

References and Notes

- (1) (a) Partially based on a Ph.D. thesis by M. C. Etter, University of Minnesota, Dec 1974; (b) National Science Foundation Predoctoral Fellow, 1970–1973, Minnesota Mining and Manufacturing Predoctoral Fellow, 1973–1974.
- (2) (a) J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.*, **4**, 230 (1972); (b) J. Z. Gougoutas and L. Lessinger, *ibid.*, **9**, 155 (1974); (c) J. Z. Gougoutas, K. H. Chang, and M. C. Etter, *ibid.*, **15**, 283 (1976); (d) J. Z. Gougoutas and D. Naae, *ibid.*, **16**, 271 (1976); (e) J. Z. Gougoutas, *Pure Appl. Chem.*, **27**, 305–325 (1971).
- (3) G. P. Baker, F. G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 3721 (1965).
- (4) M. C. Etter, *J. Solid State Chem.*, **16**, 399 (1976).
- (5) E. Shefter and W. Wolf, *Nature (London)*, **203**, 512 (1964).
- (6) $R = \sum |F_o| - |F_c| / \sum |F_o|$; the function minimized was $\sum w |F_o|^2 - |F_c|^2$, where the weight $w = 1 / [\sigma(F_o)^2]$.² Atomic scattering factors were taken from the "International Tables for X-ray Crystallography".⁷
- (7) "International Tables for X-ray Crystallography", Vol. III, C. H. MacGillavry and G. D. Riech, Ed., Kynoch Press, Birmingham, England, 1962.
- (8) After multiple recrystallizations one occasionally obtains a batch of large (~1 mm long) hollow acicular crystals. These unusual crystals have a channel about 0.1 mm in diameter extending the length of the crystal (as evidenced by "stringing" several crystals on a glass fiber). The channels are not cylindrical; they exhibit distinct trigonal, square, pentagonal, or hexagonal symmetry. X-ray photographs of these crystals showed that they were untwinned single crystals of I- β .
- (9) I am grateful to Roger Upham for his assistance in preparing special inlet systems and appropriate samples, and for running the mass spectral analyses. The samples were run on an AEI MS-30 mass spectrometer at 1000 resolution, 70 eV. Sample inlet temperature was room temperature, and source temperature 110–200 °C.
- (10) Reference samples of formaldehyde (prepared by heating paraformaldehyde) were run and the mass spectra agreed with the data given in the "Atlas of Mass Spectral Data".¹¹
- (11) S. Abrahamson, E. Stenhagen, and R. W. McLafferty, "Atlas of Mass Spectral Data", Wiley, New York, N.Y., 1969.
- (12) A pseudomorphic transformation is one in which the morphology of the reactant crystal does not change during reaction. In a single crystal to single crystal pseudomorphic transformation, the diffraction pattern of the reacting crystal changes but the dimensions and shape of the crystal itself does not (color and density changes often occur also).
- (13) M. C. Etter, Ph.D. Thesis (Appendix), University of Minnesota, 1974.
- (14) J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.*, **4**, 226–229 (1972).
- (15) The least-squares plane of the molecule was calculated using all the atomic positions except for C(12). Defined in terms of orthonormal axes x , y , and z which are directed along crystallographic axes a , b , and c^* , respectively, this plane calculates to be $0.743x + 0.558y - 0.387z = 6.16$.
- (16) A term used to describe crystals of unusual or distorted morphology resulting from intercrystal contacts during growth.¹⁷
- (17) J. S. Evans, *Discuss. Faraday Soc.*, **No. 5**, 77 (1949).
- (18) Many single crystal-gas reactions are known in which the gaseous reagent actually penetrates the crystal lattice. A review of these reactions and other organic crystal-gas reactions has appeared recently: I. C. Paul and D. Y. Curtin, *Science*, **187**, 19 (1975).
- (19) The only other known example of photolytic reduction of organic trivalent iodine is the photolysis of iodobenzene dichloride to give iodobenzene and chlorine.²⁰
- (20) D. F. Banks, *Chem. Rev.*, **66**, 249 (1966).
- (21) There is a topochemical effect²² on the kinetics of these reactions, since the I- β polymorph is much more reactive than I- α . It is difficult to relate this effect to specific structural differences between the two polymorphs, especially since there are no observable reactant-product boundaries indicative of directional product growth.
- (22) G. M. J. Schmidt and M. D. Cohen, "Reactivity of Solids", T. J. deBoer, Ed., Elsevier, Amsterdam, 1961, p 556.

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

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

Introduction

Chemical reactions in single crystals are fundamentally differing from mobile phase reactions in two respects: (1) the ordering of reactant molecules into a lattice can result in topochemical control over reaction pathways,² and (2) the reactant lattice can control the nucleation and preferential orientation of crystalline product phases. Topochemistry has been the subject of intensive research in recent years,³ but most often these solid-state reactions have not been topotactic; i.e., no crystalline product phases were formed, which had a unique orientation relative to the reactant lattice. Our studies have

focused on the single-crystal reactions of organic polyvalent iodine compounds, which generally do give oriented crystalline product phases.⁴ Because of the wide variety of reactions observed and the facility with which these single-crystal transformations occur, we have been able to study the effects of molecular packing, intermolecular coordination interactions, geometrical lattice parameters, and space group symmetry on the nature of the interlattice relationships established during reaction. Some of the significant observations concerning topotaxy in polyvalent iodine transformations are summarized here as a basis for understanding the results of the current investigation:

Table I. Crystallographic Data for Reactant and Product Lattices^a

	S.G.	a	b	c	β	V	Z	a*	b*	c*	Ref
I- α	<i>Pbca</i>	15.44	8.10	13.53	90.0	1691.0	8	0.065	0.123	0.074	6
I- β	<i>P2₁/a</i>	7.73	10.06	12.60	118.3	862.7	4	0.147	0.100	0.090	6
II	<i>P2₁/c</i>	12.89	4.10	14.05	96.73	737.5	4	0.078	0.244	0.072	16
III	<i>P2₁/c</i>	4.32	15.08	11.29	91.5	734.8	4	0.232	0.066	0.089	13

^a S.G. = space group; a, b, c, β = unit cell parameters; V = unit cell volume, Å³; Z = number of molecules per unit cell; a*, b*, c* = reciprocal cell parameters.

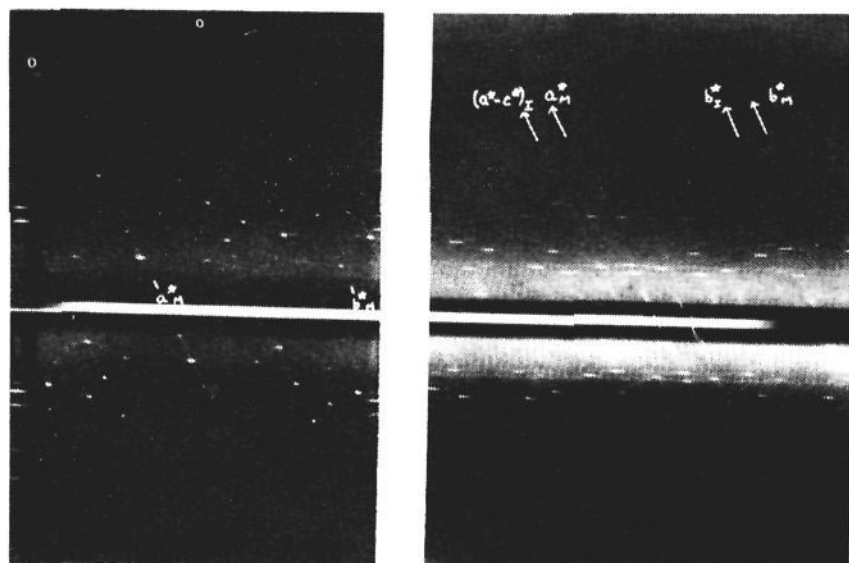


Figure 1. The x-ray diffraction patterns of $(hk0)_{I-\alpha}$ from a single crystal of I- α before reaction (left) and after decomposition (right). The pseudomorphic crystal product pattern is $(nk\bar{n})_{III}$ twinned about $(100)_{I-\alpha}$. (In the photographs, reactant axes are labeled M, and product axes are labeled I.)

(1) The topotaxy which is established is a reaction constant, unique to the chemistry and crystallography of the particular transformation.

(2) Isomorphism between reactant and product lattices is not a necessary criterion for topotaxy.

(3) Both bimolecular and unimolecular reactions can give oriented crystalline products.

(4) Multiple reaction products can be simultaneously ordered by the reactant lattice.

(5) The symmetry directions in the reactant lattice are not necessarily parallel to symmetry directions of the product lattice.

(6) When reactant and product lattice symmetry directions are not parallel, twinning of the product phase will occur such that the reactant point-group symmetry is conserved.⁵

(7) When a 4 Å axis is present in both the reactant and product lattices, the product will align such that these axes are parallel. The 4 Å axes are not necessarily unique symmetry axes.

The present study is concerned with the topotactic photolysis and hydrolysis of two polymorphs (I- α and I- β) of 1-methoxy-1,2-benziodoxolin-3-one (I). Their molecular and crystal structures and the chemistry of these single crystal transformations were presented in the preceding paper in this series.⁶ I- α and I- β have the same molecular structures and conformations, the same intermolecular coordination interactions, and undergo identical chemical reactions. Differences in the

topotactic relationships observed for the two polymorphs, therefore, result from differences in molecular packing modes, lattice parameters, and space-group symmetry. I- α is the first example of an orthorhombic reactant lattice in this series (the others being triclinic or monoclinic), providing an opportunity to test the generality of conservative twinning in a high symmetry space group.⁵ In addition, neither I- α nor I- β have 4 Å axes (the shortest axis is >7 Å) to direct alignment of the product molecules. The fact that topotaxy occurred, nevertheless, has given us new insight into the factors controlling product crystallization.

Results

I- α to *o*-Iodobenzoic Acid (III). Photolytic decomposition by x-ray radiation of a single crystal of I- α leads to crystalline III (crystal data are given in Table I), which is oriented such that none of the zero-level reciprocal lattice planes of reactant and product are parallel. Figures 1 and 2 show the $(hk0)_{I-\alpha}$ Weissenberg pattern of reactant before and after decomposition to III, and the deconvoluted map of the product pattern.⁷ From this map one can clearly see two identical product lattices, indicating the formation of at least two twin phases of product. From the measured spacings of these lattices and comparison of the relative intensities of the product reflections with those of a reference pattern of III,⁸ the presence of the $(nk\bar{n})$ lattice of III in the $(hk0)$ photograph of I- α was verified. These planes actually diverge by 0.8°, as determined by oscillation photographs. Further verification of these lattice assignments and evidence for two more twin phases⁹ was obtained by calculating the angles needed to rotate the decomposed reactant crystal in order to observe zero-level patterns of III, and then turning the pseudomorphic crystal to these settings and comparing the patterns with reference films.

The orientation of the reactant lattice relative to one of the twin lattices of product can best be represented by the transformation matrix¹⁰ (eq 1), where $\{a^*\}_R$ and $\{a^*\}_P$ are reactant and product reciprocal lattice basis sets, respectively. Evaluation of this matrix (and its inverse transform) are given in Table II (available in the microfilm edition), where τ = angle between $\sigma(10\bar{1})_P$ and $\sigma(11\bar{1})_P$, ϕ = angle between $\sigma(100)_P$ and $\sigma(10\bar{1})_P$, and θ = experimentally determined angle of 0.8°.

To test whether this product orientation was unique to the single-crystal transformation, we tried subliming III onto the surfaces of single crystals of I- α . Three large crystals of I- α , with distinctly different morphologies (one was a flat diamond-shaped crystal with a prominent (100) face, another had bipyramidal morphology, and the third was irregularly shaped)

$$\psi_1 = \begin{pmatrix} a_R a_P^* \cos \phi \cos \tau & -b_R a_P^* (\cos \phi \sin \tau \cos \theta - \sin \phi \sin \theta) & -c_R a_P^* (\cos \phi \sin \tau \sin \theta + \sin \phi \cos \theta) \\ a_R b_P^* \sin \tau & b_R b_P^* \cos \tau \cos \theta & c_R b_P^* \cos \tau \sin \theta \\ a_R c_P^* \cos (\phi + \beta_P^*) \cos \tau & -b_R c_P^* (\cos (\phi + \beta_P^*) \sin \tau \cos \theta - \sin (\phi + \beta_P^*) \sin \theta) & -c_R c_P^* (\cos (\phi + \beta_P^*) \sin \tau \sin \theta + \sin (\phi + \beta_P^*) \cos \theta) \end{pmatrix} \quad (1)$$

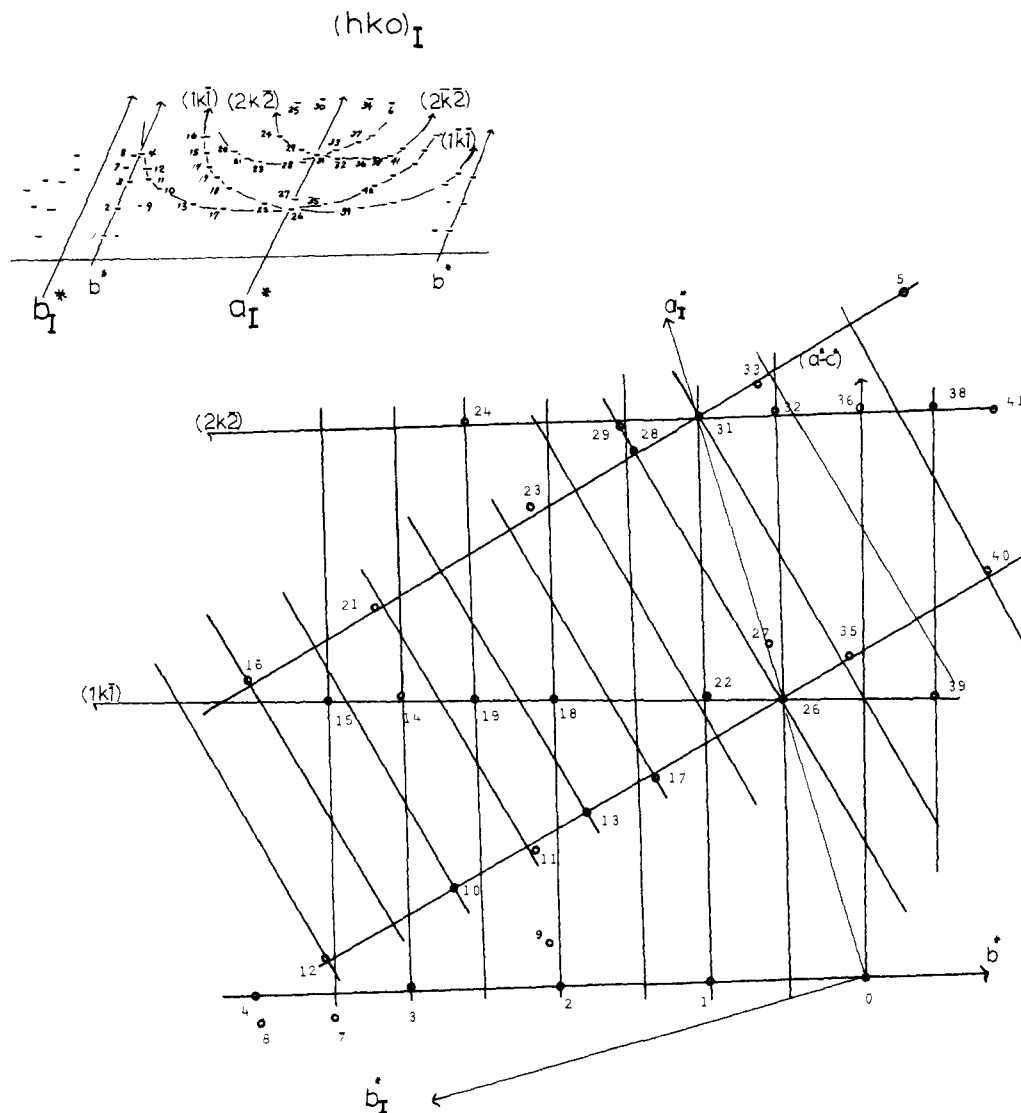


Figure 2. A graphical representation of the twinned product lattices of III in their observed orientations relative to the lattice of I- α . The reciprocal lattice-point numbers correspond to particular reflections seen in the $(hk0)_{I-\alpha}$ Weissenberg photograph of a decomposed crystal of I- α shown in Figure 1. (Axes labeled with subscripts I are reactant axes; unlabeled axes are product axes.)

were mounted on a glass slide. A sample of III was heated to 140° in the presence of these seed crystals and tiny crystallites of III grew equally well on all the faces of the seed crystals (as well as on the glass slide) and no preferred orientations were observed. Crystallization of III can also be nucleated in solution by seed crystals of I- α , but the growth of III on the seed crystals is not preferentially ordered.

I- β to III. The x-ray decomposition of single crystals of I- β leads to a highly powdered product phase for which a three-dimensional orientation could not be measured. Attempts were made to increase the product crystallinity by annealing the crystals, using different wavelength x-ray radiation, and using crystals of various sizes and histories, but no noticeable increase in product crystallinity was observed.

I- α to *o*-Iodosobenzoic Acid (II). Four product twins of equal concentration were found with their $(100)_{II}$ twin planes parallel to the $(100)_{I-\alpha}$ mirror plane. An $(h0l)$ Weissenberg pattern of I- α was shown to contain the $(hn2n)$ plane of II both by comparison of the reflection intensities of II with those of a standard film, as well as by location of the $(h0l)_{II}$ plane within the pseudomorphic crystal (an oscillation photograph about $[010]_{I-\alpha}$ in the range of $[112]_{II}$ showed that this reflection is precisely in the $(h0l)_{I-\alpha}$ plane). The transformation matrix, ψ_2 , as defined above for ψ_1 is:

$$\psi_2 = \begin{pmatrix} a_R a_P^* & 0 & 0 \\ 0 & b_R b_P^* \cos \theta & 0 \\ a_R a_P^* \cos \beta_P^* & b_R c_P^* \sin \theta \sin \beta_P^* & c_R c_P^* \sin \beta_P^* \cos \theta \end{pmatrix} \quad (2)$$

where $\theta = 60^\circ$ (the angle between $(hn2n)_{II}$ and $(h0l)_{II}$). Evaluation of this matrix is given in Table II in the microfilm edition.

I- β to II. Single-crystal hydrolysis of I- β leads to several Lonsdale twin phases of II (L-1 through L-5), which represent independent orientations of II (unrelated by the symmetry elements of reactant) and occur in unequal and variable concentrations. When I- β is hydrolyzed very slowly (1-2 years) by ambient humidity, L-2 to L-5 are formed in about equal concentrations; when I- β is hydrolyzed overnight in a saturated aqueous atmosphere at $\sim 50^\circ\text{C}$, L-1 is formed almost exclusively (if these crystals are allowed to sit on the shelf for about 6 months after being hydrolyzed, tiny brilliant crystallites of II can be seen growing out the ends of the pseudomorphic crystals, with their needle axes aligned parallel to that of the pseudomorph). L-1, which is conservatively twinned, can be formed in a very high crystalline yield in addition to being an

$$\psi_3 = \begin{pmatrix} 0 & (a_P^* \sin \theta)/b_R^* & (a_P^* \cos \theta)/c_R^* \\ -b_P^*/(a_R^* \sin \beta_R^*) & 0 & (b_P^* \cot \beta_R^*)/c_R^* \\ 0 & (c_P^* \sin (\theta - \beta_P^*))/b_R^* & (c_P^* \cos (\theta - \beta_P^*))/c_R^* \end{pmatrix} \quad (3)$$

unusually well-ordered product lattice with discrete reflections up to T values of 160° .

L-1 is oriented relative to I- β , such that its $(h0l)$ plane is parallel to $(0kl)_{I-\beta}$ and $[100]_{L-1}$ is 28° from $[001]_{I-\beta}$. This orientation is represented by ψ_3 (where $\theta = 28^\circ$):

The Lonsdale twins L-2 to L-5 occur in very low yields and are not as highly crystalline as L-1. The mosaic spread of their diffraction spots is about 4° , and there are also distinct powder rings associated with the more intense reflections. L-2 and L-3 are aligned such that their (100) planes are parallel to $(001)_{I-\beta}$, and their (010) planes are parallel to $(010)_{I-\beta}$ (necessarily aligning their glide directions, also). The $(100)_{II}$ planes are twin planes relating L-2 and L-3, which occur in equal concentrations. L-2 and L-3 differ in their relationships to I- β by their respective parallel and antiparallel alignment of \mathbf{b}_{II} relative to $\mathbf{b}_{I-\beta}$. Their topotactic matrices, derived directly from these basis set relationships are given in Table II as ψ_4 and ψ_5 .

Twins L-4 and L-5 also have their (010) planes parallel to $(010)_{I-\beta}$. Their $(100)_{II}$ planes are not twin planes, and are, respectively, 81 and 63° from $(100)_{I-\beta}$. Both twins are aligned such that their \mathbf{b} axes are antiparallel to $\mathbf{b}_{I-\beta}$ and there is no evidence that the corresponding twins with parallel \mathbf{b} axis alignments are formed. The topotactic matrices for L-4 and L-5 are given as ψ_6 and ψ_7 in Table II.

Crystalline Yields. The crystalline yield of a single-crystal reaction is a measure of the percent of crystalline reactant which has been converted to crystalline product. The yield can be calculated by comparing the ratio of the observed intensities (I_0) of a series of product reflections to their calculated absolute intensities (F_c^2) and comparing these ratios to I_0/F_c^2 for a series of reactant reflections. If the crystalline yield is quantitative, the reactant ratios should be the same as the product ratios, after correction for unit cell volume differences.

The percent yield of crystalline III can be calculated by use of the following formula:

$$\left(\frac{(tI_0/F_c^2)_{III}}{(I_0/F_c^2)_{I-\alpha}} \right) \left(\frac{V_{III}}{V_{I-\alpha}} \right) = \% \text{ yield of III}$$

where I_0 = corrected measured intensity of an hkl reflection, F_c = calculated structure factor of an hkl reflection, on an absolute scale, V = unit cell volume, and t = twinning factor (multiplicity of an hkl reflection, resulting from twinning).

From the intensities of five reactant and four product reflections, the calculated average crystalline yield of III was 23% (with specific yields ranging from 11 to 40%).

Quantitative measurements of crystalline product yields of hydrolysis reactions were not successful, since exposure to x-ray radiation prior to hydrolysis resulted in very poorly ordered product.

Discussion

The most predictable mode of product orientation in the previously studied topotactic reactions of fenziodoxole compounds has been the alignment of parallel 4 \AA axes of reactant and product.¹¹ The significance of this mode in directing product crystallization becomes important in the current investigation, since neither the I- α nor I- β reactant lattice has a 4 \AA axis, but both product lattices do. If the alignment of short axes of similar lengths is requisite for ordering product nuclei, then II and III should grow such that their 4 \AA axes align parallel to vectors in I- α and I- β whose lengths are integer

multiples of 4 \AA . However, if 4 \AA axes are parallel as a *consequence* of the parallel alignment of crystallographic planes with a 4 \AA interplanar spacing, then the 4 \AA unique axis of II should align parallel to a reciprocal space vector $\sigma(hkl)$ of I- α or I- β of length 0.25 \AA^{-1} . In the former case, this lattice-matching mode implies aligning direct-space vectors, and in the latter case, aligning reciprocal space vectors. In the transformations discussed here we have found that both modes of lattice matching occur with the important condition that the vectors of interest are either parallel to a stack of iodine atoms or normal to a layer of iodine atoms in *both* reactant and product. These vectors are usually 4 \AA long, corresponding to close-packing of the iodine atoms.

There is no evidence from the current work that specific topotactic relationships are adopted as a result of minimum molecular motion pathways. The reactant and product lattices studied were not isomorphous, and some were even in different crystal classes, so large molecular motions were needed to form crystalline products. Indeed, there is sufficient molecular mobility that the product molecules crystallize in the same forms as those obtained from solution crystallization.¹²

I- α \rightarrow III. There are four conservative twin phases of III formed in this transformation, each of which has $(nn\bar{n})$ coincident with $(h00)_{I-\alpha}$. None of the axial directions or symmetry planes of reactant are parallel to those of III, and the alignment of the 4.10 \AA \mathbf{a} axes of the twins of III appear to have no significance relative to the reactant lattice. The crystal structure of III has been solved in projection only,¹³ from which the molecules are seen to pack as centrosymmetric dimers with their molecular planes approximately parallel to $(100)_{III}$. In the reactant structure, four pairs of planar dimers occur per unit cell, but none of these planes are parallel to $(100)_{III}$. We were unable to find any molecular correspondences between reactant molecules and oriented product molecules which might have been important in directing the orientation of the product phases. In fact, *extensive molecular reorganization would have had to occur during transformation of I- α into any orientation of III.*

From reinvestigation of the x-ray diffraction patterns of a decomposing crystal of I- α , we realized that one pair of overlapping reflections occurred between an intense reflection of reactant, $[400]_{I-\alpha}$, and a similarly intense product reflection, $[11\bar{1}]_{III}$, implying that their corresponding direct-space planes contained a large fraction of the scattering matter in each structure and also had the same interplanar spacing. Indeed, the family of planes parallel to $(100)_{I-\alpha}$ with an interplanar spacing of $d(400) = 3.86 \text{ \AA}$ (here referred to as the $(400)_{I-\alpha}$ planes) do contain all the iodine atoms in the I- α structure. The $(11\bar{1})_{III}$ planes not only pass through all the iodine atoms of III and have $d(11\bar{1}) = 3.86 \text{ \AA}$, but also the $(11\bar{1})$ planes of all four product twin phases are mutually parallel. In effect, the iodine atoms in the reactant crystal and multiply twinned product crystal are in the same set of $\sim 4 \text{ \AA}$ spaced planes! This phase transformation, shown schematically in Figure 3, suggests that the motion of the heavy atoms has been restricted to these two-dimensional close-packed planes, but that the molecules could freely move about the iodines in order to establish the product crystal structure.

This concept is also consistent with those transformations in which 4 \AA axes of reactant and product were aligned, since in most cases 4 \AA iodine-containing planes were normal to the short axes. When the 4 \AA axis was not the unique monoclinic axis, it was nearly perpendicular to its (100) plane (the largest

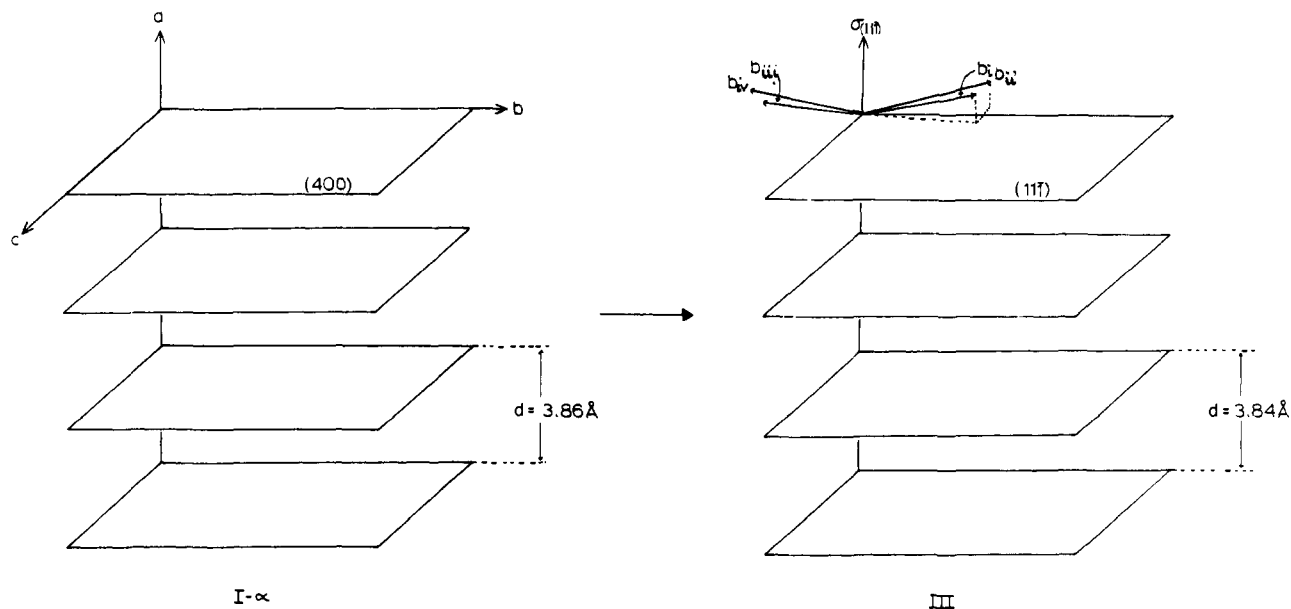


Figure 3. A schematic representation of the transformation of iodine-containing planes in I- α to those in III. The family of planes parallel to $(100)_{I-\alpha}$ with interplanar spacings of $d(400) = 3.86 \text{ \AA}$, containing all the iodine atoms of the reactant structure, are shown on the left. During transformation to III, the family of $(100)_{I-\alpha}$ planes are maintained parallel to the similarly spaced iodine-containing $(11\bar{1})$ planes ($d(11\bar{1}) = 3.84 \text{ \AA}$) of all four twin phases of III, shown on the right (b_{i-iv} are the unique symmetry axes of the four twins).

deviation observed so far being 6.7° ¹¹). For III, the short **a** axis is not precisely normal to $(100)_{III}$ ($\beta = 91.5^\circ$), but its **a** axis nevertheless had always been found parallel to a 4 \AA axis of reactant. In the transformation of I- α to III, an analogous alignment would have made \mathbf{a}_{III} parallel to $\mathbf{a}_{I-\alpha}$, with the iodine-containing $(100)_{III}$ and $(400)_{I-\alpha}$ planes 1.5° apart. In this case, however, the interplanar spacings would have been mismatched, since $d(100)_{III} = 4.31$ and $d(400)_{I-\alpha} = 3.86 \text{ \AA}$. The more closely matched set of planes, $(11\bar{1})_{III}$ and $(400)_{I-\alpha}$, were aligned instead, suggesting that *a 4 \AA axis in the product lattice is important in determining the orientation of product only when it is normal to (or nearly normal to) a set of iodine-containing planes*¹⁴ with an interplanar spacing equal to that of a set of iodine-containing reactant planes.

The alignment of $(400)_{I-\alpha}$ and $(11\bar{1})_{III}$ also demonstrates that the reactant lattice influence on the reorganization of product molecules is highly stereospecific.¹⁵ The intensities of the $(1k1)_{III}$ and $(1k\bar{1})_{III}$ festoons are very similar due to the pseudo-orthorhombic structure of III, however, no Lonsdale twin with $(111)_{III} \parallel (400)_{I-\alpha}$ is observed. The interplanar spacings of (111) and $(11\bar{1})$ are nearly identical as well (3.86 and 3.84 \AA , respectively). Since aligning parallel planes is only a one-dimensional restriction on the product orientation, the subtle differences in structure between (111) and $(11\bar{1})$ may be significant in determining the final three-dimensional alignment.

I- β \rightarrow III. III is not formed as a well-ordered preferentially oriented product phase from I- β , possibly due to the lack of similar iodine atom packing modes. The structure of I- β does have close-packed iodine-containing planes, but the 3.40 \AA spacing of these (100) planes does not match well with the spacing of iodine-containing planes of III. In addition, the 7.73 \AA **a** axis of I- β is not a close multiple of the 4.32 \AA **a** axis of III, nor is $\mathbf{a}_{I-\beta}$ normal to $(100)_{I-\beta}$ ($\beta = 118.3^\circ$). Inversion related dimers in I- β have very nearly the same intermolecular geometry as inversion related hydrogen-bonded molecules of III, so one might expect that these carboxylic acid dimers could form individually with little reactant lattice destruction. The fact that this does not occur illustrates the danger of invoking specific molecular mechanism to justify product orientation.

I- α \rightarrow II. II is formed readily as an oriented single-crystal

phase from hydrolysis of many benzyloxy-substituted benzyloxole compounds and it has always been oriented such that its 4.32 \AA **b** axis was parallel to a 4 \AA axis of reactant even though the (010) planes of II do not contain all the iodines of the product structure (the iodine atoms are layered in planes parallel to (010) with an interplanar spacing of $d(020) = 2.16 \text{ \AA}$ ¹⁶). The iodine atoms in II are also clustered about the $(100)_{II}$ planes, which have been shown to be important in determining the topotactic relations in these reactions as well as frequently being formed as a twin plane in the pseudomorphic product crystals. In the transformation of I- α to II the $(100)_{II}$ planes are again significant, since they are formed as the twin plane for all four conservative twin phases of II, and are aligned parallel to $(100)_{I-\alpha}$. In this case there is no one-dimensional correspondence between either the (100) lattice planes of I- α and II or the iodine-containing planes parallel to these (100) planes ($d(100) = 15.44$ and 12.82 \AA for I- α and II, respectively), and the spacing between the iodine-containing planes is 3.86 and 12.82 \AA , respectively). Instead, it appears that these (100) planes are forming an interphase boundary, where $(100)_{II}$ has oriented on $(100)_{I-\alpha}$ to generate several low index direct-space lattice site coincidences (Figure 4):

$$\begin{array}{ll}
 \text{A: } [\pm 3b \pm c]_{I-\alpha} = [6b + c]_{II} & [3b + c]_{I-\alpha} = 27.80 \text{ \AA} \\
 \text{E: } [\pm 2c]_{I-\alpha} = [-6b + c]_{II} & [2c]_{I-\alpha} = 27.06 \text{ \AA} \\
 & [\pm 6b + c]_{II} = 28.50 \text{ \AA} \\
 \text{B: } [\pm 2b]_{I-\alpha} = [2b + c]_{II} & [2b]_{I-\alpha} = 16.2 \text{ \AA} \\
 \text{D: } [\pm b \pm c]_{I-\alpha} = [-2b + c]_{II} & [b + c]_{I-\alpha} = 15.8 \text{ \AA} \\
 & [\pm 2b + c]_{II} = 16.3 \text{ \AA} \\
 \text{C: } [\pm 3b \pm c]_{I-\alpha} = [2c]_{II} & [3b + c]_{I-\alpha} = 27.80 \text{ \AA} \\
 & [2c]_{II} = 28.10 \text{ \AA}
 \end{array}$$

This remarkable lattice match aligns pairs of symmetry-equivalent product vectors parallel to pairs of non-symmetry-equivalent reactant vectors. The product lattice, in effect, has discovered that vectors **A** and **E**, and vectors **B** and **D**, in the reactant lattice are pseudotwin vectors which coincidentally have the same lengths. II has aligned itself such that its (010) mirror plane is parallel to **C**, the pseudotwin plane of reactant

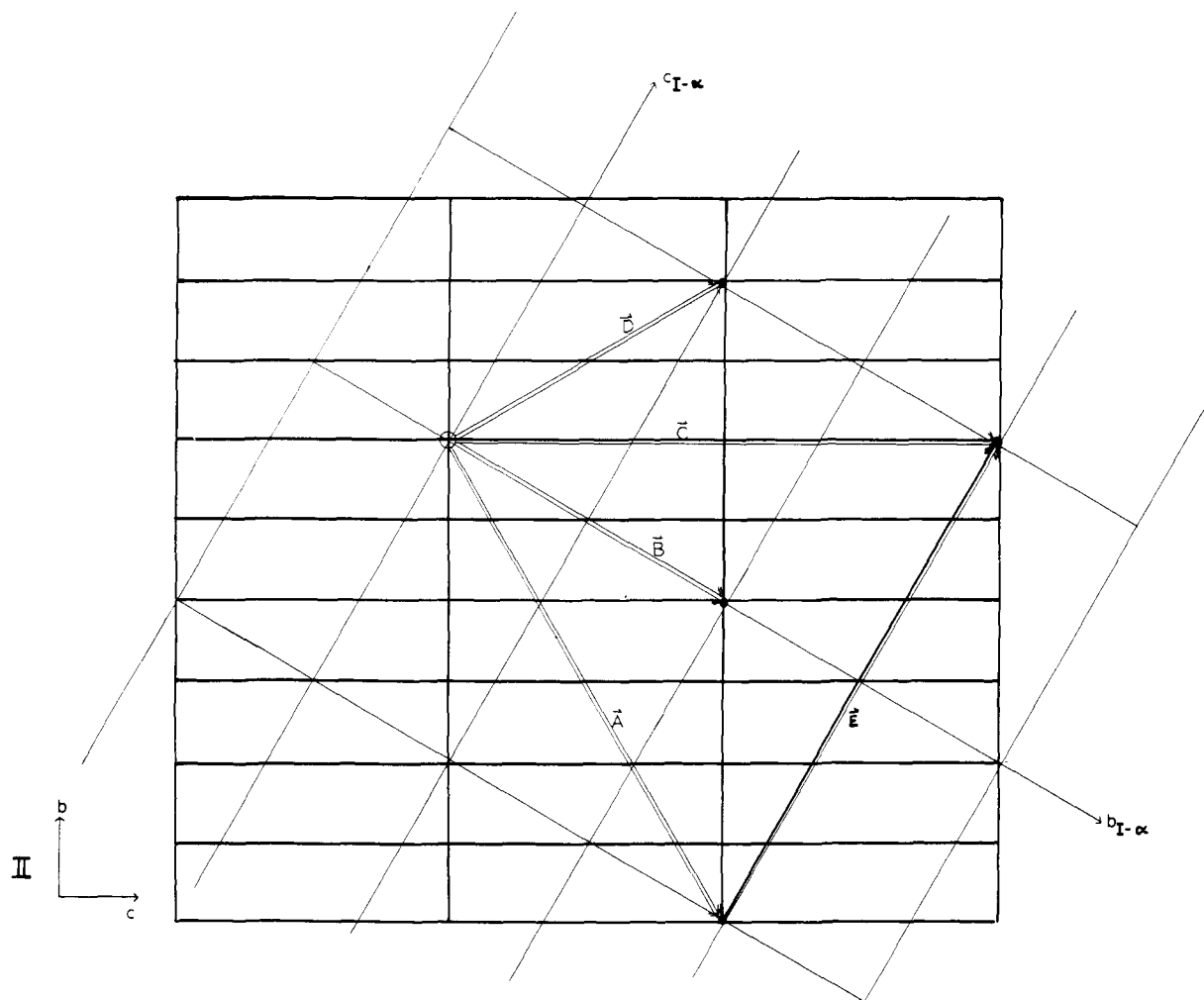


Figure 4. A possible interface between $(100)_{I-\alpha}$ and $(100)_{II}$ consistent with the observed topotactic relationships. This interface creates multiple direct-space lattice site matches, as indicated by vectors A–E. The vector pairs B–D and A–E are symmetry-equivalent vector pairs of the product, but are only coincidentally equivalent vectors of the reactant.

(this pseudotwinning is purely a geometrical effect; there is no structural equivalence between the vectors **A** and **E**, or **B** and **D**, of reactant). The product lattice has not, however, grown a second Lonsdale twin phase by actually twinning about **C**, even though such a twin would have preserved the pseudosymmetry properties of the reactant.¹⁷ If one were able to design the reverse reaction $II \rightarrow I-\alpha$, and if their (100) planes were similarly aligned, the conservative twinning imposed by **II** on the crystallization of $I-\alpha$ should generate this second Lonsdale twin relationship.¹⁸

Formation of a good lattice fit at an interface during pseudomorphic transformation implies an epitaxial mechanism whereby two discrete chemical phases form a boundary, and at least one phase is mobile enough to establish a thermodynamically favorable alignment at this boundary. This is quite different than the layering mechanisms proposed for $I-\alpha \rightarrow III$, in which it was postulated that product molecules could be formed within layers of the reactant lattice and no discrete chemical interphase was necessarily ever formed. By the latter mechanism the parallel reactant and product planes must have the same interplanar spacings, while for the former mechanism the interplanar spacing of the parallel planes forming an interphase is irrelevant. In light of these differences, it should be noted that there are several sets of mutually parallel reactant and product planes of $I-\alpha$ and **II** which have $\sim 4 \text{ \AA}$ interplanar spacings and, in fact, one of these sets contains all the iodine atoms of reactant and product. $(004)_{I-\alpha}$ and $(01\bar{2})_{II}$ are parallel with $d(hkl) = 3.38$ and 3.55 \AA , respectively. There are no isostructural features common to the molecular packing in

these reactant and product planes other than the clustering of iodine atoms about $(01\bar{2})_{II}$ and $(002)_{I-\alpha}$. Figure 5 shows the geometric relationships between these planes and the iodine positions in both structures. It is also shown that there is some similarity in the iodine positions within these planes, as every other iodine is displaced 8.1 \AA along a vector parallel to $b_{I-\alpha}$.

$I-\beta \rightarrow II$. Even though photolytic decomposition of $I-\beta$ gives powdered **III**, hydrolysis of $I-\beta$ gives well-ordered **II** in high crystalline yields. There are several distinct Lonsdale twin orientations of **II** formed from $I-\beta$. The predominant twin phase (L-1) is aligned such that $a_{1,\beta}$ is strictly parallel to b_{11} . Their vector lengths are different ($a_{1,\beta} = 7.73 \text{ \AA}$, $b_{11} = 4.10 \text{ \AA}$), but $a_{1,\beta}$ is the glide direction, so the intermolecular spacing in this direction is just 3.86 \AA . If one considers only the iodine positions in the crystal structures of $I-\beta$ and **II**, some very interesting similarities are seen, as shown schematically in Figure 6. The predominant pattern is stacking of close-packed iodine atoms pairwise into columns parallel to $a_{1,\beta}$ and b_{11} , suggesting that during the single-crystal transformation of $I-\beta$ to L-1, where these directions are parallel, the iodine atoms remain stacked within these columns. Molecular reorganization about the iodine atoms of the reactant and subsequent rotation and translation of the stacks of iodine atoms lead to the observed orientation of **II**.¹⁹ (In addition the $(01\bar{2})_{II}$ planes, which were important in the transformation of $I-\alpha$ to **II**, are parallel to the $(\bar{2}12)$ planes of $I-\beta$ which have the same interplanar spacing. In this case there is no obvious molecular correspondence between these sets of planes.)

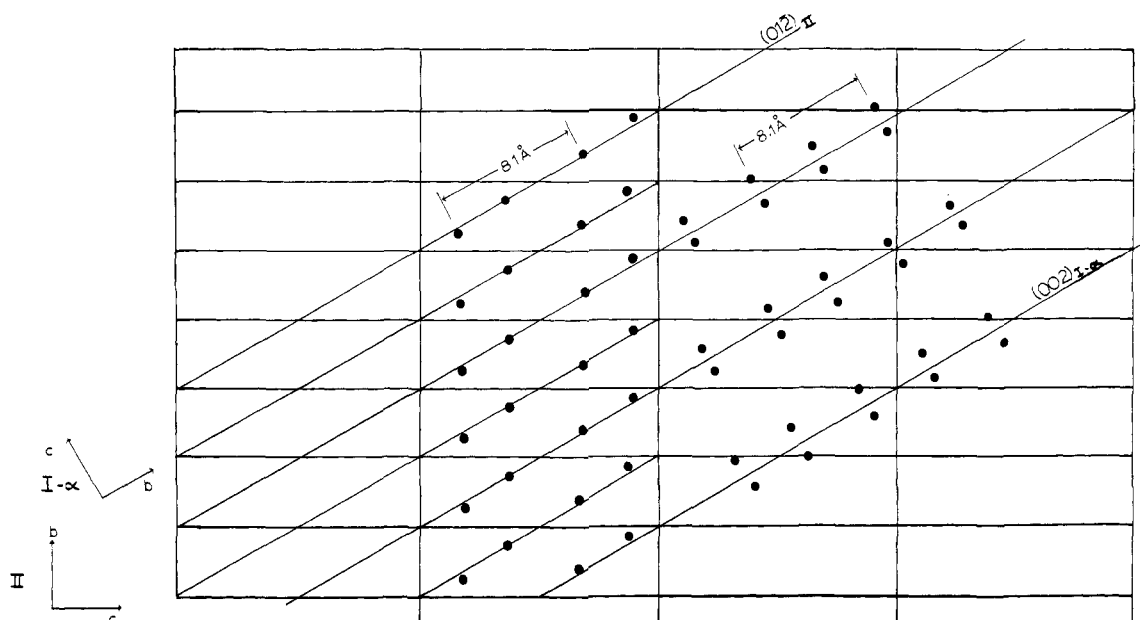


Figure 5. The observed parallel alignment of the (002) planes of I- α and the (012) planes of II showing the similar spacing between planes of iodine atoms as well as between iodine atoms aligned along $[010]_{I-\alpha}$.

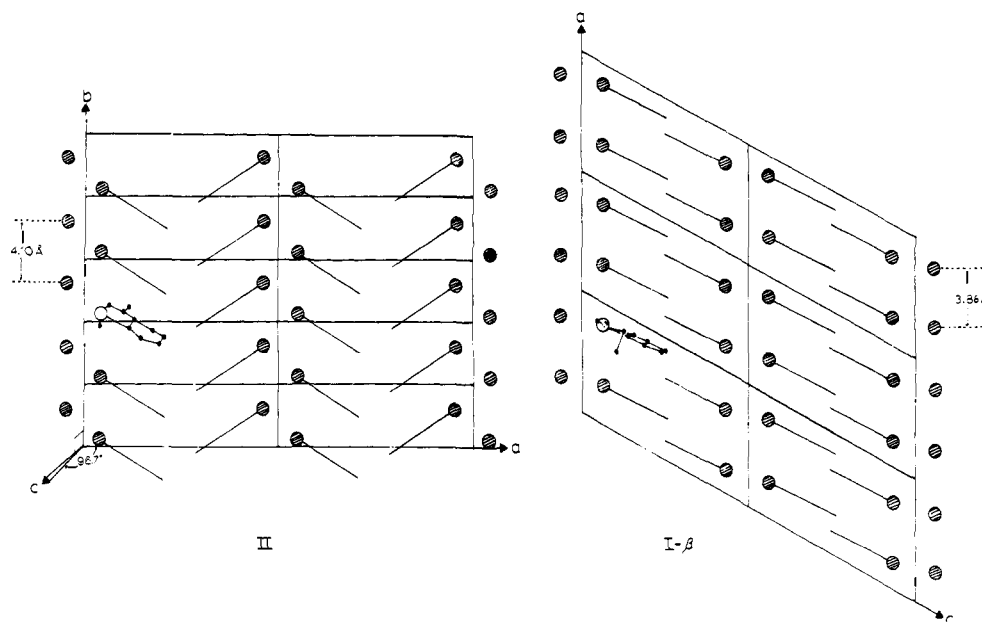


Figure 6. Stacks of close-packed iodine atoms directed along b_{II} and $a_{I-\beta}$ are found parallel in the transformation of I- β to II in Lonsdale twin orientation L-1. The iodine stacking modes are shown here in the $(001)_{II}$ and $(010)_{I-\beta}$ planes, with the iodines represented by large circles (only half of the molecules in the unit cell of II are shown, the other c glide related half also form iodine stacks parallel to b_{II} ¹⁶). For each structure, one molecule is drawn in its correct configuration and orientation and the other molecules are represented by stick figures drawn parallel to the molecular planes. The $(001)_{II}$ plane and $(010)_{I-\beta}$ planes drawn parallel here actually make an interplanar angle of 35° in the L-1 orientation of II relative to I- β .

From Figure 6, one can see that translation of the iodine stacks of product and reactant along either c_{II} or $b_{I-\beta}$, respectively, would generate layers of iodine atoms parallel to $(100)_{II}$ and $(001)_{I-\beta}$. It is these layers, with interplanar spacings of 12.82 and 11.11 Å, that are parallel for both Lonsdale twin phases L-2 and L-3, and in this orientation the $(100)_{II}$ planes are necessarily twin planes relating the product phases (in several other transformations in which multiple phases of II were formed, including the transformation of I- $\alpha \rightarrow$ II, the $(100)_{II}$ planes were also twin planes). It is possible that only one of these Lonsdale twins represents a thermodynamically favorable orientation relative to I- β , and that after formation it induces growth of its twin at a product-product interface. On the other hand, orientation of twinned product nuclei could be directed by the reactant lattice such that both twins had

favorable alignments, neither of which would necessarily have occurred had the product nuclei not been twinned prior to orientation. It is interesting in this regard that the Lonsdale twin phases L-4 and L-5 are not twinned about $(100)_{II}$ and their specific topotactic relationships relative to I- β are different than those of either L-2 or L-3.

The c glide directions of L-2 and L-3 are parallel to the a glide of reactant, and the (010) planes of reactant and product phases are also parallel.²¹ Why these axial directions are aligned is not clear, since their glide axis lengths are different, and their respective (010) planes have no apparent iodine-packing or molecular packing similarities. The (010) planes of L-4 and L-5 are also parallel to the (010) planes of I- β , L-2, and L-3, but their a glide directions and their $(100)_{II}$ planes seem to have no special significance relative to the reactant

lattice. Further analysis of interlattice relationships in reactions leading to multiphase crystalline products is in progress.

Experimental Section

Single Crystal Reactions. The stoichiometry and reaction conditions for the photolysis and hydrolysis reactions of bulk crystalline samples of $l\text{-}\alpha$ and $l\text{-}\beta$ were presented in the preceding paper.⁶ The photolysis of a single crystal was carried out by irradiating a crystal, mounted on a goniometer, with collimated x-ray radiation (Cu $K\alpha$, 45 kV, 14 mA) in the standard set-up for diffraction photographs. The reactions were followed by taking successive Weissenberg (or precession) photographs until the reactant lattice diffraction pattern had disappeared. In this manner the relative orientations of the reactant and product lattices can be readily assessed, since the crystal orientation is fixed.

Hydrolysis of single crystals was usually carried out on a batch of crystals, from which one crystal was selected which still had some transparency, indicative of the unchanged reactant lattice. The diffraction patterns of both product and reactant lattice could then be seen, in their relative orientations, from a single Weissenberg photograph. In analyzing the topotactic diffraction patterns, many independent reactant crystals with various histories and in varying degrees of decomposition were photographed and in each case the topotactic relationships between reactant and product were precisely reproducible.

The crystalline product phases were identified by comparison of their diffraction patterns with reference patterns from independently crystallized samples.

Crystalline Yields. To measure the crystalline yield of III formed from $l\text{-}\alpha$, an $(0kl)$ pattern of a single crystal of $l\text{-}\alpha$ was recorded for 24 h. The crystal was then exposed to xrays until decomposition to III was complete (~ 1 week) and the diffraction pattern of the pseudomorphic crystal was then recorded on the same film and for the same exposure time as the original reactant pattern. The intensities of several reactant and product reflections were visually estimated and corrected for Lorentz and polarization factors. To minimize relative errors due to absorption, the particular reflections chosen all fell within a limited ω range. The ratio of I_0/F_c^2 , where I_0 is the corrected measured intensity and F_c is the calculated structure factor of an (hkl) reflection, was calculated for each reflection and used to determine the crystalline yield of 23% (as described under Results).

Acknowledgment. The financial support of the National Science Foundation and the Minnesota Mining and Manufacturing Co. is gratefully acknowledged. I am also very grateful to Professor Jack Gougoutas, who introduced me to this novel field of chemistry and who has enthusiastically and critically guided much of this work.

Appendix

General Considerations in Analyzing Topotactic Relationships. Interlattice relationships which are physically significant in interpreting the observed topotaxy can readily be calculated from the transformation matrix, ϕ_{ij} , relating the direct basis set vectors \mathbf{b}_i (product lattice) and \mathbf{a}_j (reactant lattice):⁵

$$\mathbf{b}_i = \phi_{ij} \mathbf{a}_j$$

A brief outline of the methods used to determine the relationships discussed in this paper are given here.²²

(1) Transformation of reciprocal lattice basis vectors.

$$b_i^* = (\phi_{ji})^{-1} a_j^* = \psi_{ij} a_j^*$$

$$\mathbf{b}_i^* \cdot \mathbf{a}_j = \psi_{ij}$$

(2) Determination of coincident lattice sites between direct-space lattices.

$$\mathbf{V}_i = \sum_j K_j \mathbf{b}_j = \sum_j H_j \mathbf{a}_j = \mathbf{V}_j$$

$$K_i = (\phi_{ji})^{-1} H_j$$

When a particular set of integer H_j components of \mathbf{V}_j generates integer K_i components of \mathbf{V}_i , the lattice points defined

by \mathbf{V}_i and \mathbf{V}_j may be coincident. If noninteger K_i components are generated, then \mathbf{V}_i and \mathbf{V}_j are still parallel, but \mathbf{V}_i does not terminate at a lattice site.

(3) Determination of which direct-space planes of the product lattice are parallel to particular reactant planes.

This is equivalent to determining sets of parallel reciprocal lattice vectors:

$$\begin{aligned} \sigma_i &= \sum_j k_j b_j^* = \sum_j h_j a_j^* = \sigma_j \\ k_i &= \phi_{ij} h_j \end{aligned}$$

When a set of h_j components of σ_j generates integer k_i components of σ_i , the direct-space planes with Miller indices $\{h_j\}$ and $\{k_i\}$ are parallel and have the same interplanar spacings.²⁴

(4) Determination of the angle, θ , between a set of planes in the reactant direct-space lattice and a set of planes in the product direct-space lattice.

The angle between the plane normals, σ_j and σ_i , can be determined from the dot product relationship

$$\sigma_j \cdot \sigma_i = \sigma_j \sigma_i \cos \theta = \sum_i \sum_j k_i k_j (b_i^* \cdot b_j^*)$$

where σ_j and σ_i are vectors expressed in the reciprocal basis set $\{b_i^*\}$. σ_i was originally defined as a vector in the reactant basis set and its components were transformed by $k_i = \phi_{ij} h_j$.

(5) Determination of the orientations of conservatively twinned lattices.

$$C_{ki} \phi_{ij} = \phi_{kj}$$

ϕ_{ij} is the known topotactic matrix for one of the product lattice orientations. C_{ki} are matrix representations of the point-group symmetry elements of the reactant lattice, and ϕ_{kj} are the matrices relating the twinned lattices to the reactant lattice.

Supplementary Material Available: Table II, which contains all the topotactic matrices and their inverse transforms (2 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) Partially based on a Ph.D. thesis by M. C. Etter, University of Minnesota, Dec 1974; (b) National Science Foundation Predoctoral Fellow, 1970–1973, Minnesota Mining and Manufacturing Predoctoral Fellow, 1973–1974.
- (2) G. M. J. Schmidt and M. D. Cohen, "Reactivity of Solids", T. J. deBoer, Ed., Elsevier, Amsterdam, 1961, p 556.
- (3) M. D. Cohen and B. S. Green, *Chem. Br.*, **9**, 490 (1973); R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, **96**, 6329 (1974); D. Y. Curtin and I. C. Paul, *Acc. Chem. Res.*, **6**, 217 (1973); and R. H. Baughman, *J. Polym. Sci.*, **12**, 1511 (1974).
- (4) J. Z. Gougoutas, *Pure Appl. Chem.*, **27**, 305 (1971).
- (5) J. Z. Gougoutas, *Isr. J. Chem.*, **10**, 395 (1972).
- (6) M. C. Etter, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (7) G. B. Carpenter, "Principles of Crystal Structure Determination", W. A. Benjamin, New York, N.Y., 1969, p 70.
- (8) Because of the pseudo-orthorhombic character of III, the intensities of $(nk\bar{n})$ and (nkn) festoons are very similar. A careful comparison of the product reflections with the $(1k1)$, $(1k\bar{1})$, $(2k2)$, and $(2k\bar{2})$ festoons of a reference pattern of II, verified the presence of only the $(nk\bar{n})$ reflections in $(hk0)_{l\text{-}\alpha}$.
- (9) In this paper a crystalline phase is an array of molecules, which gives rise to a discrete diffraction pattern. Crystalline phases which are identical except for their orientation relative to the reactant crystal lattice are called twin lattices. In this sense, the term twin is used for two or more phases of the same structure.
- (10) There are several unidentified and generally weak product reflections (which are conservatively twinned about reactant symmetry elements) observed in reactant zero-level zones. There is a slight, but significant variation in the intensity of these anomalous reflections relative to diffraction intensities of the major product phase. They represent a distinct oriented product phase of low concentration, for which the topotactic orientation has not been solved.
- (11) J. Z. Gougoutas, K. H. Chang, and M. C. Etter, *J. Solid State Chem.* **283** (1976).
- (12) Novel crystalline forms have been trapped within transforming pseudomorphic crystals during topotactic reactions of several 2-iodo-(2'-halo)-dibenzoyl peroxides.⁴
- (13) L. Lessinger, Ph.D. Dissertation, Harvard University, Oct 1971.

- (14) Iodine-containing planes refer here to a family of planes which contain all or a large fraction of the iodine atoms in the structure and represent a predominant iodine-layering packing mode (i.e., these planes usually have an interplanar spacing of 3.4 Å or greater).
- (15) The high stereospecificity of this kind of reactant lattice control in centrosymmetric crystals of $I-\alpha$ suggests the possibility that a chiral reactant lattice could preferentially orient one enantiomeric product lattice. If a chemically racemic product were formed during a single-crystal reaction, the chiral reactant lattice might be able to effect a chemical resolution of the racemate by inducing crystallization of only one enantiomeric crystal form. Likewise, a crystallographic resolution of nonchiral product molecules which pack in enantiomeric space groups is also theoretically possible in a topotactic reaction.
- (16) E. Shefter and W. Wolf, *Nature (London)*, **203**, 512 (1964).
- (17) This would represent a Lonsdale twin phase generated by conservative twinning about the product lattice point-group symmetry elements.
- (18) Attempts to effect this conversion by diazomethane esterification of single crystals of II were unsuccessful.⁶
- (19) In the conversion of anthracene photooxide to anthraquinone, one of the first examples of an organic topotactic reaction, Lonsdale clearly demonstrated the importance of aligning molecular stacks of reactant and product molecules.²⁰ In this case the molecular stacks were defined by close-packed aromatic rings, since there were no heavy-atom substituents.
- (20) K. Lonsdale, E. Nave, and J. F. Stephens, *Philos. Trans., R. Soc. London, Ser. A*, **261**, 1 (1966).
- (21) Precisely the same topotactic relationships exist between twin phases of II formed from 3-oxo-3H-2,1-benzoxiodol-1-yl- α -fluorobenzoate, but in this case the $(100)_I$ twin plane is parallel to the mirror plane of the reactant.¹¹ The twin phases are, thus, conservative twins resulting from twinning about the point-group symmetry elements of reactant. The twin phases formed from I- β , however, are not conservatively twinned, but still occur in equal concentrations, giving credence to the postulate made by Gougoutas that the specific topotaxy between reactant and twinned product phases may be established in order to produce a favorable interphase relationship between the product twins.¹¹
- (22) The vector relationships were derived from fundamental crystallographic properties of the direct and reciprocal basis sets, as defined by Buerger.²³
- (23) M. J. Buerger, "Crystal Structure Analyses", Wiley, New York, N.Y. 1960, p 407.
- (24) The interplanar spacings are the same when both $\{h_j\}$ and $\{k_j\}$ are prime numbers; when one set is not prime the interplanar spacings are integer multiples of each other.

Molecular Criteria of Solid-State Structure in Organic Charge-Transfer Salts. 2. Effect of Methyl Substitution on Stacking Interactions of *p*-Phenylenediamine Cation Radicals

Frank B. Kaufman

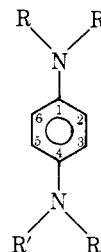
Contribution from the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598. Received April 18, 1975

Abstract: The ability of *p*-phenylenediamine cation radicals to self-associate and form sandwich dimers or higher aggregates was found to be a function of methyl substitution, $\text{TMPD}^{\cdot+}$ (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) $<$ $\text{DMPD}^{\cdot+}$ (*N,N*-dimethyl-*p*-phenylenediamine) \approx $\text{PPD}^{\cdot+}$ (*p*-phenylenediamine). The gas-phase ionization potentials or electrochemical disproportionation ($2\text{D}^{\cdot+} \rightleftharpoons \text{D}^0 + \text{D}^{2+}$) energies showed no correlation with the observed association properties. However, the enthalpy of dimerization (ΔH) was found to be proportional to the experimental unpaired π -electron spin density at the terminal ring carbons of the ion radicals. Steric considerations were shown to be relatively unimportant in the self-association processes. The relationship between these molecular data and the solid-state structure of salts formed by these cation radicals was discussed.

Since the initial discovery that certain organic ion radicals form stable solids,¹ a wide variety of these solids, displaying a surprising range of physical properties, has been synthesized and studied.² In the last 15 years, growing interest based on the pioneering research of the duPont group³ has centered on the preparation of increasingly more metallic organic charge-transfer salts. Until recently, however, synthetic efforts to prepare molecules which formed solids with specific types of physical properties have been largely guided by trial and error or structural analogy to known molecules. Fortunately, concerted attempts are currently being made to understand and control the relationship⁴⁻⁶ between molecular structure and solid-state properties for these materials in hopes of making the selection of potentially interesting molecules less haphazard.

In a general sense the connection between the molecular structure of the constituent molecules D (Donor) and A (Acceptor) and the physical properties of the resulting solid is related to the way in which the $\text{D}^{\cdot+}$ and $\text{A}^{\cdot-}$ ion radicals stack in the solid state.^{2,4} Since the most interesting solid-state effects appear to be associated with the formation of separate, equally spaced infinite stacks of planar $\text{D}^{\cdot+}$ or $\text{A}^{\cdot-}$ species,⁷ it is important to understand how changes in molecular architecture affect this type of ion-radical stacking.

To begin to answer this question we have studied the physical properties of a series of donor ion radicals which form self-stacked bromide salts, $\text{D}^{\cdot+}\text{Br}^-$. The presence of only one type of organic ion radical (i.e., donor) should minimize the presence of complicating interstack interactions. The ion-radical donors studied are a homologous series of aromatic diamines:⁸ *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD),



TMPD, $\text{R} = \text{R}' = \text{CH}_3$
 DMPD, $\text{R} = \text{H}; \text{R}' = \text{CH}_3$
 PPD, $\text{R} = \text{R}' = \text{H}$

N,N-dimethyl-*p*-phenylenediamine (DMPD), and *p*-phenylenediamine (PPD). We seek to understand why removal of two methyl groups from one side of the molecule in going from TMPD to DMPD results in a corresponding decrease in