362(6)	-0.175(3)
C(4)	0.46(1)	0.333(5)	-0.219(2)
C(5)	0.28(2)	0.219(5)	-0.227(2)
C(6)	0.21(1)	0.159(5)	-0.179(2)
C(7)	0.06(2)	0.049(7)	-0.194(3)
C(8)	0.39(2)	0.171(7)	0.015(3)
C(9)	0.53(1)	0.243(5)	0.058(2)
C(10)	0.54(1)	0.219(5)	0.110(2)
C(11)	0.73(2)	0.278(6)	0.141(3)
C(12)	0.82(1)	0.379(3)	0.130(2)
C(13)	0.81(2)	0.416(6)	0.081(3)
C(14)	0.68(2)	0.346(6)	0.046(3)
O(1)	-0.05(2)	0.019(5)	-0.229(2)
O(2)	-0.04(1)	0.011(3)	-0.146(2)
O(3)	0.39(1)	0.214(4)	-0.031(2)
O(4)	0.22(1)	0.099(5)	0.029(2)
H(1) ^a	0.54	0.332	-0.097
H(2)	0.72	0.427	-0.173
H(3)	0.48	0.386	-0.249
H(4)	0.22	0.189	-0.262
H(5)	0.40	0.156	0.124
H(6)	0.80	0.244	0.175
H(7)	0.90	0.430	0.158
H(8)	0.90	0.492	0.073

^a The experimentally unobserved hydrogen atoms have been introduced at expected positions in the phenyl planes.

sion centers. The resulting bimolecular units or "dimers" (e.g., molecules F and G in Fig. 1) are completely analogous to those found in crystal structures of IIIa and IIIb (3), III d and e,⁴ and III f (5).

The formation of "dimers" in the crystal structure of IIIc, as for all other members of the 2'-halo series of these derivatives, has

⁴ A quantitative comparison of the conformations of these dimers is presented in Table V of the preceding paper in this series (6).

resulted in a *transoid* disposition of the 2'-halo substituent and the coordinating carbonyl oxygen atom. The "dimer" of IIIc is approximately flat; the maximum atomic deviation from the least-squares plane³ of the "dimer" centered at the origin is 0.8 Å for C (11). This plane is nearly parallel to (1 $\bar{2}$ 0). Neighboring dimers related by cell translations of $\bar{a} + b$ are packed in relatively flat, infinite chains containing *interdimer* F—F approaches of 3.2 Å across inversion centers (e.g., dimers IJ and KL of Fig. 1 are part of a chain). Each dimer is inclined by $\sim 10^\circ$ to the mean chain plane (1 $\bar{1}$ 0), which in turn is inclined by $\sim 20^\circ$ to (100) (Fig. 2). Translational stacking of the chains along the 4 Å *a*-axis results in an interplanar distance of 3.5 Å between the stacked dimers.

Similar chains of dimers are present in the several crystal structures of the 2'-chloro and 2'-bromo analogs of IIIc, while the dimers in the acicular polymorph of the 2'-iodo analog pack in chains of a different configuration. In all of these structures, the relatively flat chains are stacked either translationally, with resultant 4 Å *a*-axes as in the case of IIIc, or alternately by *a*-glide symmetry operations which result in approximately doubled *a* cell axes (7.4 Å in the isostructural 2'-chloro and bromo analogs).

Topotactic Hydrolysis of IIIc

The solid-state hydrolysis of independently prepared and freshly crystallized samples of IIIc was effected by exposing single crystals (about 0.1 × 0.04 × 0.05 mm) to air saturated with water vapor at various temperatures. After ~ 10 weeks at 25°C, the originally transparent needles were opaque but apparently unchanged in external morphology. Infrared spectroscopy was used to verify the complete hydrolysis of IIIc to the expected products, II and *o*-fluorobenzoic acid. Under these conditions very little topotaxy is evident; X-ray photographs display only very faint and extensively elongated reflections due to II.

Similar treatment of fresh crystals at 45°C for ~ 2 weeks led to substantial though not complete hydrolysis, and the appearance of

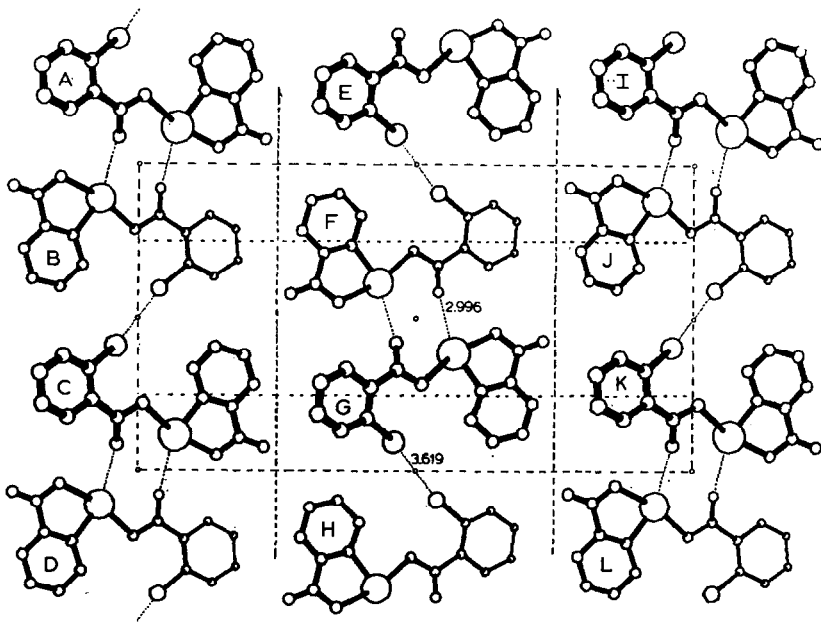


FIG. 1. A perspective drawing of the structure of IIIc, viewed along the short *a*-axis. The lettered molecules are related as: A: $-x, -y, -z$; B: x, y, z ; C: $-x, 1-y, -z$; D: $x, 1+y, z$; E: $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; F: $x, \frac{1}{2}-y, \frac{1}{2}+z$; G: $-x, \frac{1}{2}+y, \frac{1}{2}-z$; H: $x, \frac{1}{2}-y, \frac{1}{2}+z$; I: $-x, -y, 1-z$; J: $x, y, 1+z$; K: $1-x, 1-y, 1-z$; L: $1+x, 1+y, 1+z$.

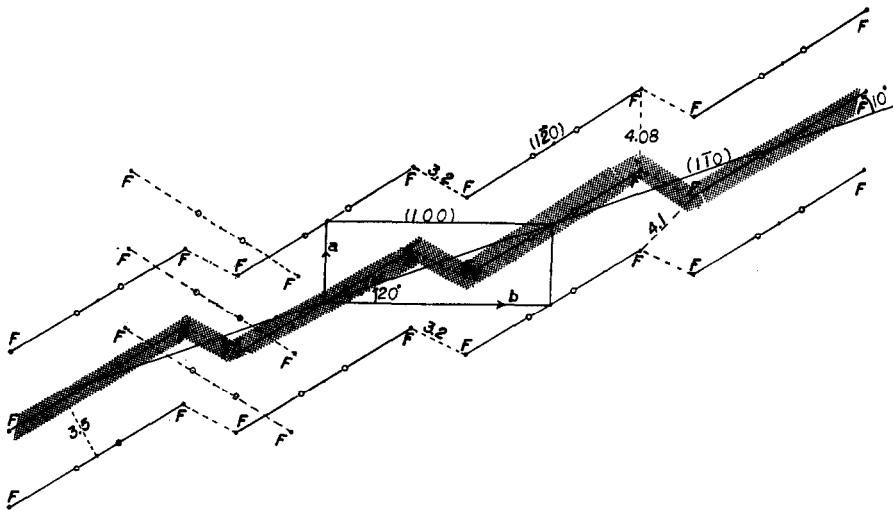


FIG. 2. A schematic drawing of the chain structure of IIIc, viewed along c^* . The solid lines terminating in F (fluorine) are dimers whose planes are approximately perpendicular to the plane of the drawing. One chain of dimers extending along $[110]$ is indicated by shading. Some fluorine-fluorine distances including the intrachain contact of 3.2 \AA are indicated. The chains consisting of solid line dimers are related by translations along *a*. The dashed dimers (also part of chains) shown in the left part of the drawing are related to the solid line chains by the *c*-glide element and therefore are displaced from the plane of the drawing.

single-crystal X-ray reflections from the three-dimensionally oriented structure (7) of II.⁵ No reflections from the known crystal structure (Table I) or *o*-fluorobenzoic acid (8) were observed, even in crystals which were completely hydrolyzed (~4 weeks) at this elevated temperature.

Although considerable randomness of orientation is indicated and the degree of topotaxy is far less than that observed in most of our other studies, a preferred orientation is clearly discernible from the maxima of reflections which extend over $\omega \cong 4^\circ$ on Weissenberg photographs.⁶ The topotactic relationship between the unit cell vectors of II(*ABC*) and IIIc(*abc*),

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} \pm 0.027 & -0.126 & \pm 0.488 \\ \pm 1.005 & 0 & 0 \\ 0 & 1.171 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

was conveniently determined from photographs of partially hydrolyzed crystals. Both monoclinic crystal structures have short ~4 Å axes which are aligned throughout the transformation. The short axis is the unique **b** monoclinic axis *only* in the product, II (Table I), which accordingly has aligned in a conservatively twinned arrangement and thus has preserved the directional point group symmetry elements of the reactant structure (4). In addition to the parallel alignment of 4 Å axes (\mathbf{a}_{IIIc} and \mathbf{b}_{II}), the specific topotaxy includes the parallel alignment of \mathbf{b}_{IIIc} and \mathbf{c}_{II} , despite the relatively large misfit of their scalar lengths, $(c_{\text{II}} - b_{\text{IIIc}})/b_{\text{IIIc}} \cong 0.17$.

⁵ The nature and extent of topotaxy in the transformation $\text{Ib} \rightarrow \text{IIIb}$ also are affected by temperature changes of this magnitude (2).

⁶ Two additional minor orientations have been observed:

$$\Phi_2 = \begin{pmatrix} \pm 0.003 & 1.067 & \pm 0.058 \\ \pm 1.005 & 0 & 0 \\ \mp 0.030 & 0 & \mp 0.535 \end{pmatrix};$$

$$\Phi_3 = \begin{pmatrix} \mp 0.006 & 1.048 & \mp 0.108 \\ \mp 1.005 & 0 & 0 \\ \pm 0.030 & 0.122 & \pm 0.532 \end{pmatrix};$$

The relative amounts of oriented II in the three modes of alignment are approximately 6:1:2. Despite the different specific topotaxy of Φ_2 , the (100) planes of the twin members of II again are parallel.

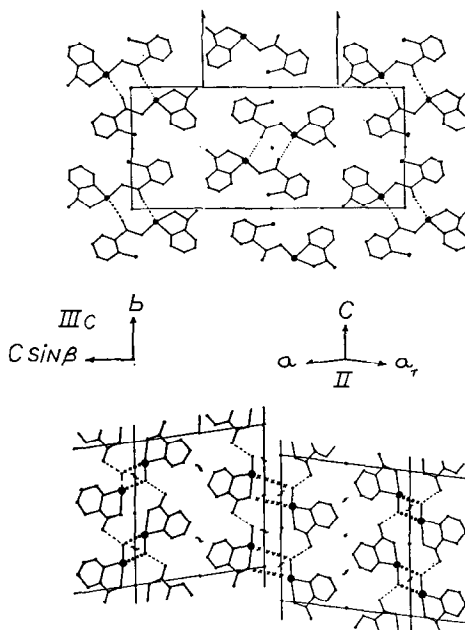


FIG. 3. The observed topotactic alignment of IIIc (top) and two conservatively twinned members of II (bottom left and right), shown in projection down their 4 Å axes. Hydrogen bonds in II are indicated by dashed lines while I—O coordination bonds are indicated by a series of dots. The x's between I and O atoms suggest possible coordination bonds across the hypothetical twin interphase (100).

The experimentally observed angular orientation of the conservatively twinned crystal structure of II relative to the reactant structure IIIc is shown in Fig. 3. Very extensive migrations of large molecular fragments must take place during the segregation of the iodine-containing *half* of the reactant structure IIIc into the oriented domains of the single-crystal structure of II, and no simple correspondence is to be expected between the initial and final molecular arrangements.

Discussion

A. Alignment of 4 Å Axes

In general, it has proved difficult to predict the specific topotaxy which will be established between a given reactant and product structure, even when both crystal structures are

known in detail. Seemingly plausible rationales gleaned from one study often are contradicted by a later study of an apparently analogous system. Therefore, considerable caution should be exercised in deriving any conclusions from an isolated study of topotaxy.

One of the few generalizations which has emerged from our studies applies to special

cases such as Ic \rightarrow IIIc, IIIc \rightarrow II in which both reactant and product have a 4 Å axis. These and more than 20 other (see Table III) related topotactic transformations in our studies suggest a useful empirical rule to which no exception has yet been found: *When topotaxy is established between a reactant and product crystal structure, both of which have the short ~ 4 Å axes characteristic of the*

TABLE III
TOPOTACTIC TRANSFORMATIONS RESULTING IN ALIGNED 4 Å AXES

1. Derivatives of Ia as the initial (parent) crystal structure						
Number	Parent	Product ^a	Parent (b) axis (Å)	Product axis (Å)	Twinning ^b	References
1	Ia	II	4.09	b = 4.10	N	(4)
2	Ib	II	4.06	4.10	L	(2)
3	Ic	II	4.20	4.10	L	(1)
4	Id	II	4.08	4.10	L	(13)
5	Ie	II	4.12	4.10	L	(13)
6	If	II	4.21	4.10	N	(4)
7	If	III f - α	4.21	a = 4.09	C	(4)
8	If	A	4.21	a = 4.32	C	(4)
9	Ie	III e - α	4.12	a = 3.99	C, L	(6, 13)
10	Ie	B	4.12	b = 4.10	L	(4)
11	Ie	X e	4.12	b = 4.05	C	(4, 6)
12	Id	C	4.08	b = 3.90	L	(13)
13	Id	X d	4.08	b = 4.00	C	(6, 13)
14	Ic	IIIc	4.20	a = 4.08	C	(1, 3)
15	Ib	D	4.06	a = 3.85	C	(2)
16	Ib	A	4.06	a = 4.32	C	(2)
17	Ib	X b	4.06	b = 4.01	?	(2)
2. Derivatives of IIIa as the initial (parent) crystal structure						
Number	Parent	Product ^a	Parent axis (Å)	Product axis (Å)	Twinning ^b	References
18	IIIc	II	a = 4.08	b = 4.10	C, L	This paper
19	III e - α	B	a = 3.99	b = 4.10	C	(4)
20	III f - α	II	a = 4.09	b = 4.10	C	Unpublished
21	III f - α	A	a = 4.09	a = 4.32	C	Unpublished
3. Miscellaneous reactants						
Number	Parent ^a	Product ^a	Parent axis (Å)	Product axis (Å)	Twinning	References
22	II	E	b = 4.10	b = 3.97	L	(12)
23	F	A	a = 4.11	a = 4.32	C	Unpublished

^a The code for structures not identified in the text: A = *o*-iodobenzoic acid; B = *o*-bromobenzoic acid; C = *o*-chlorobenzoic acid; D = *m*-chlorobenzoic acid; E = the I-O-I anhydride of II; F = II with OH replaced by Cl; X = novel polymorphs of the corresponding III.

^b Twinning of product observed during transformation. C denotes conservative twinning. L denotes Lonsdale twinning, in which case two or more symmetry-independent topotaxies are established with aligned 4 Å axes. N denotes no detectable twinning.

translational stacking modes of these relatively flat molecules, the ~ 4 Å axes will align in a parallel and/or antiparallel orientation in the pseudomorph. The favorable consequences of such an alignment, whatever their origin, clearly supersede any local symmetry considerations for in many examples the aligned 4 Å axes are not axes of space group symmetry in both the reactant and product crystal structures. That being the case, an angular divergence (often 90° as in the transformation IIIc \rightarrow II) between reactant and product axes of symmetry accompanies the preferred alignment of short translational axes and conservative twinning occurs.

Most, though by no means all, transformations in our studies involve reactant and product structures each of which has a 4 Å unit cell repeat. Applications of the above generalizations to those systems effectively reduces to two dimensions the problem of predicting a priori the observed specific topotaxies—their mutual three-dimensional phase alignment. It is of interest in this connection that 7.4 Å axes of double stacking modes in the 2'-chloro and bromo analogs align topotactically with the 4 Å axes of their peroxide precursors, while structures of IIIa and IIIb which have no comparable stacking modes do not orient readily on their solid-state precursors, Ia and Ib.

B. Twinning

The multiple orientations or twinning of product crystal structure which frequently is observed during topotactic transformations has proved to be a useful criterion for studying the template or seeding role of a particular lattice in orienting and crystallizing a product within a transforming pseudomorph (9). Implicitly, the twinning has been considered to be independent of the specific topotaxy established between the product and orienting crystal lattices. Yet, at present we have no information pertaining to the nature of the physical *distribution* of twin members of product within the pseudomorph and therefore we are not able to distinguish between: (1) an arrangement in which the twin members are physically separated by amorphous regions and are independent of one another, and (2) a

bona fide twin composed of contiguous members with an associated twin interphase. In the former case, the "twinning" is simply a *formal* relationship between two separate domains of product aligned in one of two ways relative to the orienting (seed) lattice. Possible twinning of this type will depend on the specific topotaxy, but the specific topotaxy should not depend on this "twinning." For case (2), however, the orientation established during transformation may be dependent not only upon the specific alignment of each member relative to the seed lattice, but also upon the nature of the intergrowth of twin members.

The many topotactic transformations in our studies leading to the formation of different oriented arrangements of II provide an interesting basis for comparisons of the possible interrelationship between specific topotaxy and twinning. The formation of II from hydrolyses of Ib and other peroxides usually results in two twin members having parallel (100) planes. In these cases, the twinning is of the Lonsdale type (4) in which different *specific* topotaxies obtain between the reactant and each twin member (some of the corresponding elements of the two topotactic matrices have different numerical values). The symmetry of the reactant lattice does not control the relative amount of twin members and varying ratios have been observed. Lonsdale's original conception of this type of twinning (10) focused on the different specific topotaxies between the reactant and each twin member and this may also be a determining factor in the non-conservative twinning of II from the peroxides.

By contrast, the specific topotaxies between IIIc and each twin member of II are degenerate with respect to the point group symmetry of IIIc (conservative twinning) and the twin members are always generated in equal amounts. Unlike the Lonsdale twinning, the formal or real relationship between the conservatively twinned members is completely defined by the symmetry elements of the reactant, once the specific topotaxy between IIIc and II is fixed for one "twin member." Thus, conservative twinning results in the formation of multiple orientations of

the product unit cell vectors, $(\mathbf{A})_i$ according to $(\mathbf{A})_i = \Phi C'_i(\mathbf{a})$, where C'_i is the transpose of the i th point group symmetry matrix of the seed or orienting crystal lattice (\mathbf{a}). The relationship between the crystal lattice vectors of the i th and j th twin members is therefore $(\mathbf{A})_i = \Phi C'_i C'_j \Phi^{-1}(\mathbf{A})_j = \Phi C_n \Phi^{-1}(\mathbf{A})_j$, where C_n is another point group symmetry matrix of the orienting lattice. It may readily be shown that for a specific topotaxy Φ a crystal plane $(h_1 h_2 h_3)$ of one twin member is parallel to the equivalent plane of another twin member if the corresponding reciprocal lattice vector $\sigma = \sum_m h_m \mathbf{A}_m^*$ is an eigenvector of the matrix $\Phi C_n \Phi^{-1}$. The components of σ for these "eigenplanes" are simply the *columns* of the topotactic matrix Φ . Inspection of the elements ϕ_{13} , ϕ_{23} , ϕ_{33} in the above matrix for the transformation IIIc \rightarrow II reveals that the (100) planes in all conservatively twinned members of II are parallel as a consequence both of the specific topotaxy Φ and the conservative twinning.⁶

It is apparent from the above discussion that twinned members of II with parallel (100) planes are formed in these topotactic transformations, both when the twinning is of the unrestricted Lonsdale type and when symmetry imposes the twin relationship. The latter, conservative twinning, is quite restrictive since it is clear that parallel (100) planes of twin members can result only when very specific modes of alignment of each twin member are established relative to the directional symmetry elements of the orienting lattice. We have therefore considered the somewhat convoluted possibility that specific topotaxy in some transformations may be established in such manners as to produce a favorable interphase between conservatively twinned members. Further evidence consistent with this possibility has emerged from studies of the topotactic hydrolyses of the *O*-acetyl and *O*-methyl derivatives of II (11). Neither derivative forms a crystal structure with a characteristic 4 Å axis—a feature which would have led us to expect its topotactic alignment with the *b*-axis of II (*vide supra*). Both yield conservatively twinned arrangements of II in which the (100) planes of the twin members are parallel. The effect is

manifest for the orthorhombic *O*-methyl derivative where *four* conservative-twin members of II (4) are topotactically aligned with their (100) planes in a parallel arrangement. However, in neither case are the *b* (or *c*) axes of the twin members of II also parallel. Further studies of this effect and the apparently contradictory topotaxy in the hydrolysis of IIIf are in progress.

To date, the (100) twinning mode has not been observed in crystals of II grown from solvents, but the very similar crystal structure of the anhydride of II is very commonly twinned in this manner in solvent-grown crystals.⁷ A possible molecular basis for such twinning is evident in the molecular packing of II (see Fig. 3): *c*-glide related molecules are linked through hydrogen-bonds into chains which are stacked translationally along the short *b*-axis to give layers parallel to (100). The ubiquitous intermolecular coordination bonding to trivalent iodine (6) occurs between these layers and, in the nontwinned structure, involves adjacent molecules related by screw axes between the layers. It would appear that twinning of II across the (100) planes of both members would allow for the formation of similar I^{III}—O coordination bonds *between the two twin members*, without affecting the hydrogen-bonding within the individual members. Twinning across other possible interphases parallel to (100) would also be consistent with the observed relative alignment of twin members; (200) twinning, for example, would affect neither the hydrogen bonding nor the intermolecular I—O coordination bonding within one twin member.

Acknowledgments

This research has been funded through a grant from the University of Minnesota.

References

1. J. Z. GUGOUTAS AND L. LESSINGER, *J. Solid State Chem.* **7**, 175 (1973).
2. J. Z. GUGOUTAS AND L. LESSINGER, *J. Solid State Chem.* **12**, 51 (1975).

⁷ Topotactic dehydration of II to its anhydride occurs at $\sim 197^\circ$. The crystal structure of the anhydride and its topotactic formation will be published in a future paper in this series (12).

3. J. Z. GOUGOUTAS AND L. LESSINGER, *J. Solid State Chem.* **9**, 155 (1974).
4. J. Z. GOUGOUTAS, *Isr. J. Chem.* **10**, 395 (1972).
5. J. Z. GOUGOUTAS AND J. C. CLARDY, *J. Solid State Chem.* **4**, 230 (1971).
6. J. Z. GOUGOUTAS AND D. G. NAAE, *J. Solid State Chem.* **16**, 271 (1976).
7. E. SHEFTER AND W. WOLF, *J. Pharm. Sci.* **54**, 104 (1965).
8. J. KRAUSSE AND H. DUNKEN, *Acta Crystallogr.* **20**, 67 (1966); G. FERGUSON AND K. M. S. ISLAM, *Cryst. Struct. Comm.* **4**, 389 (1975).
9. J. Z. GOUGOUTAS, Paper presented at the American Chemical Society symposium on Organic Solid-State Chemistry, New York (August 1972).
10. K. LONSDALE, *Acta Crystallogr.* **20**, 67 (1966).
11. M. ETTER, Ph.D. Thesis, University of Minnesota (1974).
12. M. ETTER, unpublished results.
13. J. Z. GOUGOUTAS, *Pure Appl. Chem.* **27**, 305 (1971).