

# Solid State Chemistry of Organic Polyvalent Iodine Compounds. IV. Topotactic Transformations of 2-Iodo-3'-Chlorodibenzoyl Peroxide and the Crystal Structure of *m*-Chlorobenzoic Acid

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Single crystals of 2-iodo-3'-chlorodibenzoyl peroxide (P) undergo several competitive and consecutive topotactic transformations: upon standing in the laboratory atmosphere or during X-ray photography at  $\sim 22^\circ\text{C}$ , crystalline P is transformed to pseudomorphs containing preferentially oriented single crystal phases of *o*-iodosobenzoic acid (E), *m*-chlorobenzoic acid (D), and an as yet unidentified novel phase, "X." (Topotactic rearrangement of P to the known acicular polymorph of its benzoxiodole isomer, 3-oxo-3H,2,1-benzoxiodol-1-yl *m*-chlorobenzoate, occurs only at elevated temperatures,  $\sim 55^\circ\text{C}$ .) In a much slower, consecutive transformation, during further continuous exposure to X-rays, "X" is photochemically reduced to *o*-iodobenzoic acid (C), which also is formed as a single crystal phase. The resulting single crystal domains of D and E in decomposed pseudomorphs of P are mutually oriented in a manner which reflects their strikingly similar crystal structures. The structure of D has been determined by single crystal X-ray analysis in order to compare the aligned molecular packing arrangements of D and C, and P and D. The mutual alignment of P and E is also presented in this report. All of these topotactic products are aligned so as to conserve the point group symmetry of the parent crystal, P (conservative twinning.)

The essentially flat molecular structure of D,  $\text{C}_7\text{H}_5\text{ClO}_2$ , crystallizes in centrosymmetric hydrogen bonded "dimer" units in a monoclinic cell with  $a = 3.845$ ,  $b = 16.038$ ,  $c = 11.203$  Å,  $\beta = 94.88^\circ$ ,  $Z = 4$ ,  $P2_1/c$ . All hydrogen atoms, including the acidic proton, were located during the analysis which converged to  $R = 0.10$  for the 1083 observed intensities. The X-ray diffraction pattern of *m*-chloroperoxybenzoic acid ( $a = 4.035$ ,  $b = 5.969$ ,  $c = 30.55$  Å,  $\beta = 91.70^\circ$ ,  $Z = 4$ ,  $P2_1/c$ ) is different from that of "X."

## Introduction

Single crystals of several derivatives of 2-iododibenzoyl peroxide, A, and the closely related benzoxiodole derivatives, B, undergo a variety of competitive and consecutive topotactic transformations (1, 2) as a result of molecular isomerization ( $A \rightarrow B$ ), hydrolysis by atmospheric moisture ( $A \rightarrow D + E$ ) and ( $B \rightarrow D + E$ ), and photochemical reduction of the trivalent iodine nucleus ( $B \rightarrow C$ ) (Fig. 1). The topotaxy in transformations of a particular peroxide derivative may be relatively simple, as in the decomposition of 2-iododibenzoyl peroxide itself, where only "orthoiodoso-

benzoic acid," E, has been observed to form as a single crystal phase under a variety of conditions. By contrast, it may be quite complex as demonstrated by the several topotactic transformations of 2-iodo-3'-chlorodibenzoyl peroxide (A with  $R = m\text{-Cl}$ ; hereafter referred to as compound P) which are described in this paper.<sup>1</sup>

In general, it is useful to distinguish between *topotactic products*, which, by definition, are crystalline and preferentially oriented relative to some single crystal matrix within the pseudomorph, and *chemical products* of a particular reaction, of which only some, and

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<sup>1</sup> Abstracted from the Ph.D. thesis of L. Lessinger, Harvard University (1971).

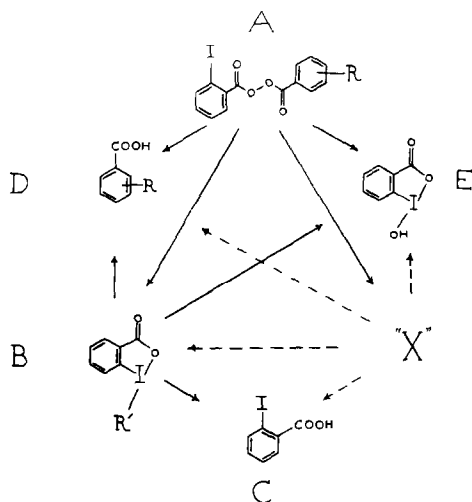


FIG. 1. Competitive and consecutive topotactic transformations of derivatives of 2-iododibenzoyl peroxide (A) and the closely related benzoxiodole structures (B).

in some cases, none may crystallize during the solid state process. Most of the topotactic products in our studies appear as crystal structures which are identical with those obtained by conventional crystallizations of the corresponding pure chemical products from solvents, but the former are usually twinned in characteristic ways which reflect their unique solid state genesis (conservative twinning) (2). While intricate twinning of this type may obscure the identity of the product phases, it is usually possible to make an unambiguous assignment of structure through comparisons with diffraction patterns from the independently crystallized samples. These diffraction techniques, however, are relatively insensitive to the presence of amorphous chemical products in the pseudomorph. The chemical composition and yield of the topotactic products, as inferred from X-ray measurements, thus do not usually correspond with the stoichiometry of the chemical reaction—a predicament which potentially is complicated further by the interesting possibility that an amorphous chemical product of a prior topotactic transformation may crystallize during another, *subsequent* topotactic transformation.

Some of the peroxides have been found to give rise to topotactic products having novel crystal structures which apparently can be formed and stabilized only within a reactant matrix. These novel product phases assume particular importance in studies of the molecular mechanisms of solid state transformations, for their formation would appear to be a direct consequence of the constraints on molecular migrations imposed by the reactant matrix.

The crystal structures of the parent peroxides (A) have been classified into 2 groups which exhibit qualitatively different solid state behavior (3). In one of these groups, topotactic isomerization (A  $\rightarrow$  B) at ambient temperatures is an especially facile process, while hydrolysis leading to the topotactic products D and E is relatively slow, even when the peroxide crystals are left exposed to the laboratory humidity during X-ray photography. 2-Iodo-3'-chlorodibenzoyl peroxide, P, is one member of the other type of crystal structures which, as a group, are more susceptible to hydrolysis. *o*-Iodosobenzoic acid (E) and, in much smaller amounts, *m*-chlorobenzoic acid (D) and a third as yet unidentified phase X, are the topotactic products in crystals of P which have been allowed to decompose in the open atmosphere. Although variable amounts of the topotactic hydrolysis products D and E are also formed during continuous X-ray photography of P at room temperature, the X-radiation appears markedly to accelerate the transformation P  $\rightarrow$  X and in some crystals, X is the predominant topotactic product at relatively early stages in the decomposition of P. Neither of the 2 known crystal structures of the benzoxiodole isomer of P (4) (B with R' = *m*-chlorobenzoyloxy; hereafter referred to as compound Q) has been observed to form as a crystalline phase under any of the above conditions.<sup>2</sup>

<sup>2</sup> Dr. Douglas Nae in this laboratory has found that P is topotactically transformed to the known acicular polymorph of Q (several orientations) upon heating at  $\sim 55^\circ\text{C}$  for several hours. An account of this topotaxy and the results of further studies of the effects of heat, moisture, and radiation on these transformations will be published in a future report.

TABLE I

CRYSTAL DATA (THE ESTIMATED UNCERTAINTY IN THE FINAL DECIMAL PLACE IS GIVEN IN PARENTHESES)

Structure <sup>a</sup>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>D</i> <sub>obs</sub> (g/cm <sup>3</sup> )	<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	<i>V</i> (Å <sup>3</sup> )	<i>Z</i>	Space group
D	3.845(1)	16.038(2)	11.203(1)	94.88(4)	1.496 <sup>b</sup>	1.511	688.3	4	<i>P</i> 2 <sub>1</sub> / <i>c</i>
P	22.28(1)	4.057(2)	15.38(1)	94.50(4)	1.90	1.930	1385.6	4	<i>P</i> 2 <sub>1</sub> / <i>c</i>
E	12.89(1)	4.10(1)	14.05(1)	96.73(5)	2.33	2.378	737.4	4	<i>P</i> 2 <sub>1</sub> / <i>c</i>
C	4.318(1)	15.083(1)	11.285(1)	91.50(4)	2.249 <sup>b</sup>	2.242	734.8	4	<i>P</i> 2 <sub>1</sub> / <i>c</i>
F	4.034(1)	5.969(1)	30.552(2)	91.70(4)	1.51	1.558	735.4	4	<i>P</i> 2 <sub>1</sub> / <i>c</i>
X	13.051(2)	4.005(6)	15.427(2)	104.20(4)	—	—	781.7	—	—

<sup>a</sup> All measurements were made at 21–22°C. Structure key: D = *m*-chlorobenzoic acid; P = 2-iodo-3'-chlorodibenzoyl peroxide; E = *o*-iodosobenzoic acid; C = *o*-iodobenzoic acid; F = *m*-chloroperoxybenzoic acid; X = the unidentified phase.

<sup>b</sup> Reported in Ref. (5).

Still another topotactic product, *o*-iodobenzoic acid (C), is formed gradually in pseudomorphs containing primarily X and some oriented D and E, during further prolonged exposure to X-radiation. The resulting mutual orientation of C and D first drew our attention to the striking similarity of their unit cell parameters (Table I). The crystal structure of D (Appendix I) has been determined in order to compare the molecular arrangements in the topotactically aligned crystal structures of D and C,<sup>3</sup> and D and P (3).

Initially, we were led to consider whether

<sup>3</sup> The crystal structure of C has been examined no less than four times. In a very early effort, Klug (6) determined the coordinates of the iodine atom. Later, Khotsyanova and Struchkov (7) attempted to solve the structure in projection along the short *a* axis; while successful in locating the iodine and thereby confirming Klug's results, they were unable to determine the positions of the carbon and oxygen atoms. Krause and Haase (8) succeeded in obtaining an approximate solution to the structure in (100) projection. Unfortunately, while a figure showing the orientations of the molecules was given in their paper, no atomic coordinates were presented. The 2-dimensional structure presented in this paper is based on Clardy's (9) independent X-ray determination of the *y* and *z* coordinates of all atoms by hydrogen (to be published in a separate report), in which he assumed Klug's values for the unit cell constants. We independently obtained the more accurate constants presented in Table I.

the novel phase X might be still another hydrolysis product. However, of the two peroxybenzoic acids—*o*-iodo-, and *m*-chloroperoxybenzoic acids—which may be expected to result directly from the hydrolytic cleavage of P, only the latter is known and we have shown it to be different from X (see Appendix II). The former peroxyacid undoubtedly is quite unstable and is expected either to rearrange to its isomer, E, or to undergo further hydrolysis to give C. We have found that crystalline *o*-bromoperoxybenzoic acid decomposes at room temperature to give solid *o*-bromobenzoic acid and further have considered that it may be crystallographically isostructural with the unknown *o*-iodoperoxybenzoic acid. In any case, its diffraction pattern also is different from that of X. To date, a crystal structure analysis based on the limited and relatively low quality intensity data of X from P has not been possible, but preliminary results of a structure analysis of the seemingly analogous phase formed in the topotactic decomposition of 2-iodo-2'-chlorodibenzoyl peroxide suggest that these intermediate-structures are *novel* polymorphs of the corresponding benzoxiodole isomers (B) (10). In support of this possibility, we have recently found that the trivalent iodine atoms in several benzoxiodole structures readily undergo solid state photochemical reduction resulting in the topotactic formation of C (11).

### Topotactic Formation of D, E, X, and C

The crystal structure of every one of the topotactic products D, E, X, and C, has a short  $\sim 4 \text{ \AA}$  lattice repeat which aligns strictly parallel (or *antiparallel*, *vide infra*) to the  $\sim 4 \text{ \AA}$  translation of the decomposing parent crystal structure, P. All of the transformations thus were conveniently studied by continuous Weissenberg photography of crystals mounted along the  $b$  axis of P, without change in crystal alignment.<sup>4</sup> For the several individual studies, suitable single crystals of P were randomly selected from various crops, glued to thin glass fibres (Duco cement thinned with amyl acetate), and left exposed to the atmosphere at  $\sim 22^\circ\text{C}$  throughout the entire X-ray experiments. The gradually diminishing peroxide X-ray reflections remain sharp and discrete on Weissenberg and rotation photographs until their complete disappearance,  $\sim 160$  hr after initial exposure to X-rays.

Although the previously reported (2) topotactic matrices defining the specific angular phase alignment of D and E relative to P were derived from X-ray measurements of a pseudomorph which contained predominantly these stable products, the particular choice of pseudomorph is not important since no variation in the specific mode of phase alignment of *any* product relative to P was observed at any time. The experimentally observed angular alignments of the molecular arrays of P and E (12), and P and D are shown in Figs. 2 and 3.

The conversion  $P \rightarrow X$  predominates in freshly crystallized samples of P, at room temperature in the X-ray beam ( $\text{CuK}\alpha$  X-radiation; 50 kV, 14 mA); however, small amounts of D and E usually are also formed before the complete disappearance of P. X displays  $2/m$  diffraction symmetry. The accurately known length of the peroxide  $b$  axis was used to calibrate measurements of the apparent symmetry axis,  $b_x$ , from  $[010]$  oscillation photographs of partially transformed peroxide crystals, while  $a$ ,  $c$ , and  $\beta$

<sup>4</sup> Weissenberg photographs of various stages of the topotactic transformations of P have been deposited (see footnote 6).

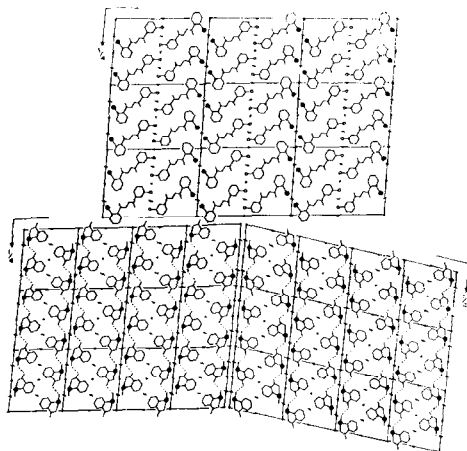


FIG. 2. The experimentally observed angular alignment of P (top) and E. The latter is formed in 2 orientations relative to P. All structures are shown in projection down the mutually aligned  $b$  axes.

for X (Table I) were derived from a least squares analysis of 187 independent values of  $\theta(h0l)_x$ , obtained from calibrated Weissenberg photographs. Comparisons of the considerably more diffuse reciprocal lattice level  $(h1l)_x$  with  $(h0l)_x$ , suggest no systematic absences on either level and twinning is not apparent. The

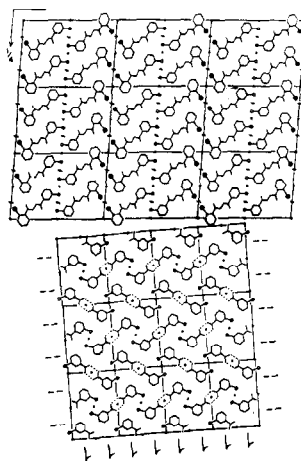


FIG. 3. The experimentally observed angular alignment of D (bottom) and P. The crystal structures are shown in projection down the coincident directions  $[010]_D$ ,  $[100]_D$ , and  $[100]_P$ .

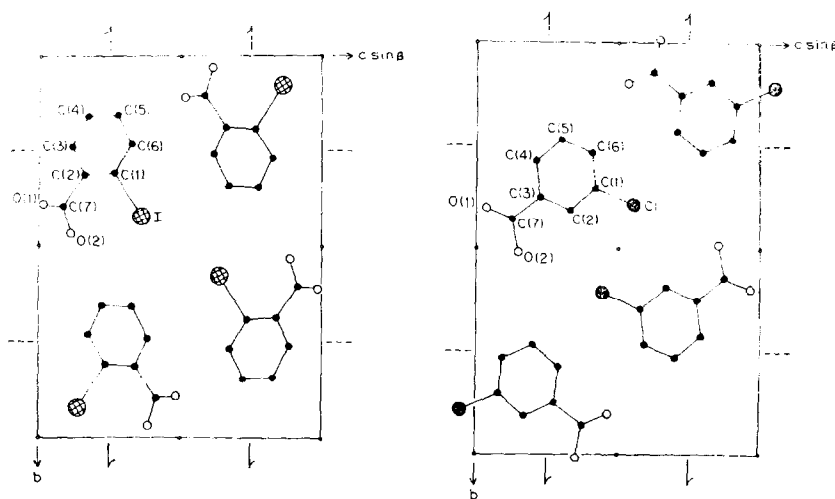


FIG. 4. The observed angular alignment and molecular correspondence of C (left) and D (right) in pseudomorphs of P. The twinned structures are shown in projections down their aligned  $\pm a$  axes.

matrix relationship which defines the topotaxy between X and P is

$$\begin{pmatrix} \mathbf{A} \\ \mathbf{B} \\ \mathbf{C} \end{pmatrix} = \begin{pmatrix} .580 & 0 & .204 \\ 0 & .987 & 0 \\ -.278 & 0 & .888 \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}$$

where  $(\mathbf{ABC})$  and  $(\mathbf{abc})$  are the unit cell vectors of X and P, respectively.

Further continuous X-ray photography reveals the gradual disappearance of X and the formation of C in a closely aligned orientation relative to the already present crystal structure of D. In addition, the amount of oriented D appears to increase somewhat during this consecutive transformation. This step is essentially complete after  $\sim 560$  hr total exposure of P to X-rays. Even though the final pseudomorph is a rather severe mosaic of the aligned structures ( $7\text{--}16^\circ$  mosaic spread perpendicular to the short axis), comparisons with diffraction photographs of authentic crystals of D and C allow for an unambiguous identification.<sup>4</sup> The topotactic matrix defining the angular alignment of C relative to P has already been presented (2); the mutual phase alignment of D and C, and their alignment relative to X, may be obtained by multiplication of the appropriate topotactic matrices. Figure 4 illustrates the close correspondence

between the molecular packing arrays in the oriented crystal structures of D and C.

We wish to emphasize that our measurements of the topotaxy in these systems define only the 3-dimensional *angular* orientation of the various crystal structures. The *translational* (phase) relationship between any two angularly oriented crystal structures ordinarily is not recoverable from the X-ray experiments because the (large) domains of the component structures diffract essentially independently of one another. Therefore, the molecular structure at the interphase boundary(s) between the domains is not defined by our measurements, and, in principle, the domains can be merged in several different ways while preserving the observed *angular* alignment. One way, which results in an interphase parallel to (010) of both structures, allows for contiguous hydrogen bonding *across* the interphase, as an extension of the hydrogen bonding *within* the domains of the separate crystal structures (Fig. 5a). However, the disparity in the monoclinic angle  $\beta$  for the 2 structures and the consequent mismatch of the 2 *a-c* lattice grids (Fig. 6) would appear to limit the extent and stability of such an interphase. Similar contiguous hydrogen-bonded arrays may be established across an interphase parallel to (001) of both structures

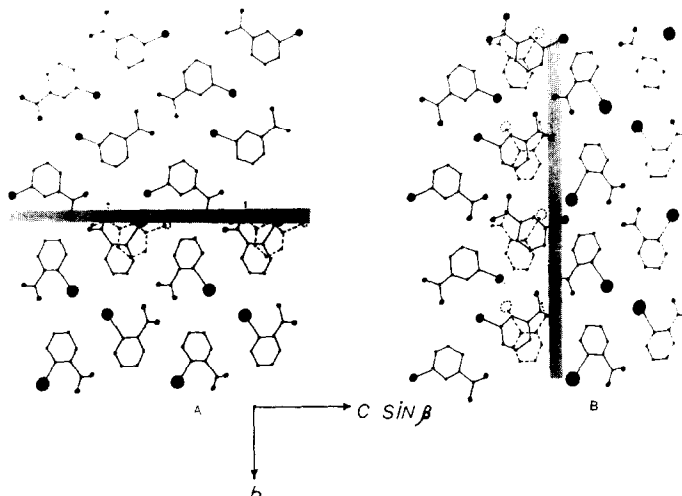


FIG. 5. Two hypothetical intergrowths of D and C, consistent with the observed angular alignment (Fig. 4), which allow for contiguous hydrogen bonding across the interphase boundary (shaded region). (a—left): interphase parallel to (010) of both structures. The dashed molecules in the lower (C) structure define equivalent positions of D, as an extension of its ordered structure (top) across the interphase. (b—right): interphase parallel to (001) of both structures. The dashed molecules to the left of the interphase define equivalent positions of C, as an extension of its ordered structure (right) across the interphase.

(Fig. 5b) and, in this case, the close match of the 2 rectangular  $a$ - $b$  lattice grids extends over a greater area of the potential interphase. Further considerations of these and other possible structures of the interphase have

been postponed until the 3-dimensional structure of C has been determined.

### Conservative Twinning

The initial monoclinic reactant crystal structure P is characterized by one unique direction of symmetry ( $b$ ) which, in this case, is also the short 4 Å axis. While each of the product crystal structures C, D, and E also is monoclinic with one equally short lattice repeat, only in the last structure is the short axis also the symmetry axis. The alignment of 4 Å axes in pseudomorphs of P consequently is accompanied by conservative twinning (2) of the topotactic products C and D. Thus, although the mirror and twofold rotational (point group) symmetry elements of the initial crystal cannot be locally retained in homogeneous single crystal domains of either C or D aligned with their  $a$  axes parallel to  $b_p$ , they are conserved as macroscopic symmetry elements of the *total* pseudomorph through the generation of an essentially equal number of single crystal domains of these products aligned with their  $a$  axes *antiparallel* to  $b_p$ .

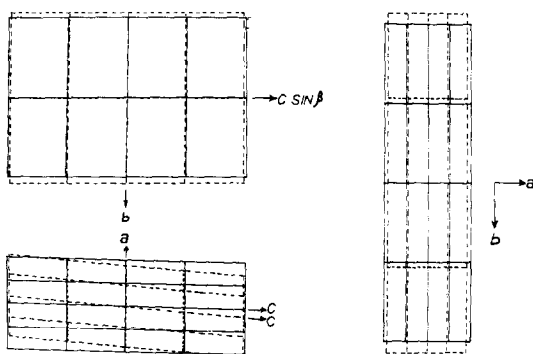


FIG. 6. The reticular correspondence of the lattices of D and C, angularly aligned in accord with the observed topotaxy. The lower left drawing represents the implied lattice match for an interphase parallel to (010) (see Fig. 5a). The drawing on the right represents the implied lattice match for an interphase parallel to (001) (see Fig. 5b). —: *o*-iodobenzoic acid; ----: *m*-chlorobenzoic acid.

The observed alignment of the unique axes of P and E allows for both local and overall preservation of the symmetry of P, within and between domains of E, without conservative twinning.<sup>5</sup> An antiparallel alignment of these axes, without twinning, similarly preserves the initial symmetry and, in general, the relative frequency of occurrence of these 2 modes of alignment is not controlled by the symmetry of P. Both a parallel and an antiparallel alignment, each defining a different specific topotaxy, are realized in the transformation  $P \rightarrow E$ ; however, the topotactic transformation of 2-iododibenzoyl peroxide to E results in only one of the two modes of alignment of unique axes (2).

These twinning modes represent another potential source of confusion in our diffraction studies of X. Since any triclinic crystal structure generated as a topotactic product of a monoclinic reactant may be *expected* to twin conservatively, and thereby display the initial  $2/m$  diffraction symmetry, we are somewhat reluctant to assign X unequivocally to the monoclinic crystal system. On the other hand, X may in fact be monoclinic but with a 4 Å unique axis which is aligned *both* parallel and antiparallel to  $b_p$ , with unequal frequency, and in such manner as to conceal its true  $a-c$  lattice grid.

While the conservative twinning of C is consistent with the alignment of C relative to the twinned structure of D, we cannot exclude the alternative possibility that topotaxy in the formation of C is established relative to X.

<sup>5</sup> Our experience over the past several years lends support to Bernal's insightful suggestion that "topotaxy is very widespread and may be the commonest method of transformation in solid state reactions" (13). However, in our general use of the term topotaxy, we have not adhered to his notion that topotaxy is characterized by the retention of some crystallographic symmetry axes of the reactant in the crystal structure of the product (we take this to mean a *local* preservation such as in the transformation  $P \rightarrow E$  and not the *overall* preservation which is manifest in the widespread conservative twinning modes), nor have we used the recently described terminology (14) to distinguish between the various types of mutual crystal orientation.

## Appendix I

### *Crystal Structure Analysis of m-Chlorobenzoic Acid (D)*

Crystallizations of commercial *m*-chlorobenzoic acid from water-acetone solvent mixtures gave colorless needles elongated along  $a$ . Unit cell parameters (Table I) were determined from least squares analyses of  $\theta(hkl)$  values from  $hk0$ ,  $h0l$ , and  $0kl$  Weissenberg photographs calibrated with Al powder. The  $2/m$  diffraction symmetry and systematically absent classes of reflections ( $h0l$ ,  $l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ ), together with the previously reported crystal density (5) indicated the presence of 4 molecules of D in general positions of space group  $P2_1/c$ .

Independent non-extinct intensities (1368) ( $0kl-3kl$ ) from a single crystal of dimensions  $0.17 \times 0.13 \times 0.17$  mm were recorded at 21°C by the multiple-film equi-inclination Weissenberg method ( $\text{CuK}\alpha$ ,  $\lambda = 1.542$  Å) and estimated by visual comparison with a graduated series of exposures of a representative reflection. Intensities from the cross levels  $hk0$  and  $h0l$  were examined in order to correlate and adjust the data to a common scale. The intensities were corrected for absorption and the Lorentz and polarization factors and assigned estimated standard deviations in terms of the minimum observable intensity,  $I'$ , according to:  $\sigma(I) = 0.3 I'$  for  $I > 53 I'$ ;  $\sigma(I) = 0.2$  for  $3.5 I' < I \leq 53 I'$ ;  $\sigma(I) = 0.83 I'$  for  $I \leq 3.5 I'$ . Of the 1368 (88% of the 1556 reflections within the  $\text{CuK}\alpha$  sphere) recorded intensities, 285 were unobserved and therefore assigned an intensity of  $0.5 I'$  with an estimated error of  $0.83 I'$ . The intensities of 50 broad reflections at low  $\nu$  values on upper level photographs (mostly  $2kl$  and  $3kl$ ) were more difficult to estimate and accordingly were assigned greater uncertainties, typically 2 or 3 times the estimated error for a reflection of the same intensity at higher  $\nu$  values.

Solution of the structure by Patterson and Fourier techniques was straightforward; the conventional agreement index for a trial structure consisting of only the chlorine atom ( $R = 0.53$ ) was lowered to 0.24 when all 10 non hydrogen atoms were included in the structure factor calculation. Six cycles of

least-squares refinements of all coordinates, individual anisotropic temperature parameters, and scale factors reduced  $R$  to 0.130. When the positions of all 5 hydrogen atoms, clearly evident in a 3-dimensional difference Fourier synthesis, were introduced with an isotropic temperature factor of  $B = 4.5 \text{ \AA}^2$ ,  $R$  fell slightly to 0.125. Two further cycles of refinements of all parameters (H atoms were varied isotropically) reduced  $R$  to its final value of 0.117 for the 1368 recorded reflections.<sup>6</sup> Omission of the unobserved reflections resulted in  $R = 0.10$ . Parameter shifts during the final refinement were less than one-tenth of the corresponding estimated standard deviations obtained from the inverse matrix. Since a final 3-dimensional difference map based on all 15 atoms showed no significant features, the analysis was terminated.

Fractional atomic coordinates and individual temperature factors are presented in Tables II and III.

#### The Molecular Structure of D

The calculated bond distances and valence angles are shown in Fig. 7 which also illustrates the characteristic dimeric arrangement of mutually hydrogen-bonded pairs of the acid molecules across a crystallographic inversion center. The mean aromatic C—C bond length is 1.394 Å with deviations from this value ranging up to 0.021 Å. The C—Cl bond length of 1.744 Å is in reasonable agreement with the values reported for the related structures: 1.737 Å in *o*-chlorobenzoic acid

<sup>6</sup> In all least-squares refinements, the quantity minimized was  $\sum w(|F_o|^2 - |F_c|^2)^2$  with  $w = 1/[\sigma(F_o^2)]^2$ . Atomic scattering factors for Cl, C, O and H were taken from the "International Tables for X-ray Crystallography", Vol. III, (C. H. MacGillavry and G. D. Rieck, Eds.), pp. 202–203, The Kynoch Press, Birmingham, 1962. Tables of the observed and calculated structure factors, least-squares planes, and intermolecular contacts, as well as several Weissenberg photographs of the transformations of P have been deposited. See NAPS document # 02335 for 34 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications.

TABLE II  
FRACTIONAL ATOMIC COORDINATES FOR D<sup>a</sup>

Atom	x	y	z
Cl	0.8418(4)	0.39289(8)	0.5547(1)
C(1)	0.649(1)	0.3529(3)	0.4202(4)
C(2)	0.524(1)	0.4073(3)	0.3305(4)
C(3)	0.359(1)	0.3745(3)	0.2237(4)
C(4)	0.328(1)	0.2871(3)	0.2091(4)
C(5)	0.461(1)	0.2353(3)	0.3003(5)
C(6)	0.623(1)	0.2673(3)	0.4065(4)
C(7)	0.205(1)	0.4293(3)	0.1265(4)
O(1)	0.058(1)	0.4018(2)	0.0338(3)
O(2)	0.245(1)	0.5089(2)	0.1466(4)
H(1)	0.57(1)	0.461(2)	0.334(3)
H(2)	0.19(1)	0.261(3)	0.138(4)
H(3)	0.38(1)	0.175(3)	0.303(4)
H(4)	0.72(1)	0.231(3)	0.467(3)
H(5)	0.15(1)	0.544(3)	0.089(4)

<sup>a</sup> Uncertainties in the final significant figures are given in parentheses.

(15), 1.753 Å in 2-chloro-5-nitrobenzoic acid (16), 1.725 Å in 2-chlorobiphenyl-4-carboxylic acid (17). The seemingly short bond distances and small temperature factors for the hydrogen atoms, for the most part attributable to the incorrect assumption of a spherical electron density about the hydrogen atoms, are in reasonable agreement with the more accurate results from neutron studies when corrected by +.09 Å and +2.3 Å<sup>2</sup>, respectively (18).

The conformations of D and its hydrogen-bonded "dimer" unit were examined by computing several weighted least-squares planes through various groups of atoms. A table of the least-squares planes is included in the deposit described in footnote 6. Although the entire "dimer" unit is essentially planar (plane A), the molecular conformation is more precisely described by 2 least-squares planes: plane C—the 6 phenyl carbon atoms; plane D—the carboxyl group. The dihedral angle between planes C and D is 1.8°. The geometry of the centrosymmetric hydrogen bonding conforms to the general patterns described by Jeffrey and Sax (19) and Donohue (20), with an interplanar distance of 0.06 Å between the necessarily parallel planes of the 2 carboxyl



TABLE III  
TEMPERATURE FACTOR PARAMETERS FOR D<sup>a</sup>

A. Heavy atoms with anisotropic factors of the form $\exp[-.001(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$						
Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl	50(1)	5.47(5)	8.97(9)	3.5(4)	-8.0(5)	-0.5(1)
C(1)	10(4)	4.9(2)	9.7(4)	2(1)	3(2)	-0.5(4)
C(2)	23(4)	3.8(2)	9.8(4)	5(1)	1(2)	0.4(4)
C(3)	33(4)	4.1(2)	7.8(3)	4(1)	5(2)	0.4(4)
C(4)	38(5)	4.4(2)	9.0(4)	-1(2)	2(2)	-0.5(4)
C(5)	48(5)	4.6(2)	11.0(5)	2(2)	5(2)	1.0(5)
C(6)	34(5)	5.4(2)	9.0(4)	7(2)	7(2)	2.4(5)
C(7)	9(4)	4.4(2)	9.9(4)	-1(1)	-4(2)	1.0(4)
O(1)	93(4)	4.6(1)	9.3(3)	-5(1)	-20(2)	1.7(3)
O(2)	101(4)	4.0(1)	12.0(4)	-5(1)	-24(2)	2.4(4)

B. Hydrogen atoms with isotropic factors of the form $\exp[-B \sin^2\theta/\lambda^2]$ with B expressed in $\text{\AA}^2$ .	
Atom	B
H(1)	0.7(8)
H(2)	1.6(9)
H(3)	2.2(10)
H(4)	1.2(9)
H(5)	1.7(9)

<sup>a</sup> Uncertainties in the final significant figures are given in parentheses.

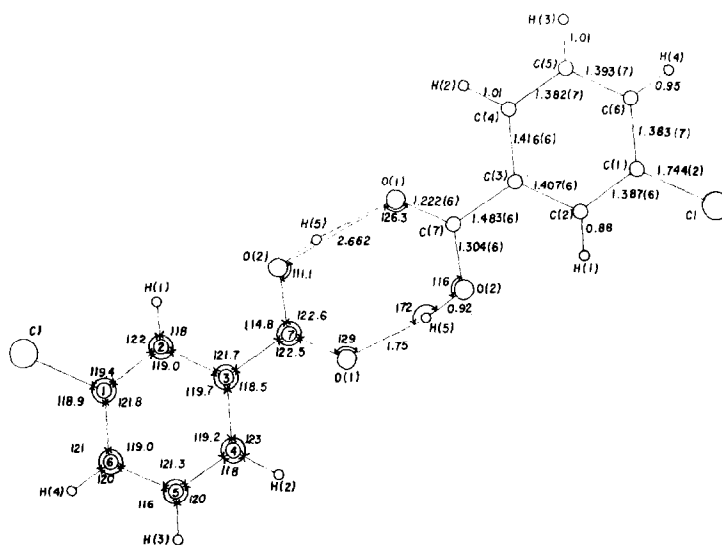


FIG. 7. Bond lengths and valence angles in the centrosymmetric hydrogen bonded dimer unit of D. The numbers in parentheses are the estimated uncertainties in the final decimal place. All of the e.s.d.'s for valence angles not involving hydrogen fall in the range 0.4-0.5°. E.s.d.'s for valence angles and bond lengths involving the hydrogen atoms are  $\sim 2.8^\circ$  and  $\sim 0.04 \text{ \AA}$ , respectively.

groups of the dimer unit (the distance from the inversion center at  $(0, \frac{1}{2}, 0)$  to plane C is  $0.03 \text{ \AA}$ ).

The difference in C–O bond lengths, the pattern of valence angles about C(7) (15), and the well-defined position of the acidic hydrogen atom, H(5), clearly identify O(1) as the carbonyl atom, and therefore the Cl and O(1) atoms have adopted a *transoid* disposition about the C(3)–C(7) bond. In *o*-halobenzoic acids, the halogen and carbonyl oxygen atoms adopt a *cisoid* conformation, apparently in response to steric factors associated with the differences in C–O bond lengths and C–C–O angles, and despite the resulting unfavorable alignment of the C=O and C–halogen bond dipoles (21). However, in general there is little if any basis for *intramolecular* steric discrimination between the approximately planar *cisoid* and *transoid* conformers of *m*-halobenzoate groups, and a consistent preference for one type of conformer is not evident in comparisons of D with *m*-halobenzoate groups in other, more extensive molecular structures. The reactant peroxide, P, and the 2 known polymorphic forms of Q contain *cisoid* *m*-chlorobenzoate groups. Although their *transoid* conformers, which have significantly different overall shapes, have not been observed, the *o*-iodo analog of Q crystallizes in both conformers, and in that case, the conformational change is clearly dependent on the modes of *intermolecular* coordination bonding to the trivalent iodine atom (22).

The choice between a *cisoid* and *transoid* conformer of the halobenzoate group, in the larger structures, thus appears to be a consequence of differences in crystal packing requirements and possible *intermolecular* coordination modes of the *overall* molecular conformations. This, however, is not the case for the centrosymmetric hydrogen-bonded dimer units of simple *m*-halobenzoic acids, the *cisoid* and *transoid* conformers of which may form virtually identical dimers of similar *interdimer* packing requirements. Small *intramolecular* dipole–dipole effects therefore may be especially manifest in the crystalline dimers and it is of interest in this connection that 2-chlorobiphenyl-4-carboxylic acid (17), like D, adopts a *transoid*

conformation in the solid state with an *anti*-parallel alignment of the polar C=O and C–Cl bonds. Unfortunately, more direct comparisons with other members of the series of *m*-halobenzoic acid crystal structures cannot be made because only *m*-bromobenzoic acid (not isostructural with D) appears to have been studied (23) and, in that case, hydrogen atoms were not located and no distinction was made between the 2 oxygen atoms. We have found no report of a *cisoid* conformer in simple structures of this type.

#### *Molecular Packing in Crystalline D*

With the exception of the above-mentioned hydrogen bonds within the centrosymmetric "dimer" unit, all *intermolecular* approach distances<sup>6</sup> correspond to normal van der Waals interactions. Since the virtually planar dimer unit (plane A) is nearly parallel to the crystallographic *b* axis, all molecules in the crystal lie in essentially parallel planes. These planes define a dihedral angle of  $28^\circ$  with (100) and are nearly parallel to  $(20\bar{3})$ . The crystals are composed of infinite layers of molecules with  $(10\bar{2})$  as the mean layer plane; the dimer plane A is inclined by  $7.6^\circ$  to the mean layer plane, thus reducing the perpendicular distance between molecules in adjacent layers to  $3.526 \text{ \AA}$ .

*Intermolecular* contacts within each layer are shown in Fig. 8 while Fig. 9 presents a schematic illustration of the layered structure and provides further clarification of the relationships between the dimer and mean layer planes.

#### Appendix II

##### *Unit Cell Data for m-Chloroperoxybenzoic Acid (F)*

A brief survey of this potential hydrolysis product of P was made in order to compare its X-ray diffraction pattern with that of X.

Commercial (85%) *m*-chloroperoxybenzoic acid ( $C_7H_5O_3Cl$ ) was recrystallized several times by dissolving the solid in dichloromethane and, without mixing, superposing a layer of low boiling petroleum ether over the solution. The crystals which formed after cooling in a freezer for several hours melted at  $88\text{--}90^\circ\text{C}$  (24). The colorless laths are elongated along *a*

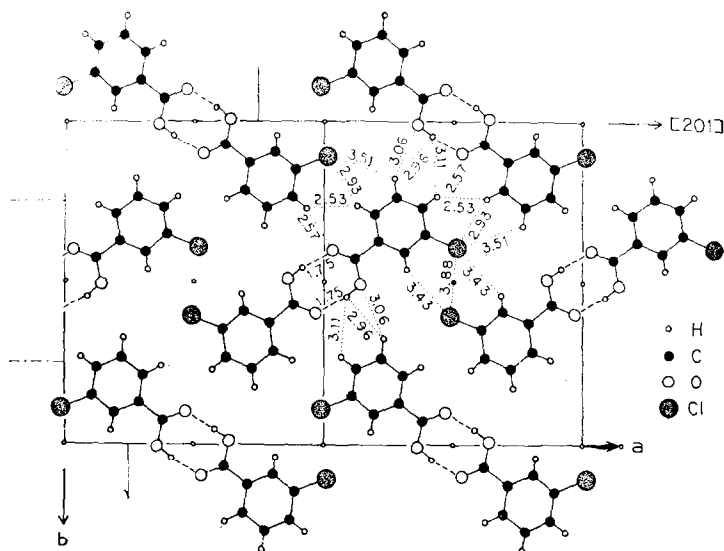


FIG. 8. The molecular packing of D in the mean layer plane (102).

and frequently twinned across (001). Their systematically absent X-ray reflections for classes  $h0l$  ( $l = 2n + 1$ ) and  $0k0$  ( $k = 2n + 1$ ) together with the observed  $2/m$  diffraction symmetry uniquely determined space group  $P2_1/c$ . Unit cell parameters and estimated standard deviations (Table I) were determined from least-squares analyses of many  $\theta(hkl)$  values obtained from  $h0l$  and  $0kl$  Weissenberg photographs calibrated with Al powder reflections ( $\text{CuK}\alpha$ ;  $\lambda = 1.542 \text{ \AA}$ ). The approximate crystal density, measured with considerable difficulty by flotation in aqueous

cadmium nitrate solution, indicates the presence of 4 molecules in general positions of the unit cell. Extensive crystal decomposition and sublimation into the open atmosphere were evident after approximately 24 hr exposure to the X-ray beam.

It is clear that the diffraction patterns of these crystals and X are different.

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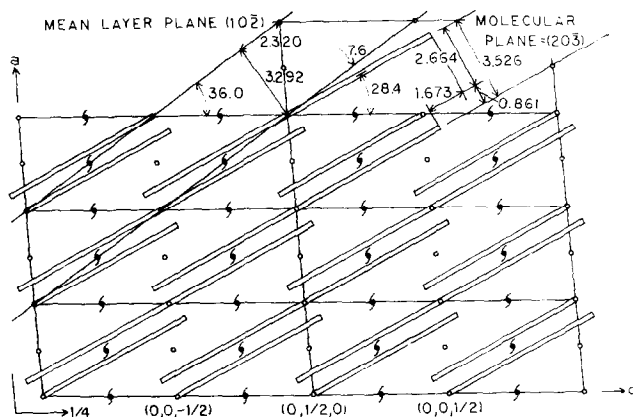


FIG. 9. A schematic illustration of the layered crystal structure of D, viewed in projection along [010].

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