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Solid State Chemistry of Organic Polyvalent Iodine Compounds
II. The Crystal Structure of 2-Iodo-3′-chlorodibenzoyl Peroxide

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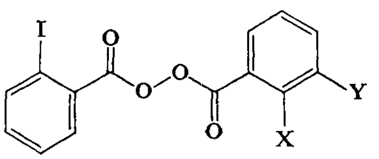
The monoclinic crystal structures of 2-iododibenzoyl peroxide derivatives which undergo topotactic solid state transformations have very similar b as well as c axial lengths. The structures accordingly are composed of similarly packed molecular layers parallel to their respective (100) planes. However, they differ through the manner in which these layers are stacked to form the three dimensional structures. *Translational* stacking in the **a** direction characterizes one group (A) of peroxides, all of whose members are transformed to single crystals of the corresponding benzoxiodole isomers. The previously reported structure of bis-(orthoiodobenzoyl) peroxide belongs to this group. The second group (B) of peroxide structures, exemplified by the here-described 2-iodo-3′-chlorodibenzoyl peroxide structure, ($C_{14}H_8ClIO_4$; $a = 22.28$, $b = 4.06$, $c = 15.38$ Å, $\beta = 94.5°$, $P2_1/c$, $Z = 4$), is characterized by an alternate stacking of the layers through inversion centers. The a axial lengths of group A structures accordingly are approximately half those of group B structures. Instead of isomerizing, at ~22°C the latter are usually hydrolyzed to single crystal phases of "orthoiodosobenzoic acid." Considerations of close interlayer iodine–oxygen and iodine–halogen distances suggest that group B structures are predisposed toward other intermolecular reactions and cannot readily form the crystal structures of their isomeric benzoxiodole phases.

The oxygen–oxygen bond (1.46 Å) in 2-iodo-3′-chlorodibenzoyl peroxide is coplanar with each of the carbonyl groups and the dihedral angle of the peroxide linkage is 117°. The dihedral angle between the two benzene planes is 5°.

Introduction

The 2-iododibenzoyl peroxide derivatives Ia–f undergo topotactic single-crystal phase transformations as a result of chemical isomerization and hydrolysis reactions (*1*).



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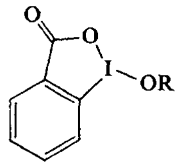

II

Group A		Group B		
X	Y	X	Y	R
(a) I	H	(d) F	H	(a) 3′-chlorobenzoyl
(b) Br	H	(e) H	H	(b) 2′-iodobenzoyl
(c) Cl	H	(f) H	Cl	(c) hydrogen
				(d) 2′-fluorobenzoyl

The uniformly monoclinic "reactant" peroxide crystal structures have a short (~4 Å) unique b axis and similar c axial lengths (~15.4 Å) which reflect their equivalent types of intermolecular packing contacts between c-glide related molecules. The structures differ however in the lengths of their a axes which generally fall in one of two groups. The previously reported peroxide structures Ia–c (*2*) comprise one group (A) having an a axial length approximately half that of the second group, (B) Id–f.

Whereas *topotactic isomerization* to the corresponding, independently known, benzoxiodole crystal structure (e.g., Ia → IIb) commonly is observed in solid state transformations of every one of the group A peroxides, it has been observed only in the case of Id of the group B peroxides. Members of the latter group at ~22°C appear to be particularly susceptible to hydrolysis by atmospheric moisture, and usually are transformed instead to single crystal phases of "orthoiodosobenzoic acid" (IIc, 1-hydroxy-3-oxo-3*H*, 2-1-benzoxiodole). We describe here the crystal

TABLE I

CRYSTAL DATA

Structure	a(Å)	b(Å)	c(Å)	β(°)	Space group	Z	Ref.
Ia	13.05	4.21	15.47	121.1	Pc	2	(*2*)
Ib	12.96	4.12	15.38	121.2	Pc	2	(*2*)
Ic	13.00	4.08	15.38	120.9	Pc	2	(*2*)
Id	21.41	4.20	15.46	93.7	$P2_1/c$	4	(*9*)
Ie	20.81	4.09	15.41	94.7	$P2_1/c$	4	(*1*)
If	22.28(1)	4.057(4)	15.38(1)	94.50(4)	$P2_1/c$	4	(*3*)
IIa-α	6.38	10.55	20.07	92.0	$P2_1/n$	4	(*3*)
IIa-β	5.06	13.04	10.34	99.5	Pc	2	(*3*)
IIb-α	4.21	30.86	22.52	93.3	Cc	8	(*11*)
IIb-β	8.03	12.58	13.74	91.6	$P2_1/c$	4	(*11*)
IId	4.07	12.00	26.27	90.5	$P2_1/c$	4	(*9*)

structure of If[1] as a representative of the closely analogous group B structures and examine possible reasons for the disparate solid state behavior of the two groups.

Experimental Methods

If was synthesized from commercially available 85% *m*-chloroperoxybenzoic acid and *o*-iodobenzoyl chloride. The latter (8 g) in three times its volume of diethyl ether was added to a stirred solution of the peracid (6 g) and sodium carbonate (10 g) in 150 ml of water at 0°C. The peroxide which had precipitated after stirring at 0°C for 2 hr was collected and washed with cold saturated sodium bicarbonate solution, water, and methanol. Further purification was effected by dissolving the solid in cold dichloromethane and reprecipitating with ice-cold methanol. Although the peroxide may be stored for extended periods in desiccators at 0°C without appreciable decomposition, fresh crystals were grown prior to each diffraction study by dissolving small batches of the peroxide in chloroform, carefully adding methanol without mixing, and allowing the mixture to stand at 0°C. Colorless needles elongated along the monoclinic *b* axis were obtained in a period of from 1 to 4 hr. The crystals melt with apparent decomposition at 95–97°C; upon further heating, the decomposition product or products resolidify and eventually melt in the vicinity of 190–200°C.

The unit cell parameters and space group (Table I), determined from calibrated Weissenberg photographs, together with the crystal density of 1.90 g/cm^3, measured by flotation in aqueous zinc chloride solution, indicated four molecules in general positions of the unit cell. Intensities from reciprocal lattice levels $h0l$, $h1l$, $h2l$, $hk0$, $0kl$, were recorded using the multiple film equi-inclination Weissenberg method (Cu$K\alpha$; $\lambda = 1.542$ Å). Since the peroxide decomposes under these conditions (exposed to the ~21°C atmosphere), a fresh specimen (typically 0.10 × 0.18 × 0.08 mm) was used to obtain each level of data. Exposure times, estimated so as to compromise between sufficient accumulation of intensity on the film and errors caused by crystal decomposition, ranged from 24 to 48 hr. The intensities were estimated through visual comparisons with a standard scale and assigned standard deviations in terms of the minimum observable intensity $I_{\min}$ as follows:

$$\sigma(I_{\text{obs}}) = (0.3)I_{\text{obs}} \text{ for } I_{\text{obs}} > (50)I_{\min},$$

$$\sigma(I_{\text{obs}}) = (0.2)I_{\text{obs}} \text{ for } (5)I_{\min} < I_{\text{obs}} \leqq (50)I_{\min},$$

$$\sigma(I_{\text{obs}}) = I_{\min} \text{ for } I_{\text{obs}} \leqq (5)I_{\min}.$$

Unobserved reflections were assigned an intensity equal to $I_{\min}/2$ and standard deviation equal to $I_{\min}$. Of the 3158 independent nonextinct reflections within the copper sphere of reflection, 2126 (67%) were recorded and estimated. Of these, 1452 (68%) were observed and 674 were unobserved. The intensities were corrected for the Lorentz and polarization factors and absorption corrections were applied using a

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[1] Abstracted from the PhD thesis of L.L. (*3*).

Gaussian quadrature numerical integration method (*4*).[2]

The data were merged to a common scale which was adjusted to the absolute scale using Wilson's method (*5*). Conventional Patterson and Fourier methods clearly revealed all of the carbon, oxygen, and halogen atomic positions, but no attempt was made to locate the hydrogen atoms. Two cycles of least squares refinements[3] of all coordinates and isotropic temperature factors reduced the value of R to 0.17. Several additional parameter refinements in which the halogen atom thermal parameters were allowed to vary anisotropically reduced R to its final value of 0.14[4]. No attempt was made to refine a completely anisotropic model. In the last cycle of refinement, the parameter shifts generally ranged from 0.01 to 0.05 of the standard deviations estimated from the least squares inverse matrix.

The final atomic coordinates and temperature factor parameters are given in Tables II and III.

TABLE II

FRACTIONAL ATOMIC COORDINATES FOR If[a]

Atom	x	y	z
I	0.04614(5)	0.1558(3)	0.33895(7)
C(1)	0.1034(7)	0.333(4)	0.439(1)
C(2)	0.0811(8)	0.360(4)	0.523(1)
C(3)	0.1207(9)	0.519(5)	0.591(1)
C(4)	0.1779(8)	0.617(4)	0.578(1)
C(5)	0.1980(7)	0.592(4)	0.499(1)
C(6)	0.1620(7)	0.453(4)	0.427(1)
C(7)	0.1864(8)	0.440(4)	0.341(1)
O(1)	0.1637(7)	0.565(4)	0.272(1)
O(2)	0.2413(7)	0.304(3)	0.348(1)
O(3)	0.2698(7)	0.325(3)	0.266(1)
O(4)	0.3364(7)	0.640(3)	0.343(1)
C(8)	0.3175(9)	0.505(5)	0.276(1)
C(9)	0.3483(8)	0.533(5)	0.193(1)
C(10)	0.4042(9)	0.677(4)	0.197(1)
C(11)	0.4337(8)	0.699(4)	0.121(1)
C(12)	0.4073(9)	0.588(4)	0.041(1)
C(13)	0.3501(10)	0.447(5)	0.039(1)
C(14)	0.3191(8)	0.406(4)	0.118(1)
Cl	0.5051(2)	0.866(1)	0.1232(4)

[a] Estimated errors in the final significant figures are given in parentheses.

The Molecular Structure of If

The mean C—C bond lengths and internal ring angles with root mean square deviations from the means are 1.41 ± 0.05 Å and 120 ± 2°, respectively, for the iodosubstituted benzene ring, and 1.40 ± 0.02 Å and 120 ± 3° for the chlorosubstituted benzene ring. The calculated C–I bond length of 2.05 ± 0.01 Å agrees with the average value described by Sutton (*7*). The calculated C–Cl bond length of 1.73 ± 0.02 Å which also has been found in the structure of the benzoxiodole isomer of If is in close agreement with the more precise value of 1.744 ± 0.005 Å observed in the crystal structure of *m*-chlorobenzoic acid.[5] The O–O peroxide bond length of 1.46 ± 0.02 Å is similar to that found in other covalent peroxides (*2*, *3*).

Several interesting aspects of the molecular conformation are conveniently described in terms of the least squares planes presented in Table IV. The steric crowding of the *ortho* iodine atom and the proximate carbonyl oxygen atom primarily is relieved through a rotation of the carboxyl group about the exocyclic C–C bond through approximately 53° relative to the plane of the benzene ring. However, the iodine and double bonded carbonyl oxygen atom still occur in a *cisoid* relationship with an I–O distance of 3.33 Å.[6] Corresponding rotations of the carboxyl group through 38 and 46° were found in the similarly *cisoid* molecular structure of Ia. By contrast, the other carboxyl group of If is rotated only 9° from the plane of its benzene

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[2] The accuracy of the structure factor amplitudes was heavily dependent on the accuracy with which the absorption corrections were made since the transmission factors ranged from 0.055 to 0.464.

[3] The function minimized by the least squares procedure was $\Sigma w(|F_{obs}|^2 - |F_{calc}|^2)^2$, where the weight $w = 1/[\sigma(|F_{obs}|^2)]^2$. Atomic scattering factors for I, Cl, C, and O were taken from the "International Tables for X-Ray Crystallography" (*6*).

[4] A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-02082 with the ASIS National Auxiliary Publication Service, c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. A copy may be secured by citing the document number and by remitting $11.60 for photocopies or $1.50 for microfiche. Advance payment is required. Make check or money order payable to Microfiche Publications.

[5] See the following papers in this series.

[6] Some interaction of the carboxyl group and adjacent iodine atom may be indicated by the apparent distortion from the expected planarity of the carbonyl carbon atom and the three atoms to which it is bonded (see Table A).

TABLE III

TEMPERATURE PARAMETERS

1. Anisotropic temperature factor parameters

The anisotropic temperature factor is expressed in the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. Estimated uncertainties in the final significant figures are given in parentheses.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	0.00286(2)	0.085(1)	0.00536(4)	−0.0006(3)	−0.00048(5)	−0.0015(4)
Cl	0.0033(1)	0.142(7)	0.0082(3)	−0.010(1)	0.0008(3)	−0.004(2)

2. Principal axis lengths and orientations of thermal ellipsoids

Values of $B_0 = 8\pi^2\bar{u}^2$, and $(\bar{u}^2)^{1/2}$, the root mean square amplitude of vibration (Å) along the principal axes of the anisotropic thermal ellipsoids are listed below. The direction cosines of the principal axes are given with respect to the monoclinic cell axes *a*, *b*, *c*.

Atom	B	$(\bar{u}^2)^{1/2}$	cos A	cos B	cos C
I	6.21	0.28	−0.8503	−0.0130	0.5911
	5.61	0.27	0.1177	−0.9790	0.1563
	4.55	0.24	0.5129	0.2031	0.7913
Cl	10.29	0.36	0.4293	−0.8895	0.1223
	7.67	0.31	−0.1720	0.0896	0.9915
	5.60	0.27	0.8866	0.4481	0.0446

3. Isotropic temperature factor parameters

The isotropic temperature factor is expressed in the form $T = \exp(-B\sin^2\theta/\lambda^2)$, where $B = 8\pi^2\bar{u}^2$ and has dimensions Å^2. Estimated uncertainties in the final significant figures are given in parentheses.

Atom	B	$(\bar{u}^2)^{1/2}$	Atom	B	$(\bar{u}^2)^{1/2}$
C(1)	4.4(3)	0.24	O(3)	7.2(3)	0.30
C(2)	5.4(3)	0.26	O(4)	8.6(4)	0.33
C(3)	6.5(4)	0.29	C(8)	6.2(4)	0.28
C(4)	5.7(4)	0.27	C(9)	5.6(4)	0.27
C(5)	5.1(3)	0.25	C(10)	6.0(4)	0.27
C(6)	4.6(3)	0.24	C(11)	5.9(4)	0.27
C(7)	5.7(4)	0.27	C(12)	6.6(4)	0.29
O(1)	9.3(4)	0.34	C(13)	7.2(4)	0.30
O(2)	7.5(3)	0.31	C(14)	6.1(4)	0.28

ring containing the nonobstructing *meta* chloro substituent. The chlorine atom and the carbonyl oxygen atom in that half of the molecule also occur in the *cisoid* relationship. The O–O bond is strictly coplanar with each of the two (C═O) carbonyl groups. The latter, however, are not coplanar and the C–O–O–C dihedral angle of the peroxide linkage is 117°. This represents the largest deviation from an orthogonal peroxide dihedral angle yet observed in dibenzoyl peroxide derivatives (*2*). The dihedral angle between the two benzene planes is 5°.

Figure 1 depicts two perspective views of the molecular conformation and some of the angular relationships of the least squares planes.

Molecular Crystal Packing

The molecular packing, viewed in projection down the short *b* axis, is shown in Fig. 2. With the interesting exception of the short I---I distance described below, all other intermolecular approach distances (Fig. 2 and Table V) correspond to normal van der Waals separations, after

TABLE IV

LEAST SQUARES PLANES IN If

	Dev. (Å)		Dev. (Å)
Plane: $0.353X - 0.903Y + 0.247Z = 1.064$[a]			
C(1)[b]	0.01	C(6)[b]	−0.01
C(2)[b]	0.01	C(7)	−0.06
C(3)[b]	−0.03	O(1)	−0.93
C(4)[b]	0.02	O(2)	0.89
C(5)[b]	0.00	I	−0.13
Plane: $0.527X - 0.811Y + 0.254Z = 2.965$[a]			
O(2)[b]	0.00	C(8)[b]	0.00
O(3)[b]	0.00	C(9)[b]	0.00
O(4)[b]	0.00		
Plane: $0.411X - 0.894Y + 0.176Z = 1.688$[a]			
O(3)	0.19	C(11)[b]	0.01
O(4)	−0.17	C(12)[b]	0.00
C(8)	−0.00	C(13)[b]	−0.02
C(9)[b]	−0.01	C(14)[b]	0.02
C(10)[b]	−0.01	Cl	0.07
Plane: $0.421X + 0.883Y + 0.206Z = 4.264$[a]			
C(6)[b]	0.01	O(2)[b]	0.01
C(7)[b]	−0.04	O(3)	0.14
O(1)[b]	0.01		

[a] Planes are defined in terms of the orthonormal axes, X, Y, Z which are directed along the crystallographic axes a, b, and c^*, respectively.

[b] These atoms were used to calculate the plane.

due allowance is made for the undetermined hydrogen atom positions.

Considered individually, the intermolecular approach distances define the initial proximity of reactive sites in the molecules. Collectively, they indicate the overall manner in which the structure is composed of molecular chains and layers. The packing differences between the two groups of peroxide crystal structures may be conveniently described in terms of the set of close packed[7] molecular layers in the structure of If which contains the crystal planes (400) and $(\bar{4}00)$. These layers are comprised of molecules related by the *b* lattice translations and the *c*-glide symmetry operations; they are polar both in and normal to the layer plane. In group B structures, the layers are stacked by screw axes and inversion centers with an interlayer distance of $(a/2) \sin \beta$ (11.105 Å in If). The *a* lattice translation is complete when three layers are stacked in this manner. The group A peroxide structures, which have essentially identical packing arrangements *within* layers of this type, by contrast, are defined by simple a *translational* stacking of the layers. Accordingly, group A structures have *a* axial lengths approximately half those of the group B structures (e.g., $a \sin \beta = 11.17$ Å for Ia).

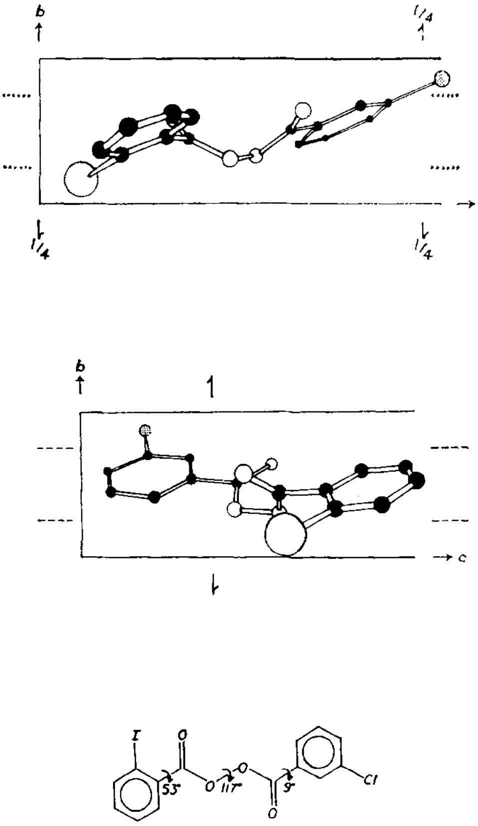

FIG. 1. (Top) The molecular conformation of If, viewed along the normal to the (001) plane. (Middle) The structure viewed along the normal to the (100) plane. (Bottom) Selected dihedral angles in If.

The short I---I distance (3.87 Å) occurs between adjacent layers related by the screw axes in the (100) planes. Very similar iodine–halogen interactions have been found in peroxides Ia (3.88 Å), Ie, and in Ib and Ic, where the contacts involve iodine with bromine and chlorine, respectively.[8]

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[7] Several sets of molecular layers which satisfy the principles of close packing theory (*8*) can be identified.

[8] Although the crystal structure analysis of *Id* is not complete, the unit cell constants and the general distribution of *h0l* intensities suggest a structure which is completely analogous to that of the closely related Ie and f structures (*9*).

TABLE V

INTERMOLECULAR APPROACH DISTANCES[a]

Atom a	Atom b	Pos.	Distance (Å)	Atom a	Atom b	Pos.	Distance (Å)
1. Short distances between atoms in molecules related by the *b* translation							
I	I	Q	4.06	O(1)	O(3)	Q	3.89
I	C(1)	J	3.85	O(2)	O(4)	J	3.44
I	C(2)	J	4.32	O(2)	C(8)	J	3.86
I	C(6)	J	4.01	O(3)	O(4)	J	3.33
I	C(7)	J	4.27	O(3)	C(8)	J	3.49
I	O(1)	J	3.76	O(3)	C(9)	J	3.87
C(1)	C(4)	J	3.90	O(4)	C(8)	Q	3.68
C(1)	C(5)	J	3.74	C(9)	C(14)	Q	3.77
C(1)	C(6)	J	3.81	C(9)	C(10)	J	3.69
C(2)	C(3)	J	3.66	C(10)	C(14)	Q	3.67
C(2)	C(4)	J	3.77	C(11)	C(12)	Q	3.84
C(3)	C(4)	J	3.89	C(11)	C(13)	Q	3.72
C(5)	C(6)	Q	3.73	C(11)	C(14)	Q	3.84
C(5)	O(2)	Q	3.88	C(11)	Cl	J	3.74
C(7)	O(2)	Q	3.71	C(12)	C(13)	Q	3.71
C(7)	O(1)	J	3.73	C(12)	Cl	J	3.81
O(1)	O(2)	Q	3.61				
2. Other short intermolecular approach distances							
I	C(3)	D	4.33	C(5)	C(14)	M	3.73
I	C(2)	K	4.23	C(5)	C(13)	G	3.88
I	C(2)	B	4.17	C(5)	C(14)	G	3.74
I	C(3)	B	4.16	O(2)	C(13)	M	3.81
I	I	C	3.87	O(4)	C(13)	M	3.84
C(2)	C(2)	B	3.80	O(4)	C(12)	G	3.50
C(3)	O(1)	M	3.72	O(4)	C(13)	G	3.45
C(3)	O(1)	G	3.33	O(4)	Cl	P	3.70
C(4)	O(3)	M	3.85	C(10)	Cl	P	3.53
C(4)	C(14)	M	3.80	C(12)	Cl	O	3.79
C(4)	O(1)	G	3.29	C(12)	Cl	E	3.98
C(4)	C(14)	G	3.70	Cl	Cl	E	3.93
3. Iodine–oxygen distances							
I	O(1)	A	3.33	I	O(3)	C	7.22
I	O(1)	J	3.76	I	O(3)	M	7.87
I	O(1)	C	4.86	I	O(4)	A	6.75
I	O(2)	J	5.55	I	O(4)	J	6.80
I	O(3)	A	5.24	I	O(4)	M	9.77
I	O(3)	J	6.19				

[a] Molecule A is closely approached by molecules B–Q. In the above, atom a is part of molecule A; atom b is in one of the molecular positions (Pos.) B–Q.

A: x, y, z
B: $-x, -y+1, -z+1$
C: $-x, y-1/2, -z+1/2$
D: $x, -y+1/2, z-1/2$
E: $-x+1, -y+2, -z$
F: $-x+1, y+1/2, -z+1/2$
G: $x, -y+3/2, z+1/2$
H: $-x, y+1/2, -z+1/2$
J: $x, y-1, z$
K: $-x, -y, -z+1$
M: $x, -y+1/2, z+1/2$
N: $x, -y+3/2, z-1/2$
O: $-x+1, -y+1, -z$
P: $-x+1, y-1/2, -z+1/2$
Q: $x, y+1, z$

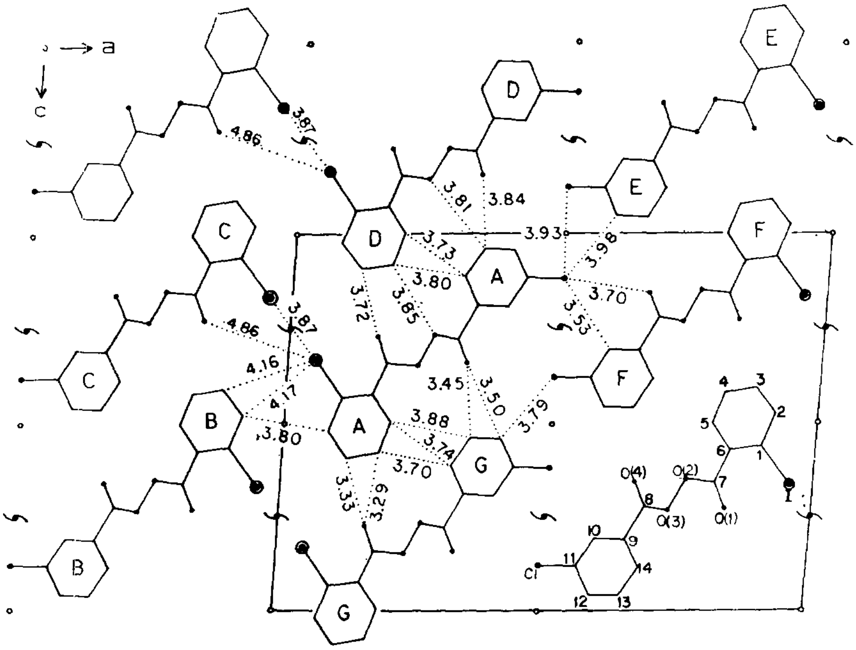

FIG. 2. The crystal structure of If, projected onto (010). The lettered molecules are related as A: x, y, z; B: $-x, 1-y, 1-z$; C: $-x, -1/2+y, 1/2-z$; D: $x, 1/2-y, -1/2+z$; E: $1-x, 2-y, -z$; F: $1-x, 1/2+y, 1/2-z$; G: $x, 3/2-y, 1/2+z$. The atomic numbering scheme is shown in the lower right molecule. The close intermolecular I---I and I---O approaches, considered further in Fig. 3, are shown between molecules A and C.

The interhalogen distances suggest a radius for iodine (1.93 Å) which lies at the lower end of the range of values (1.95–2.05 Å) suggested by Bondi (*10*) and some interaction of the iodines is indicated. Directionally invariant close contacts commonly occur in crystal structures containing coordinated *polyvalent* iodine atoms and it appears that ~1.6 Å is a more appropriate "intermolecular radius" for higher valence states of this halogen (*11*). In this connection, the crystal structure of the β polymorph of IIb (*12*) provides an interesting comparison. Instead of the common I---O coordination mode which obtains in the structure of IIb-α, the heterocyclic *trivalent* iodine atom in IIb-β is intermolecularly coordinated with the monovalent iodine atom across a distance of 3.70 Å. Further, the C—I---I angle is 143° in IIb-β, 139° in If, 120 and 173° in Ia. [The corresponding angle in the I---O coordination mode falls in the range 158 ± 4° (*11*).]

A possible role for this interhalogen interaction in the solid state transformations of the peroxides is considered below. It is particularly interesting to note that, in our studies, the only 2-iododibenzoyl peroxide derivative (2-iodo-4′-nitrodibenzoyl peroxide) which does not appear to undergo any type of topotactic transformation has an entirely different crystal structure with no comparable interhalogen interaction (*3*).

Chemical Consequences of the Differences in Peroxide Crystal Structures

Topotactic transformation to the corresponding isomeric benzoxiodole phases is a facile process in all of the group A crystal structures, while the occasional formation of small amounts of the single crystal phase of IIc, through hydrolysis by atmospheric moisture, by comparison, is slow. In group B crystal structures at ~22°C, both the relative rates and the overall yields of oriented crystalline products of these two competing processes appear to be reversed: the single crystal phase of IIc forms very readily in all structures of the group and, in the case of Ie and If, apparently to the complete exclusion of any crystalline phase of the corresponding benzoxiodole isomers.[9] These differences in part may be

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[9] The benzoxiodole isomers of Ie and If form isostructural crystals from a variety of solvents. IIc is the *only* crystalline product which has been observed in decompositions of crystalline Ie. The apparent absence of an isomeric benzoxiodole product phase in the case of If cannot be regarded as firmly established until the structure of an as yet unidentified intermediate phase

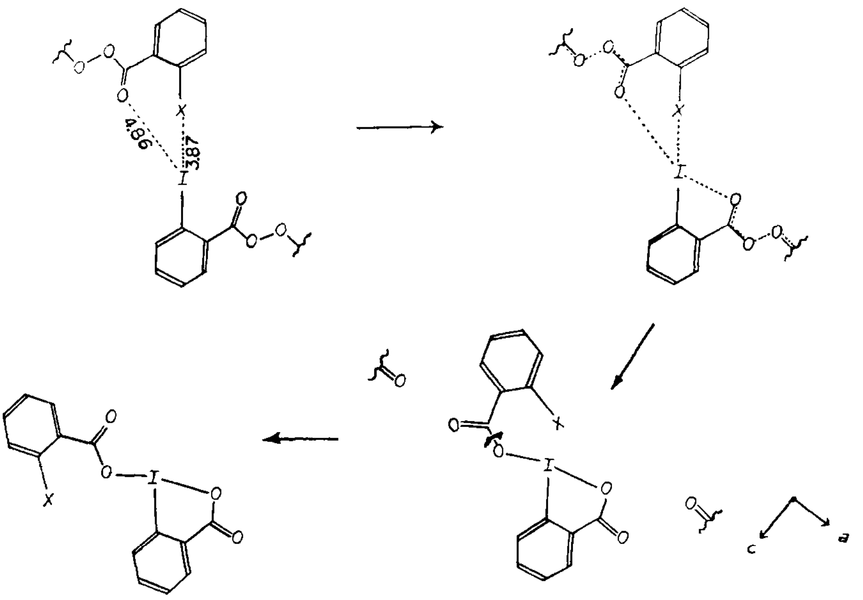

FIG. 3. A possible intermolecular bond redistribution scheme for the formation of benzoxiodole structures within the crystal structures of the peroxides. In group A peroxides, X is the other halogen atom while in group B peroxides, X is a symmetry related iodine atom. The initial arrangement of the two peroxide molecules (top) conforms with the observed crystal packing in Ia(*2*) and If (molecules A and C of Fig. 2), viewed in (010) projection. The indicated distances (Å) are essentially identical in Ia and If. As shown, a flip of one of the benzoate groups is necessary in order to arrive at the molecular conformation of product actually observed in the solid state transformations of Ia–Ic (*1*).

has been elucidated. While it does not appear to have any of the known structures of expected products (e.g., IIa-α and IIa-β), we cannot yet exclude the possibility that unusual conservative twinning (*13*) of some known phase is masking its identity.

attributed to the two types of molecular packing modes which characterize the two groups of structures.

In principle, both the 3′-chloro- and 2′-iodo-benzoxiodole molecular structures IIa and IIb can be formed from atomic constituents originally present within the crystal structure of If. Closure of the heterocyclic ring for both structures would require *intra*molecular bond formation between the iodine atom and either O(1) or O(2). In the case of IIa, the other (exocyclic) I–O bond may be formed *intra*molecularly between the iodine and either oxygen atom of the carboxyl group attached to the chlorosubstituted phenyl ring, or alternatively, through an *inter*molecular combination of these atoms. The nearest I---O approach (5.24 Å) (see Table 5) for this potential reaction path occurs *intra*molecularly and involves the oxygen atom O(3) of the peroxide linkage. Formation of the exocyclic I–O bond in the molecular structure IIb necessarily would require an *inter*molecular reaction in the crystal structure of If. Both of the close distances (3.76 and 4.86 Å) between atoms potentially involved in the formation of this bond for IIb are less than all *inter*molecular and *intra*molecular I–O distances considered for its formation for IIa. Thus, on the limited basis of initial static proximity of reactive sites, the crystal structure of If is predisposed towards the formation of molecular IIb rather than IIa.

The above, shortest *inter*molecular iodine–oxygen separation (3.76 Å) obtains between molecules related by the *b* translation and therefore is present in every one of the peroxide crystal structures Ia–f. However, its possible role in the formation of crystallographically ordered benzoxiodole structures clearly is admissible only in the case of the reactant crystal structure Ia.[10] The other, (4.86 Å) close *inter*molecular I---O approach occurs between an iodine of one molecule at *xyz* and O(1) of a

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[10] I–O bond formation across this distance obviously would yield IIb. Although several characteristic reflections of the X-ray spectrum of IIb have been tentatively identified in some decomposing crystals of the group A structure Ic, no fully authenticated example of such an intermolecular "crossing" resulting in an ordered product phase has emerged from our studies.

second molecule at $-x$, $y-1/2$, $1/2-z$, (molecules A and C, respectively, in Fig. 2) and therefore merits additional consideration since the close I---I contact also occurs between these same two molecules. Again, closely analogous iodine–oxygen (4.87 Å in Ia) approaches and the above described iodine–halogen interactions are present in all of these peroxide crystal structures. But, an important difference in the crystallographic symmetry relationship between the interacting molecules further characterizes the two groups of peroxides. For both groups, the two benzoate moieties (designated I and X) of a given peroxide molecule (I–X) occupy opposite sides (I and X) of their common, (400)-type molecular layers. The interacting iodine atom is exposed on the "I" face of every layer.

In group A structures, the other interacting halogen atom (=iodine only in the case of Ia) and the O(1) type oxygen are part of the same benzoate group of the other half of the molecular structure and, accordingly, are exposed on the opposite, X face of a layer. The **a** translational stacking of these layers results in an ---I–X---I–X---I—X molecular sequence of benzoate groups in the crystallographic *a* direction. Formation of the exocyclic I–O bond along the 4.86 Å approach between layers therefore would result in the benzoxiodole product which is isomeric with the reactant peroxide. A possible bond redistribution scheme of this type in which these neighboring oxygen and interacting halogen atoms anchimerically assist peroxide decomposition is shown in Fig. 3. Further, since the interactions occur between *every pair of adjacent layer faces, the entire peroxide crystal structure could transform to the isomeric product, as*

---I—X---I—X---I—X--- → —I, X—I, X—I, X—

(see Fig. 4). Isotopic labeling experiments have been designed to test this *inter*molecular mechanism for the topotactic isomerization of the group A peroxides.

By contrast, in group B structures the O(1) type oxygens and both of the halogen atoms (two iodines) for the interactions are contributed only by the *o*-iodobenzoate half of the molecular structure. The interactions therefore involve the I but not the X face of a layer. The inversion and screw axis stacking of the layers results in a ,X—I---I—X, X—I---I—X, sequence of benzoate groups along the *a* lattice translation with the 4.86 Å I---O approach occurring between *every other* pair of adjacent layer faces (i.e., only between the I faces). If reaction indeed occurred in the manner depicted in Fig. 3, only the iodine-containing half of a group B peroxide structure would become involved in (IIb) benzoxiodole formation while the other (X) half of the molecular and crystal structure would suffer other types of decomposition. Thus (see Fig. 4),

,X—I---I—X, X—I---I—X, →
?X, I—I ,X, ?X,I—I ,X, ?

In the case of the If reactant lattice, the resulting molecules of IIb (shown as I–I above) initially would be localized in widely separated (~22 Å) layered regions, approximately containing the (100) unit cell planes of If, and sandwiched between parallel regions containing the chlorobenzoate groups. The very extensive solid state reorganization necessary to segregate the bulky chlorobenzoate groups renders unlikely the possibility that IIb would appear as an ordered crystal structure. While there is no direct evidence in support of the intermediate formation of amorphous IIb in group B peroxides which are topotactically transformed to IIc, it seems reasonable to suppose that such benzoxiodole molecules could be hydrolyzed to IIc more readily than their three dimensionally ordered phases.

Although the above considerations reasonably account for the qualitative differences in the solid state behavior of the two types of molecular packing which characterize the peroxide groups, undoubtedly other factors also are important. In general, topotactic chemical transformations involve two distinct, though obviously interrelated processes—chemical reaction of the ordered parent structure and solid state recrystallization of the product molecules. With regard to the former, the proximity of reactive sites in the *idealized* crystal structure of the reactant, in some cases, may be a poor, indeed misleading, indication of the preferred solid state reaction path. Even the repeatedly verified topochemical principles of solid state dimerization (*14*) have had to be reexamined in cases where crystal defects significantly perturb the idealized reactant structure (*15–21*). The separate question of the topotaxy which occurs after chemical reaction requires a definition of the extent of product reorganization which can be tolerated within an environment which, by definition, retains some knowledge of the pre-

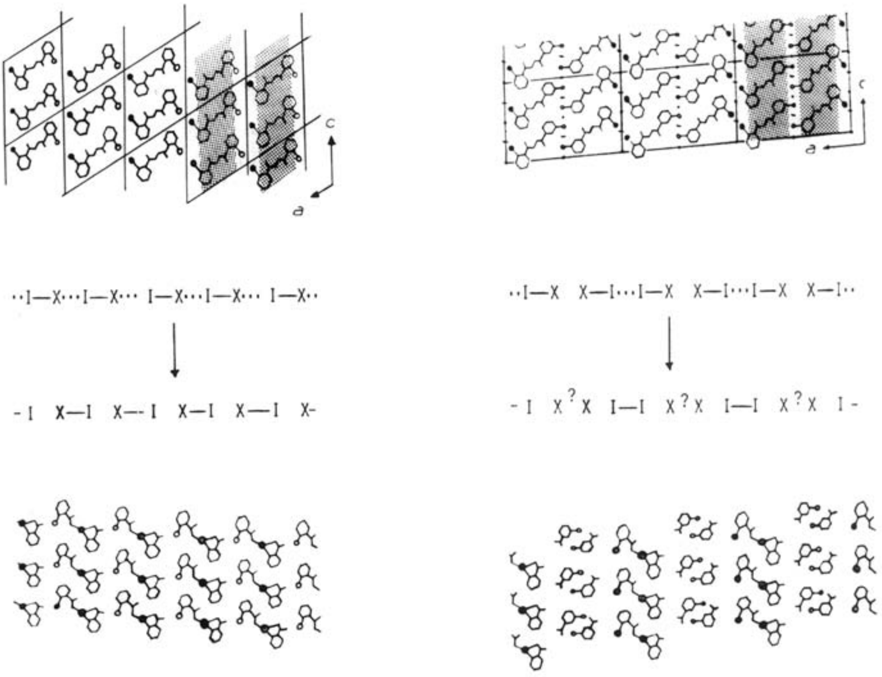

FIG. 4. The observed packing in peroxide structures (top left: group A; top right: group B) is shown in (010) projection. In each group, the shaded areas represent a cross section of two of the close-packed molecular layers which are parallel to (100) and extend throughout the crystals along the directions ±**c** and ±**b**. As drawn, the left and right sides of the group A layers are "I" and "X" faces, respectively. The intermolecular iodine–halogen and iodine–oxygen interactions occur between each pair of adjacent layers (schematically designated as I—X---I—X below the group A structure). Chemical reaction in the manner depicted in Fig. 3 would result in the isomerization of the entire crystal (left part of figure). *Reorganization of this arrangement of product molecules* (lower left) *is required to arrive at the actual packing arrangements observed in transformations of this group (1).*

The close-packed layers in group B structures are alternately stacked and only two "X" or two "I" but not "I" and "X" faces are in contact. The space between the two shaded layers represents contact of two X faces. The intermolecular iodine–iodine and iodine–oxygen interactions occur between two "I" faces (schematically designed as I---I below the group B structure). Chemical reaction according to Fig. 3 would result in the formation of isolated layers of molecular IIb (bottom right).

reaction crystallographic order. The single crystal transformations of the above peroxides to IIc (*1*) clearly demonstrate that major solid state segregation and recrystallization, at least for molecular products approximately half as bulky as IIa and IIb, can occur without randomizing the initial reactant lattice.

The absence of an ordered, isomeric benzoxiodole phase in decomposed pseudomorphs of Ie supports the above rationalizations of the differences in peroxide behavior, and comparable support is indicated by the example of If.[9] However, the group B peroxide Id is an exception; although the transformation Id → IIc appears to be the usual fate of this structure, the topotactic formation of its isomeric IId phase has been observed in some crystals. In the final analysis, this anomalous case may serve to demonstrate that these considerations of the reactant crystal structure on an intimate molecular level present an oversimplified view of topotactic processes. Cooperative movements of entire groups of molecules are necessary even for the reaction and formation of a single molecule. The topotactic growth of a product phase within the reactant lattice presumably also requires group movement in order to achieve a "good fit" between the reactant and product lattices. The behavior of Id may simply prove to be attributable to the existence of such a good fit where none exists between the structure of If and either of its two isomeric structures IIaα and β. The latter will be considered in the next paper in this series.

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