measured the thresholds for hydride abstraction by protonated acetaldehyde and propionaldehyde. The former compound was observed to abstract hydride from 2-methylbutane, but not from 2-methylpropane; the latter was noted to react endothermically with both methylcyclohexane and methylcyclopentane. The resulting affinities, 234.0 kcal/mol for protonated acetaldehyde and \leq 229.4 kcal/mol for protonated propionaldehyde, both appear to be within 2 kcal/mol of their known literature values (see ref 13).

(15) Methylenimine has been the subject of several previous theoretical investigations: (a) J. M. Lehn, B. Munsch, and P. Millie, *Theor. Chim. Acta*, **12**, 91 (1968); (b) J. M. Lehn, B. Munsch, and P. Millie, *Ibid.*, **16**, 351 (1970); (c) B. Levy, P. Millie, J. M. Lehn, and B. Munsch, *ibid.*, **18**, 143 (1970); (d) E. Kochanski, J. M. Lehn, and B. Levy, *ibid.*, **22**, 111 (1971); (e) J. Vinh, B. Levy, and P. Millie, *Mol. Phys.*, **21**, 345 (1971); (f) L. Radom, W. J. Hehre, and J. A. Pople, J. Am. Chem. Soc., **93**, 289 (1971); (g) R. Ditchfield and J. E. Del Bene, *ibid.*, **94**, 703 (1972); (h) P. Botschwina, *Chem. Phys. Lett.*, **29**, 580 (1974); (i) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle,

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and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974); (j) S. Wolf, H. B. Schlegel, and M. H. Whangbo, *Can. J. Chem.*, **54**, 795 (1976).

- (16) Calculations have been performed at the split-valence-shell 4-31G level¹⁷ of single determinant ab initio molecular orbital theory and using the Gaussian 70 series of computer programs.¹⁸ Equilibrium geometries have been optimized.
- (17) R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 54, 724 (1971).
- (18) W. J. Hehre, W. A. Lathen, M. D. Newton, R. Ditchfield, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
- Indiana University, Bloomington, Ind.
 ΔE values have been corrected for zero point vibrational energy. Experimental frequencies from T. Shimanouchi, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 39 (1972); except methylenimine, from ref 2d.
- (20) Heats of formation (at 300 K) from S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley-Interscience, New York, N.Y., 1976.

Solid State Chemistry of Organic Polyvalent Iodine Compounds. 11. Topotactic Transformations of 2-Iodo-2'-chlorodibenzoyl Peroxide

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Single crystals of 2-iodo-2'-chlorodibenzoyl peroxide, Pa, undergo topotactic transformations to twinned single crystal phases of the corresponding benzoxiodole isomer, ISa, o-iodosobenzoic acid, IO, o-chloro- and o-iodobenzoic acids, BAa, c, and a novel triclinic phase, Xa. IR spectroscopic evidence and a two-dimensional analysis of 110 hol x-ray intensities from Xa (R = 0.12) suggest that Xa is comprised of intermolecularly coordinated benzoxiodole "bimolecular units" similar to those found in the known monoclinic structure of ISa. Despite the apparent similarities in the structures of ISa and Xa, it is clear that they are formed through two distinct topotactic pathways of rearrangement. The novel phase Xa is formed during *photolytic* (UV or x-ray wavelengths) decompositions of crystalline Pa while the monoclinic ISa structure is formed via a *thermal* pathway of rearrangement. Further prolonged exposure to x-rays results in the photochemical reduction of Xa to BAa and BAc. These two acids cocrystallize topotactically as a solid solution phase which has the same crystal structure as that of pure BAa.

Introduction

Despite their very similar crystal structures, peroxides Pa-c exhibit markedly different patterns of behavior



during solid state isomerization ($P \rightarrow IS$), hydrolysis (P,

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IS \rightarrow BA, IO), and consecutive photochemical reduction (IS \rightarrow BA).

These topotactic processes are considerably more complex for the unsymmetrical peroxides Pa, b than for the previously studied¹ symmetrical prototype Pc. Thus, topotactic isomerization of Pc under a variety of conditions was found to yield only the monoclinic crystal structure of ISc which also can be obtained independently by crystallization of ISc from solvents.² Although x rays accelerate the solid state isomerization of Pc, they do not alter the crystallographic aspects of the transformation. By contrast, the topotactic formation of the independently known crystal structures of ISa, b in single crystals of Pa, b in earlier studies was found to be accompanied by the joint formation of *novel* single crystal phases Xa, b whenever x-ray photography had been used to monitor the progress of the solid state transformation.¹

It is now clear that ISa, b and Xa, b are formed through distinct thermal and photochemical topotactic pathways of rearrangement: (a) under thermal conditions (room temperature $\rightarrow 85$ °C) in the absence of x rays, ISa, b are formed without Xa, b; (b) during continuous exposure to x rays, or more effectively by exposure to UV light, Pa, b are transformed to Xa, b with little if any contamination by ISa, b.³

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Structure	<i>a</i> , Å	b , A	<i>c</i> , Å	α , deg	β, deg	γ , deg	<i>V</i> , Å ³	Z	Space group
Pa	13.02	4.07	15.39	90	120.9	90	700	2	Pc
\mathbf{Pb}	12.96	4.12	15.38	90	121.2	90	700	2	Pc
Pc	13.02	4.22	15.43	90	121.1	90	726	2	Pc
ISa	7.403	13.88	13.12	90	102.1	90	1318	4	$P2_1/a$
ISc	4.09	30.75	22.47	90	93.3	90	2821	8	Cc
Xa	13.86	4.00	13.89	100	114	84	691	2	$P\overline{1}$
BAa	14.73	3.90	25.50	90	112.7	90	1352	8	C2/c
\mathbf{BAb}	14.82	4.10	25.90	90	118.3	90	1386	8	C2/c
BAc	4.32	15.08	11.29	90	91.5	90	735	4	$P2_1/c$
\mathbf{S}^{a}	14.99	4.06	26.41	90	119.0	90	1406	8	C2/c
· IO	12.89	4.10	14.05	90	96.7	90	737	4	$P2_1/c$

TABLE I: Crystal Data

 a S is the solid solution of BAa and BAc formed through topotactic reduction of Xa.

TABLE II: Topotactic Matrices

No. ^a	Φ_{11}	Φ_{12}	Φ ₁₃	Φ 21	Φ 22	Φ ₂₃	Φ 31	Φ_{32}	Φ_{33}	Φ
1	0	1.816	0	±0.667	0	±1.051	±0.971	-0.675	∓0.025	1.884
2	0	1.816	0	0	0	± 0.902	± 1.150	-0.675	± 0.499	1.884
3	0	1.816	0	± 0.306	0	± 1.008	± 1.114	-0.675	-0.721	1.884
4	0	1.816	0	± 1.323	0	± 0.408	Ŧ0.162	-0.675	Ŧ0.896	1.884
5	1.049	0.345	-0.018	0	0.982	0	0.173	-0.576	0.956	0.990
6	0	0	0.975	0	-0.996	0	2.071	0	0.067	2.010
7	0	0	0.958	0	-0.957	0	2.109	0	0.277	1.932
8a	1.148	0	0.596	0	-1.006	0.	0	0	-0.914	1.054
8b	1.148	0	0.400	0	1.006	• 0	0	0	0.914	1.054
.9a	0.706	0	0.970	0	1.006	0	-1.081	0	0	1.054
9b	0.473	0	0.970	0	-1.006	0	1.081	0	0	1.054
10	± 0.034	0.925	± 0.092	± 0.554	0	0	∓0.407	-0.027	∓1.095	0.560

^a Numbers refer to transformations described in the text according to: 1, $Pa \rightarrow ISa$ (major orientation, thermal); 2 and 3, $Pa \rightarrow ISa$ (minor orientations, thermal); 4, $Pa \rightarrow ISa$ (Xa present); 5, $Pa \rightarrow Xa$; 6, $Pa \rightarrow S$; 7, $Pa \rightarrow BAa$ (hydrolysis); 8, 9, $Pa \rightarrow IO$ (hydrolysis); 10, IO relative to ISa in Pa.

The formation and probable structure of Xa, b raise interesting questions concerning the mechanisms of the solid state rearrangements. In addition, these novel phases appear to influence the preferred modes of mutual phase alignment of ISa, b in Pa, b under conditions where both topotactic pathways of transformation are followed.

In this paper we shall concentrate on Pa; the behavior of Pb is complicated further by the existence and topotactic formation of an additional polymorph of Pb.

Further prolonged exposure to x rays brings about the consecutive topotactic reduction of the first-formed products, IS, X to the corresponding substituted benzoic acids, BA. Here again the crystallographic aspects of the topotaxy for ISc \rightarrow BAc were found to be relatively straightforward since the reduction of ISc gives only one (o-iodo) benzoic acid derivative. The previously reported⁴ behavior of the unsymmetrical peroxide Pf with regard to this sequential topotactic reduction process is an example in which reduction of the intermediate novel phase (Xf) yields two different halobenzoic acids, each of which crystallizes topotactically in its own crystal structure.

An analogous phase separation of the corresponding acid products BAa and BAc was expected during the consecutive topotactic reduction of Xa, for the (monoclinic) crystal structures of these acids are entirely different; the short 4-Å unit cell axis common to all of these halobenzoic acid crystal structures is the unique b symmetry axis only for the crystallographically isostructural derivatives BAa, b. Instead, BAa and BAc from Xa crystallize together as a *solid solution phase*, S, having an average structure similar to that of pure BAa (and BAb).

Competitive topotactic transformation of Pa to BAa and IO also occurs to a variable extent when the peroxide crystals are not protected from atmospheric moisture. It is of interest that the resulting crystal structure of "pure" BAa and the solid solution phase S can coexist without mixing in pseudomorphs which have been exposed to the variety of conditions which bring about the various competitive and sequential transformations of Pa.

A summary of the topotactic transformations of Pa which are described in this paper is presented in Figure 1.

Thermal Topotactic Isomerizations

The sole form of ISa which grows from solvents⁵ is formed topotactically in single crystals of Pa which have been allowed to decompose (~4 weeks at 24 °C) thermally in the absence of x rays. Three by three matrices Φ defining the experimentally observed angular relationship between the unit cell vectors (one by three column matrices) of the product, (B), and parent, (A), crystal structures, according to $(\vec{B}) = \Phi(\vec{A})$ for this and the other topotactic transformations described in this paper are presented in Table II. Despite the very similar crystal structures of Pa and Pc, ISa is not isostructural with ISc (Table I) and the high specificity of topotactic alignment in $Pc \rightarrow ISc$ does not obtain in $Pa \rightarrow ISa$. Four different topotactic modes of alignment of ISa are evident, but in each, the 7.4-Å a axis of ISa aligns with the unique symmetry axis b = 4.07 of Pa. This reflects the previously noted⁶ tendency for layered structures of these relatively flat molecules to align with a common direction of layer stacking, which in this case occurs in spite of the mismatch of the scalar lengths $(a_{ISa} - 2b_{Pa})/2b_{Pa} = -0.09$. Since the symmetry axes of the monoclinic parent and product are not aligned, conservative twinning accompanies each specific topotaxy.

The relative distribution (yield) of ISa among the four simultaneously present though distinct modes of alignment is approximately 20:2:1:1, as estimated from the relative intensities of their x-ray reflections. The predominant orientation (matrix 1 and Figure 2) includes a virtually parallel arrangement of the (010) planes (d(010) = 13.88 Å) of ISa and the (001) planes (d(001) = 13.20 Å) of Pa.



Figure 1. A summary of the topotactic transformations observed for Pa.

Two of the minor orientations are defined further through the relationships: (matrix 2) d(001) = 12.82 Å of ISa parallel to d(100) = 11.15 Å of Pa; (matrix 3) d(010) of ISa parallel to $d(\overline{1}04) = \frac{1}{4}(14.91$ Å) of Pa. Unlike the other relatively discrete modes of alignment, the fourth type is continuous over an angular range ($0^{\circ} < \theta < 14^{\circ}$) according to eq 1 with locally preferred alignments at $\theta = 0$ and $\sim 8^{\circ}$. The (010) planes of ISa are parallel to (100) planes (d(100)= 11.15 Å) of Pa for $\theta = 0^{\circ}$, and this appears to be but another minor orientation established relative to Pa. However, the other topotaxy (matrix 4 = matrix eq 1 with $\theta = 8.1^{\circ}$) is less readily understood in terms of the parent lattice Pa, but appears at least in part to be associated with other topotactic processes which are described below.

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In comparisons of the molecular arrangements in this and the other topotactic transformations, it is important to note the present uncertainty regarding the specific arrangement of the pseudosymmetrical molecules in the crystal structure of Pa.⁷ The ordered structure depicted in this paper has two molecules in a unit cell of space group Pc. However, least-squares refinements based on the h0lintensities (present only for l = even) suggest a disordered two-dimensional crystal structure in which a random selection of the peroxide molecules are rotated by 180° *in the plane* of the drawing of the figures.⁸ Comparable positional disorder (halogen interchange) in the unsymmetrical isomeric molecular structure of ISa is not expected, for heterocyclic trivalent chlorine compounds of this type are unknown.

The Novel Photochemical Phases Xa and Ua

The above course of topotactic isomerization of Pa is altered markedly by radiation of x-ray or UV wavelengths. During continuous exposure to x rays over a 2–3-day period at ~ 23 °C, a single crystal of Pa is smoothly transformed to a novel single crystal phase, Xa, which is not detectable in crystals of Pa which have transformed (thermally) to ISa in the absence of x rays. UV light effects the solid state photochemical transformation Pa \rightarrow Xa in \sim 15 h at 24 °C and results in material containing little if any of the crystalline products (ISa, IO, BAa) from the other competing topotactic pathways of decompositions. Since the infrared absorption spectrum of several UV-transformed pseudomorphs was very similar to the spectrum of ISa displayed by thermally transformed pseudomorphs of Pa, it appeared that rearrangement of Pa to benzoxiodole isomers, IS, also occurred under photochemical conditions of topotactic decomposition. The novel phase, however, could not be recovered from solvent recrystallizations of small batches of phototransformed pseudomorphs. The only crystalline benzoxiodole product obtained from the attempted recrystallizations of Xa had the usual monoclinic structure of ISa (hereafter referred to only as ISa). It thus seemed likely that Xa was a novel polymorph of ISa formed uniquely through solid state photochemical decomposition of Pa.





Figure 2. The preferred mode of topotactic alignment of ISa (right) in thermally isomerized crystals of Pa (left). The parallel axes, b_{Pa} and a_{ISa}, are perpendicular to the drawing.



Figure 3. The two-dimensional structure of Xa (right), derived from Fourier analysis of h0/diffraction data, is shown in the observed topotactic mode of alignment relative to Pa (left). The parallel b axes of both structures are perpendicular to the drawing.

A second *novel* photochemical phase, Ua, also is formed topotactically together with Xa. Although their crystal structures appear to be very similar, Ua in fact is formed only to a relatively minor extent in most pseudomorphs. We shall here concentrate on the predominant product Xa, and consider below its possible link with Ua.

In the majority of topotactic transformations studied to date, it is clear that crystal lattice restrictions on molecular mobility are relaxed sufficiently to allow the formation of the same arrangement of product molecules which obtains in their crystal structures grown from solvents, and it is accordingly difficult to evaluate the extent to which the preferred mode of mutual phase alignment reflects directionally specific mechanisms of molecular reorganization, a good geometrical match of the two lattices, or both. However, the exceptional transformations which yield novel crystal structures of products appear to be subject to a much higher degree of lattice control. Thus, in the transformation of $Pa \rightarrow Xa$, (matrix 5) it would appear that the unit cell parameters of Xa (Table I) have been established in close accord with the cell parameters of the parent Pa lattice. Unlike the monoclinic ISa which has no lattice translation shorter than a = 7.4 Å, triclinic Xa has a short 4-Å repeat, b, which aligns strictly parallel to the 4-Å b axis of the parent Pa. Moreover, its essentially identical a and c axes (13.9 Å) are generated near to the a (13.00 Å) and c (15.38 Å) peroxide axes (6° between a's and 13° between c's), such that (001) of Xa (d(001) = 12.5Å) and (001) of Pa (d(001) = 13.2 Å) are virtually parallel. This imposed template effect raised the interesting possibility that a close correspondence exists between the arrangements of halobenzoate groups in the initial and final mutually oriented phases. Efforts therefore were directed toward the determination of the crystal structure of Xa.

Although many h1l reflections have been observed, only a two-dimensional analysis of the structure in projection down its short lattice repeat was undertaken. Patterson and Fourier analyses have led to a plausible structural interpretation of the observed h0l structure factors. The arrangement of halobenzoate groups about an assumed inversion center for space group $P\bar{1}$ suggests mutual intermolecular I--O coordination to form "dimers" analogous to those observed in ISa, and all other derivatives of the general type IS which have been examined in this series.⁵ Here, as in all ortho-substituted derivatives ISa-d, an unusual molecular conformation in which the ortho monovalent halogen and the carbonyl oxygen atom (O(18)) are disposed in a *transoid* conformation about the C(16)-C(17) bond has been adopted in order to allow "dimer" formation.

The topotactic alignment of the *idealized* crystal structures of Pa and Xa is shown in Figure 3, where it is apparent that half of the halobenzoate groups of Pa necessarily have "flipped" over (rotations through $\sim 180^{\circ}$ about an axis parallel to the plane of the drawing) to form the *transoid* "dimers" of Xa, contrary to our early expectation that the novel formation of Xa represented a "minimum motion" topotactic rearrangement not requiring the remarkable flipping between closely stacked layers of peroxide molecules. "Dimer" formation thus appears to be ubiquitous in these topotactic isomerizations.

Sequential Topotaxy. Photochemical Reduction of Xa

Sequential topotactic transformations were first observed in Pc, wherein the initially formed ISc is slowly transformed to the *known* single crystal structure of *o*iodobenzoic acid, BAc^9 (Table I). It was early thought¹ that BAc resulted only from hydrolysis of Pc and ISc, even though the other product of hydrolysis, IO, was not observed as an ordered phase in the final pseudomorph. We have since come to expect the crystallization of IO whenever it is formed through hydrolysis of the heterocyclic benzoxiodole group of these structures, a process which in fact can be prevented completely only through careful exclusion of moisture.

Solid state photochemical reduction of the trivalent iodine group to BAc, the other common fate of the heterocyclic ring, has been well established through studies of the topotactic transformations of O-alkyl derivatives of IO,¹⁰ and undoubtedly it also occurs, albeit at a much slower rate, in crystals of the O-acyl derivatives, IS. In some cases, e.g., Pa and Pb, the stoichiometry of the topotactic reductions is further masked by the variable crystallographic forms which BAa may assume. Except for this interesting variation, the sequential photochemical topotactic behavior of Pa is similar to that reported for Pf,⁴ wherein the initially formed novel phase is slowly reduced in the x-ray beam to the benzoic acid derivatives BAc and BAf. Despite their different patterns of phenyl substitution, these two acids have similar crystal structures which are mutually aligned, though distinct, in the final pseudomorph.

The slow photochemical reduction of Xa in the x-ray beam gives rise to a new single-crystal phase, S, whose diffraction spacings and intensities closely resemble those of o-bromobenzoic acid, BAb:¹¹ There is no evidence for the formation of the conventional crystal structure of BAc. Typically, the time scale for the topotactic sequence of photochemical events observed during continuous x-ray photography of a fresh crystal of Pa is as follows: after 15 h, mostly Pa, but prominent Xa reflections; 50 h, essentially only reflections of Xa; 70 h, faint reflections from S begin to appear; 380 h, Xa and S equally present; 480 h, essentially only the relatively broad single crystal reflections of S.

The crystal structure of o-chlorobenzoic acid,¹² BAa, which was expected on chemical grounds, has the same space group and modes of molecular packing as BAb, but slightly shorter unit cell axes; corresponding hol reflections of the two structures at low θ values have similar relative intensities, with the obvious exceptions of the very weak 400 and 408 of BAa. Qualitatively, their diffraction patterns are most readily distinguished by virtue of the 6° difference in the monoclinic angle, β (Table I); however, this difference is obscured somewhat in the horizontally broadened reflections of S on hol Weissenberg photographs. Therefore, in order to facilitate further comparisons, and to obtain calibrated cell constants for S (Table I), a film was multiply exposed to diffraction from S and an authentic single crystal of BAb.

The observed and calculated 2θ values are presented in Table III together with the corresponding values calculated for BAa and BAb. The calculated unit cell volume (1406 \pm 10 Å³) of S is virtually the average of the crystal volumes independently occupied by eight molecules of BAa (1352 Å³) and BAc (1470 Å³), and we therefore have concluded that S is a substitution solid solution of BAc in the crystal structure of BAa.

The 4-Å symmetry axis of monoclinic S is generated precisely in the direction previously defined by the aligned 4-Å axes of Pa and Xa; consequently (010) of S is parallel to (010) of the parent Pa, but not of Xa. The prior genesis of triclinic Xa introduces no new symmetry in the pseudomorph, and therefore the absence of conservative twinning of S is consistent¹³ with specific topotaxy established relative to either Pa (matrix 6: (001) of S parallel to (100) of Pa and (100) of S nearly parallel to (001) of Pa) or Xa. Indeed it is probable that both serve to orient S, whose large mosaic spread from the above, locally preferred orientation includes a significant amount of ordering with (001) of Xa parallel to (100) of S.

There is no doubt that the bulk of S crystallizes during the decomposition of Xa, well after the disappearance of Pa. However, variable, though usually very minor amounts of the oriented crystal structure of "pure" BAa (and IO) are also observed early in the series of photochemical transformations, due to competing hydrolyses by atmospheric moisture (described below). Therefore the orienting influence of Pa on S probably is exerted indirectly through the oriented structure of BAa.

It is of considerable interest that o-chlorobenzoic acid in these pseudomorphs may be simultaneously present both in its "pure" form BAa, and in solid solution with BAc, in S, without a uniform continuum of phases of intermediate BAc composition.¹⁴ Typically, the amount of S predominates over BAa by a factor of ~20 in the completely reduced pseudomorphs. Qualitatively the two phases appear to be discrete, as evidenced by the sharp differences in corresponding 2θ values observed on Weissenberg films, especially obvious for the three strongest h0l reflections of BAa: $40\overline{10}$, 600, $40\overline{4}$. It would appear therefore that the composition of S is fixed by the stoichiometry of the photochemical reduction, and that solid state mixing of the two phases, if it occurs at all, is a slow process. The minor phase Ua also is reduced under these conditions.

Topotactic Hydrolysis

This usually bothersome side reaction was promoted by storing fresh crystals of Pa in air saturated with water vapor at room temperature for varying time intervals. The susceptibility to solid state hydrolysis is much less in the (group A) peroxides Pa-c, than in the (group B) structures Pd-g, which under these conditions yield IO, and in some cases also the corresponding acid, BA, as the only topotactic products. These humid conditions serve only to increase the relative amounts of hydrolysis products in the group A peroxides. Thermal topotactic isomerization still competes effectively, and in the case of Pa, after 16 days the total amount of ISa distributed over the above described orientations is approximately equal to the amount of oriented IO and BAa. A discrete parent phase Pa was still present after this time, but the photochemical phases Xa and Ua were absent. At no time have we observed the topotactic crystallization of the conventional crystal structure of BAc. Our continuing studies suggest that crystalline ISa is hydrolyzed at a slower rate than Pa, at least in its presumably less defective forms grown from solvents, and therefore IO and BAa probably arise primarily from peroxide hydrolysis.

Weissenberg hol photographs of the partially hydrolyzed crystals display the complicated pattern of ten simultaneously present single crystal phases: ISa (4 orientations), BAa (1), IO (4), and Pa. Calibrated measurements of 2θ values using the sharp reflections of Pa as an internal standard suggest unit cell parameters for BAa which differ only slightly from the values determined using solventgrown crystals. However, some distortion of its structure is implied by the slight though characteristic "arcing" of its horizontally broadened reflections toward higher 2θ values. It is likely that this "pure" BAa also contains o-iodobenzoic acid, BAc, from peroxide hydrolysis, in low and continuously variable concentrations. There is no evidence of the clearly distinguishable reflections of the solid solution phase S, which probably contains much higher concentrations of BAc. We have assumed the independently known cell parameters of BAa in deriving the topotactic matrix (no. 7) of "pure" BAa relative to Pa. The close similarity in the orientation and packing of halobenzoate groups in the topotactically aligned structures of Pa and BAa (see ref 1 for molecular comparisons in the closely related topotaxy of $Pb \rightarrow BAb$) requires no further comment.

The four observed orientations of IO, formed in the relative amounts 15:7:5:1, define different specific topotaxies relative to Pa (matrices 8a, 8b, 9a, and 9b). All are established such that the 4-Å symmetry axes of parent and product are either parallel or antiparallel. The observed lattice parameters of all four members are identical within experimental error to the parameters independently determined from solvent-grown crystals.¹⁶ Solid solutions of any of the other products in the entirely different crystal structure of IO therefore appear not to be formed topo-tactically to any appreciable extent.

The matrices are grouped pairwise since orientations 8b and 9b are related to 8a and 9a respectively through the commonly observed⁶ (100) twinning of IO. The predominant orientation 8, in which the (100) planes of Pa and IO are parallel, is essentially the only mode of to-



Figure 4. The observed topotactic alignment of ISc and Pc. The parallel axes, a ISa and b Pc, are perpendicular to the drawing.

potactic alignment of IO in hydrolyzed crystals of Pc and all of the group B peroxides. (The molecular aspects of this common mode have been presented in several earlier papers.)

The topotaxies of orientations 9 include the parallel alignment of (100) of IO (d = 12.80 Å) and (001) of Pa (d= 13.20 Å); however, since this mode of alignment has not been observed in hydrolyses of the other peroxide structures, it is of interest briefly to consider other possible lattice templates within the pseudomorph which also might serve to orient this IO. As described above, the (010)planes of the predominant orientation of ISa (Φ_1) also are generated nearly parallel (1.5° divergence) to (001) of Pa and therefore they are at the same time parallel to (001)of IO in the partially hydrolyzed pseudomorphs. The two matrices relating 9a and 9b to ISa, which are readily obtained by appropriate matrix multiplications, essentially differ only in the signs of the first and third columns (matrices 10). Thus although 9a and 9b represent different specific topotaxies with respect to the parent lattice Pa, they define two symmetry equivalent modes of alignment relative to ISa. However, the amounts of oriented IO in 9a and 9b clearly are not equal, an equality which would be expected if the topotaxy were established at numerous nucleation sites, solely relative to ISa (conservative twinning). Independent solid state hydrolyses of single crystals of ISa grown from solvents are under investigation in order to determine if matrix 10 represents a preferred alignment of IO relative to ISa.

Thermal Vs. Photochemical Topotactic Pathways in Pa

In considering possible origins of distinct photochemical and thermal pathways for topotactic rearrangement in crystalline Pa, it is useful to recall the behavior of Pc (Figure 4) and its failure to form a corresponding novel photochemical phase. Since the disordered crystal structure of Pa on the average closely resembles that of Pc, their different behaviors presumably reflect the fundamentally different chemical reactivities of the two halobenzoate groups of Pa, vis a vis their chemical equivalence in Pc. This difference however would not necessarily have crystallographic consequences if an *intra*molecular mechanism of isomerization obtains, since only one *o*-iodobenzoate group becomes oxidized to the trivalent iodine moiety of IS. On the other hand, an intermolecular mechanism of rearrangement could result in a mixture of molecular ISa and ISc in crystals of Pa, while in the symmetric structure of Pc, only ISc could be formed. Xa accordingly could be a solid solution phase of ISa and ISc which uniquely is formed and stabilized through topotactic alignment on its parent structure Pa. Comparisons of the "molecular volumes" (unit cell volume + molecules per cell) of Xa (346 Å³), ISa (330), ISb (336 α form; 344 β form), and ISc (353 α form; 347 β form) lend some support to this notion.

By contrast, the *thermal* topotactic formation of ISa is comparatively uncomplicated. Molecular integrity apparently is maintained with no scrambling of halobenzoate groups during the solid state process. The observed unit cell parameters for orientations 1–4 are identical within experimental error to the independently known parameters, and there is no other compelling evidence for the formation of solid solutions.

It is thus possible that solid state peroxide rearrangement occurs via an intramolecular mechanism under thermal conditions, and via an intermolecular mechanism under photochemical conditions of decomposition. Comparisons of the observed relative molecular arrangements which result from the two topotactic pathways of rearrangement in Pa (Figures 2 and 3) indicate that both transformations require cleavage of the peroxide bonds, the formation of new bonds between iodine and oxygen atoms, and "flipping" of half of the halobenzoate groups. It is this last feature and possibly its sequence in the mechanisms of phase isomerization which represents a major difference in the modes of alignment of product molecules relative to Pa. None of the iodobenzoate groups of Pa which become the heterocyclic trivalent iodobenzoate groups of Xa have "flipped over", while the (thermal) formation of ISa results in an equal number of "flipped and unflipped" heterocyclic rings.

This difference may reflect specific constraints on "flipping" of some halobenzoate groups, perhaps imposed through geometrical changes associated with the prior formation of some type of photoexcited complex. Accordingly, the crystallographically identical behavior of Pc under photochemical and thermal conditions of isomerization may simply be a consequence of the chemical equivalence of its halobenzoate groups, any one of which may remain monovalent, become trivalent, flip or not flip to form only ISc during either *intra*- or *inter*molecular

ΤA	BLE	III:	Obser	ved an	d Calcu	lated	Values	of
2θ	(h0l)	for §	S, BAa,	BAb,	Ua, and	l Xa		

		20	S	BAa	BAb
h	l	(obsd)	(calcd)	(calcd)	(calcd)
4	$^{-4}$	24.0	23.9	24.7	24.2
4	0	27.1	27.2	26.2	27.3
4	-8	29.6	29.7	31.6	30.3
0	8	31.0	31.0	30.4	31.4
-2	10	34.4	34.4	35.2	35.0
4	-10	35.0	35.0	37.2	35.8
6	4	36.1	36.2	36.6	36.6
6	0	41.3	41.3	39.8	41.5
4	6	44.1	44.1	41.3	44.3
8	-4	49.9	49.9	49. 8	50.4
8	-10	50.4	50.3	52.9	51.1
			2	θ	
				Ua	Xa
h	l	Obsd		(calcd)	(calcd)
2	- 2	16.1		16.3	15.4
1	- 3	20.6		20.7	19.5
0	3	21.7		22.0	21.3
3	1	23.9		23.9	24.9
4	0	27.2		27.3	28.3
1	-4	27.8		27.9	26.4
2	-4	27.9		28.0	26.2
5	-1	32.3		32.5	33.3
3	3	35.0		35.0	35.9
1	5	40.0		40.1	39.9
4	3	40.9		40.9	42.3
3	4	41.6		41.6	42.4
4	-6	44.1		44.1	41.1
0	6	45.1		44.9	43.3
7	-2	45.8		45.7	46.5
5	-6	46.7		46.7	43.7
4	4	47.7		47.3	48.5

^a All values are given in degrees. The estimated error of measurement is $\pm 0.1^{\circ}$.

phase isomerization. We would expect the ratio of products ISa:ISc from an *inter*molecular mechanism of recombination of halobenzoate groups in Pa to depend on the extent of short-range order in the disordered parent crystal. To a first approximation, ISc would constitute one-third of the intermolecularly formed benzoxiodoles in a randomly disordered arrangement of molecular Pa in the idealized (space group Pc) crystal structure. Intermolecular chemical reactions between fortuitously adjacent chlorobenzoate groups in this sense would be unproductive.

Of interest in this connection is the growth of transparent whiskers on the surfaces of some photodecomposed crystals of Pa. There are no discernable reflections from the tiny whiskers among the single crystal reflections of Xa. Although slightly larger crystals of the volatile whiskers were obtained by sublimation they also could not be well characterized by single crystal methods. Preliminary chemical and spectroscopic evidence suggests that the whiskers are a mixture of BAa and o-chloroperoxybenzoic acid.

Variations in the initial packing disorder may be reponsible for the variations occasionally observed in decomposition of different crystals of Pa. The most commonly observed variation¹⁷ pertains to the formation of the two novel phases Xa and Ua. Undoubtedly the two structures are closely related, for their corresponding h0lreflections have very similar relative intensities and comparable spacings; moreover, both phases are similarly aligned relative to the parent Pa. These factors combine to give a characteristic "split" appearance to reflections, which for most corresponding h and l indices, are measurable resolved in 2θ (Table III). The derived lattice constants for Ua are d(100) = 13.08 Å, d(100) = 12.11 Å, $\beta^* = 70.3^\circ$ (12.62, 12.52 Å, $\beta^* = 66.2^\circ$ respectively for Xa). The relative amounts of Ua and Xa range from the normally observed ratio of 1:20 to an extreme 2:1 ratio which was found in one crystal. This behavior is reminiscent of the joint formation of the solid solution phase S and "pure" BAa, and it is possible that both Xa and Ua are solid solutions which differ only in the relative concentrations of the components.

The formation and topotactic transformations of solid solutions of Pa and Pc, as well as the possible formation of solid solutions of ISa and ISc during crystallization of mixtures of the pure components are under investigation.

The Minor Topotactic Orientation of ISa in Pa

Attempts to reduce the mosaicity, and thus improve the quality of x-ray reflections of Xa, through alternate heating and cooling of photodecomposed pseudomorphs of Pa were unsuccessful; however, these annealing experiments provided insight into the topotaxy of the fourth orientation of ISa (matrix 4, vide supra) observed as a minor component during thermal isomerization of Pa. Fresh single crystals of Pa where phototransformed to pseudomorphs exhibiting the characteristic reflections of Xa and Ua, but none from ISa. When heated at 55 °C for 24 h, cooled to room temperature, and rephotographed, the pseudomorphs were found to contain, in addition to Xa and Ua, the topotactic orientation of ISa represented by matrix 4, but no detectable amounts of the other orientations. The amount of ordered ISa did not appear to increase after heating for an additional 72 h and it is probable that this ISa arose from small amounts of amorphous ISa, or undecomposed Pa in the pseudomorphs, but not from the crystalline Xa or Ua. The latter two phases are quite stable thermally; their single crystal structures in other photodecomposed pseudomorphs were essentially unchanged after storage for several days at 100-140 °C.

The topotactic alignments of ISa *relative to Xa* which are suggested by these observations may be derived from the matrix relationships between Pa and Xa (matrix 5) and between Pa and ISa (matrix 4). The (010) planes of ISa are parallel to the (100) planes of Xa (Figure 5), an alignment which differs by 90° from that which might have been expected ((001) of ISa parallel to (100) of Xa) on the basis of the apparent similarities in their crystal structures.

Experimental Section

A. General Methods. The synthesis and crystallization of Pa and ISa have been described in previous reports of the corresponding crystal structure determinations.^{2,7} Weissenberg, Laue, rotation, and precession x-ray photography (Cu Kα x rays: 1.54 Å; 45 kV, 14 mA) of crystals having dimensions in the range 0.05-0.15 mm were used to study the various topotactic transformations. For photographic purposes the crystals were mounted on glass fibers with Duco cement and continuously exposed to the ambient atmospheric conditions of the laboratory during exposure to x rays. The consecutive photochemical transformations $Pa \rightarrow Xa \rightarrow S$ were effected and studied under these same experimental conditions. The formation of Xa was also effected by UV light from a Fluorolight lamp (2537 Å) held 4 in. from several crystals of Pa spread out on a microscope slide and exposed to the ambient laboratory conditions. KBr disks of the UV decomposed crystals were used to measure the IR spectrum of Xa.

Since each of the topotactic transformations occurs slowly and continuously over a period of several hours, it was possible to obtain x-ray photographs of partially transformed crystals from which the mutual angular orientations of parent and product phases could be derived.



Figure 5. The topotactic alignment of Xa (right) and ISa (left) observed when ISa crystallizes in a pseudomorph containing Xa (and Ua) as the predominant oriented product phase from decomposition of Pa.

TABLE IV: Atomic Parameters for Xa^a

 Atom	x	<i>z</i>	Atom	x	Z	Atom	x	<i>z</i>	
 тт	0.120(2)	0.158(1)	C(6)	0.32(1)	0.35(1)	C(14)	-0.35(1)	0.08(1)	
ĈI	-0.092(3)	0.363(3)	$\mathbf{C}(7)$	0.37(1)	0.26(1)	C(15)	-0.28(1)	0.04(1)	
C(1)	0.21(1)	0.31(1)	O(8)	0.281(7)	0.164(6)	C(16)	-0.21(1)	0.14(1)	
C(2)	0.17(1)	0.40(1)	O(9)	0.439(7)	0.250(6)	C(17)	-0.11(1)	0.14(1)	
C(3)	0.23(1)	0.48(1)	C(11)	-0.18(1)	0.28(1)	O(18)	-0.076(7)	0.078(6)	
C(4)	0.35(1)	0.50(1)	C(12)	-0.28(1)	0.25(1)	O(19)	0.002(7)	0.193(6)	
C(5)	0.42(1)	0.45(1)	C(13)	-0.36(1)	0.17(1)				

^a Except for I which was found to have $\beta_{11} = 0.26(2)$, $\beta_{33} = 0.016(2)$, $\beta_{13} = 0.010(1)$ in the anisotropic temperature factor $\exp(-\Sigma \Sigma \beta_{ij}h_ih_j)$, and Cl which was found to have an isotropic B = 4.4 Å², the atoms were assigned a fixed isotropic B = 4.75 Å².

TABLE V: Observed and Calculated hol Structure Factors for Xa on the Absolute Scale

h	l	Fo	F _c	h	l	Fo		h	l	Fo	F _c	h	l	Fo	F _c
-1	4	159	-141	4	3	37	41	1	5	55	52	3	1	33	-42
-5	10	42	35	2	4	41	40	0	11	21	10	2	7	17	- 30
2	2	104	-87	-4	2	48	44	-4	9	34	27	1	3	33	- 34
-4	10	42	36	8	0	26	12	-7	6	40	35	-4	7	19	-16
-2	2	112	96	1	2	56	-46	2	5	49	46	-8	4	16	-10
-6	10	37	26	-2	7	32	31	0	4	64	- 68	- 5	7	18	-13
-2	4	91	-79	6	1	32	28	8	3	25	-25	2	0	32	- 36
0	3	98	-103	-3	8	27	33	5	0	53	-50	5	3	17	19
-6	2	69	- 56	-4	5	38	-31	6	2	39	31	-1	6	20	31
-6	8	46	-45	7	4	19	-10	3	8	25	-20	3	0	28	-27
4	Ō	84	-81	-2	6	36	-18	0	9	28	- 29	7	0	16	1
1	6	58	55	$-\frac{1}{4}$	1	44	-39	-6	5	44	47	0	7	16	15
0	$\overline{2}$	99	-79	7	3	21	-18	- 5	1	54	-51	2	6	16	15
-5	$\overline{4}$	69	70	-7	9	19	-15	0	10	23	-23	-2	1	29	31
- 3	2	91	91	9	0	19	14	-7	5	39	30	6	0	16	-16
-7	2	55	-58	8	- 3	24	-21	-9	6	27	25	5	2	16	11
-8	6	43	44	1	8	20	-21	-1	7	38	42	0	5	18	6
-1	1	102	93	-9	4	20	-11	3	8	22	- 20	-1	5	18	-14
-6	4	58	57	- 3	9	20	22	7	1	31	21	2	1	20	-17
3	4	58	51	-5	5	29	18	3	- 3	46	39	1	4	15	- 21
-4	6	58	-66	-2	5	34	-31	4	4	49	41	- 3	5	14	-12
1	0	97	100	-9	5	18	-13	-6	7	31	-17	-5	2	14	6
0	6	55	53	- 5	9	18	15	-6	1	39	- 33	- 3	3	13	$^{-1}$
-3	6	56	-58	- 3	7	25	-24	-1	8	28	31	-1	2	14	-15
-2	8	41	45	3	2	32	- 30	- 5	8	28	-21	-2	3	10	16
-5	6	50	-48	-7	3	22	-32	0	1	64	45	1	1	8	5
4	4	46	45	-4	3	31	30	-1	3	55	- 58				
-7	8	34	-34	. 7	2	17	15	-7	4	33	31				

The corresponding topotactic matrices express the observed average relative orientations as obtained by angular measurements from the center or maximum of the parent and product single crystal reflections. Typically, the approximate angular (ω) widths of the reflections on Weissenberg films (originally h0l of Pa) are 1.5° for Pa, 2° for ISa, 4° for Xa, 4° for IO, and 14° for S.

The relative amounts of a particular product crystallizing in more than one orientation were estimated by comparing several intensities of reflections from the various orientations. Through similar comparisons it is possible to obtain a crude estimate of the "yield" of a topotactic transformation (i.e., the relative amount of crystalline oriented product formed from the starting quantity of parent crystal) when the structure factor amplitudes of both phases are known. Thus, the isomeric Pa and Xa have essentially equal unit cell volumes and $F_c^2(202)_{\rm Pe} \simeq$ $F_{c}^{2}(202)_{Xa}$. (These reflections are nearly coincident in space.) It was found that the intensity of the (202) reflections of Xa shortly after the disappearance of the peroxide reflections was 60% of the original intensity of the (202) reflection of Pa. Other comparisons suggest a similar "vield".

Unit cell parameters of the various product phases were obtained through least-squares analyses of several values of 2θ measured from Weissenberg films. Except for the 2θ values of S which were calibrated relative to a superimposed pattern of o-bromobenzoic acid, the 2θ values for the other product phases were calibrated relative to those for the parent Pa reflections.

Although a microscopic study of the transforming crystals was not undertaken, a few qualitative observations were made. The original crystal shape is maintained throughout the various transformations, with the exception of the UV-induced formation of Xa which results in the growth of whiskers having no specific orientation relative to the parent crystal. In all cases, the originally clear colorless crystals gradually become opaque, while remaining colorless, during the initial several hours of exposure to the various conditions for transformation.

B. Structural Studies of Xa. The lattice parameters a^* , c^* , and β^* were determined from a least-squares analysis of 26 values of 2θ measured from Al-calibrated h0lWeissenberg photographs. Although the initial 2/mdiffraction symmetry of Pa is retained in crystals which have transformed to Xa, it is clear from h1l photographs that Xa is in fact triclinic and conservatively twinned about (010) of Pa. Similar least-squares analyses of Υ values from several h1l reflections were used to obtain the other triclinic cell parameters. These upper level reflections are quite diffuse however and the derived cell constants are not well determined. (The better defined values of a^* , c^* , and β^* from hol data were not allowed to vary in the latter analyses.)

In view of the limited and very low quality intensity data available from h1l photographs, the structure was examined only in (010) projection. The intensities of 110 observable reflections $(2\theta_{\text{max}} \sim 84^{\circ})$ on multiple-pack Weissenberg films were visually estimated by comparisons with a standard scale. Successive Fourier maps assuming space group $P\overline{1}$ (R = 0.37, I only; R = 0.31, I and Cl) contained peaks consistent with the 20 atoms of the benzoxiodole isomer (R = 0.24). The derived molecular arrangement about space group inversion centers is strongly suggestive of the bimolecular units found in nearly all crystal structures of compounds IS.

Least-squares refinements of all x and z coordinates, anisotropic thermal parameters for I, and isotropic B for Cl (the other atoms were assigned a fixed value of B = 4.75Å²) gave R = 0.12 (Tables IV and V). Further refinements with more variables were not pursued because of the limited quality and quantity of the intensity data. (Although refinements of the site occupancy factor for Cl gave values somewhat larger than unity, the estimated error is large and we place no reliance on this possible indication of the presence of molecular ISc in Xa.)

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References and Notes

- (1) J. Z. Gougoutas, Pure Appl. Chem., 27, 305 (1971).
- J. Z. Gougoutas and J. C. Clardy, J. Solid State Chem., 4, 230 (1972). (3) In order to eliminate possible variations in behavior due to crystal sampling, one single crystal was cleaved and the two halves were transformed independently. The UV-irradiated half gave only Xa while the thermally isomerized part gave only the conventional monoclinic cystal structure of ISa.
- J. Z. Gougoutas and L. Lessinger, J. Solid State Chem., 12, 51 (1975).
 J. Z. Gougoutas and D. G. Naae, J. Solid State Chem., 16, 271 (1976).
- J. Z. Gougoutas, K. H. Chang, and M. C. Etter, J. Solid State Chem., (6)
- 16, 283 (1976). (7) J. Z. Gougoutas and J. C. Clardy, Acta Crystallogr., Sect. B, 26, 1999 (1970).
- The p-chloroiodo-, dichloro-, dibromo-, and bromochlorobenzenes (8) form an isomorphous series of crystal structures having similar halogen disorder for the unsymmetrical molecular structures. D. Britton, Acta disorder for the unsymmetrical molecular structures. D. Britton, Acta Crystallogr., Sect. B, 32, 976 (1976).
 (9) J. Z. Gougoutas, Cryst. Struct. Commun., in press.
 (10) M. C. Etter, J. Am. Chem. Soc., 98, 5331 (1976).
 (11) G. Ferguson and G. A. Sim, Acta Crystallogr., 15, 346 (1962).
 (12) G. Ferguson and G. A. Sim, Acta Crystallogr., 14, 1262 (1961).
 (13) J. Z. Gougoutas, J. Am. Chem. Soc., 99, 127 (1977).
 (14) The variation of unit cell parameters of BAa with increasing BAc composition has not heap examined. Continuous solid solution

- composition has not been examined. Continuous solid solution formation between BAa and BAc seems unlikely in view of their different crystal structures. However, a solubility discontinuity is not apparent in their published¹⁵ phase diagram. H. Lettre and P. Lehmann, *Berichte*, **71**, 416 (1938). E. Shefter and W. Wolf, *J. Pharm. Sci.*, **54**, 104 (1965). Some early observations¹ on the behavior of Pa are relevant to this
- (15)
- (16)
- (17) point. Although x-ray decompositions of some crystals of Pa gave primarily Xa, the characteristic single crystal pattern of the acicular form of ISc also was evident in Weissenberg photographs of the rearranged pseudomorphs. Other "abnormal" crystals decomposed to Xa and a phase similar to ISc.