Table V. Percentage of Deuterium Incorporation and Hydrolysis Rate Constants of Selected Vinyl Selenides

compd	% D incorptn[a]	$k_{H_3O^+}$, s^{-1}
$C_6H_5-C(SeCH_3)=CH_2$	31	5.29×10^{-3} [c]
p-$NO_2C_6H_4-C(SeC_6H_5)=CH_2$	4[b]	
$C_6H_5-C(SeC_6H_5)=CH_2$	32	3.43×10^{-4} [c]
$CH_3-C(SeC_6H_5)=CH_2$	5	1.5×10^{-3} [c]
$H-C(SeC_6H_5)=CH_2$	0	3.08×10^{-4} [d]
$H-C(SeCH_3)=CH_2$	7.5	4.59×10^{-3} [d]

[a] Determined on the recovered vinyl selenide after ~50% conversion. [b] Hydrolysis conversion was only ~10%. [c] In 60/40 v/v dioxane/water (1 M in $HClO_4$) at 30 °C. [d] In 60/40 v/v dioxane/water (1 M in $HClO_4$) at 60 °C.

group and also that the former should be more basic than the latter. Therefore intermediate **3** is more likely to accumulate during hydrolysis of phenyl vinyl selenides than in the case of methyl vinyl selenides. Yet, reversibility is only observed for the latter. Futher support for this is provided by the observation that α-(phenylseleno)styrene incorporates about the same amount of deuterium (~32%, see below) as does α-(methylseleno)styrene (Table IV).

Selenium-Stabilized Carbonium Ions. From measurements of hydrolysis rates of phenyl vinyl ethers, sulfides, and selenides McClelland and Leung have concluded that phenoxy, phenylthio, and phenylseleno groups possess carbonium ion stabilizing properties described by a σ_P^+ parameter of value −0.62, −0.54, and −0.47, respectively.[13]

Although qualitatively in some respect, additional information to this problem can be gained from our rate and deuterium incorporation measurements. The most relevant results are summarized in Table V.

Several interesting conclusions can be drawn from these data. As was already pointed out, entries 2–4 show that even phenyl vinyl selenides can hydrolyze with a reversible protonation step, provided the intermediate carbonium ion be sufficiently stable. Thus the presence of a methyl group (entry 4) or even of a p-nitrophenyl group (entry 2) at the α-position of the vinyl moiety appears to stabilize the carbonium ion enough to allow the observation of some reversibility as indicated by the nonzero values of the percentages of deuterium incorporation.

On the other hand, comparison of the appropriate hydrolysis rate constants provide a quantitative measure of the stabilization of carbonium ions by α-alkyl- and/or α-arylseleno groups. Entries 1 and 3 show that α-(methylseleno)styrene hydrolyzes 15.4 times faster than α-(phenylseleno)styrene. Because of the much lower reactivity of phenyl vinyl selenide[25] rate comparison between this compound and methyl vinyl selenide had to be effected at 60 °C (entries 5 and 6). In spite of this difference, we found a rate enhancement by a factor of 14.9 in favor of methyl vinyl selenide as compared to phenyl vinyl selenide. Since essentially the same rate ratio is found for two different pairs of compounds under different conditions, we can safely consider that this factor of ~15 reflects the carbonium ion stabilizing ability of the methylseleno group as compared to that of the phenylseleno group. Together, with relative rates of hydrolysis for vinyl ethers and vinyl sulfides reported[5b] by Mc Clelland, we obtain the following series of ratios: $CH_3O/C_6H_5O = 133$, $CH_3S/C_6H_5S = 41$, and $CH_3Se/C_6H_5Se = 15$.

Finally, entries 3 and 4 show that 2-(phenylseleno)propene hydrolyzes 4.3 times faster than does α-(phenylseleno)styrene. A very similar observation was made by Kresge and co-workers[41] in the vinyl ether series and interpreted as arising mainly from initial-state stabilization differences.

Acknowledgment. Financial support of this work from "Fonds National de la Recherche Scientifique" (FNRS, Belgium) is gratefully acknowledged.

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[25] We could not reproduce the rate constant given for this compound in Table II of ref 13.

Chemical Consequences of a Polar Axis in a Solid–Gas Reaction. Reaction of *p*-Bromobenzoic Anhydride Crystals with Ammonia Gas. The Absolute Direction of a Polar Unitropic Reaction and the Relationship of Absolute Configuration with Crystal Morphology

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Received July 14, 1980

Abstract: The reaction of crystalline p-bromobenzoic anhydride with ammonia gas has been found to be highly anisotropic and to occur preferentially from one side; that is, a front forms which proceeds in only one direction along the polar axis. (Such a reaction is classified as a polar unitropic reaction.) The absolute direction of the polar axis has been determined by X-ray methods and correlated with the internal structure of the crystal; the preferential attack of ammonia molecules from the side of the carbonyl oxygen atoms can be explained by a mechanism in which the ammonia molecule undergoing reaction is hydrogen bonded to a carbonyl oxygen and thus correctly oriented for attack at the sp^2 carbon atom of the other carbonyl group in the same anhydride molecule. Determination of the direction of the polar axis gives at the same time the absolute configuration of the anhydride single crystal (space group $C2$), and the absolute configuration has been related to crystal morphology. It is proposed that the *RS* notation be extended to include absolute configurations of molecules such as p-bromobenzoic anhydride held rigidly in a chiral conformation in the crystalline state.

Although the first reactions of crystalline organic solids with gaseous reagents were described more than 100 years ago, it is only relatively recently that the improved ease of structure determination has given impetus to studies correlating chemical

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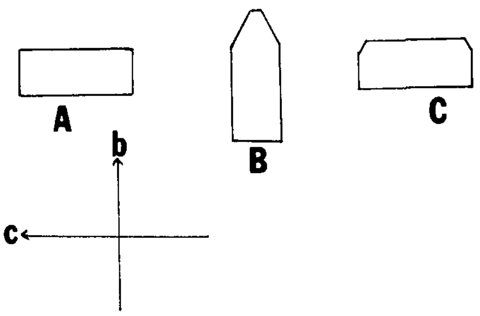

Figure 1. Projection on the *bc* plane of the three types of crystals of *p*-bromobenzoic anhydride obtained at various times in our laboratories: (A) tablets on (100) elongated along *c*; (B) very thin plates on (100) elongated along *b*; (C) tablets similar to A but with additional corner faces revealing the existance of a polar axis (the *b* axis).

reactivity with crystal structure.[1] Benzoic acid and related compounds have shown remarkable anisotropy in their reactions with ammonia gas.[1] Their characteristically platelike crystals typically have eight-membered hydrogen-bonded carboxyl dimer units exposed to the ammonia gas at the "sides" of the crystals, thus permitting ready reaction from the sides and in directions parallel to the "top" (major) faces. Reaction normal to the major faces is slow, however, since the layered structure has benzenoid layers alternating with the carboxyl dimer units and reaction in directions necessitating penetration of these inert benzenoid layers is rapidly attenuated. Reactions of this type characterized by frontal migration in two dimensions have been classified as "ditropic".[2a] A further limitation of reaction direction has been observed with certain acids which have hydrogen-bonded chain structures instead of the more common eight-membered carboxyl dimer. In these cases the preferred reaction direction is the chain direction. Such crystals whose rearrangement proceeds in one dimension have been said to react by a "unitropic" path.[1,2]

Acid anhydrides such as *p*-chloro- and *p*-bromobenzoic anhydride had been found to have layered crystal structures[3,4] similar to those of the acids and to show similar anisotropy when single crystals were treated with ammonia gas.[5] The products were microcrystalline aggregates of equimolar amounts of the acid amide and ammonium salt.[5] An additional point of interest was found in the case of *p*-bromobenzoic anhydride. The crystals of this anhydride were tiny colorless tablets; it was initially reported[5] that these crystals, when exposed to ammonia gas, underwent reaction preferentially at the side faces. Subsequent and more careful investigation showed that the reaction front moved mainly from only one side of the crystal and in a direction parallel to the *b* axis.[6] In contrast to *p*-chlorobenzoic anhydride whose crystal structure (space group $P2/c$, point group $2/m$) is centrosymmetric, the bromoanhydride crystal structure (space group $C2$, point group 2) is both polar and chiral; that is, an idealized single crystal is formed of molecules of a single chirality with the carbonyl groups oriented preferentially along one direction of the polar *b* axis. The absolute direction of the polar axis was unknown as was, of course, the absolute configuration of molecules in a given crystal. In this paper we report the details of the study of this polar unitropic reaction of *p*-bromobenzoic anhydride with ammonia gas and the determination of the absolute direction of the polar axis together with the relationship of the polar direction to the preferred direction of the reaction. The absolute configuration of molecules in a single crystal and the relationship of the chirality and polar direction to the crystal morphology have also been elucidated.

Experimental Section

Crystallization of *p*-Bromobenzoic Anhydride. The original crystallization[5] in our laboratory (at Urbana, IL) by slow evaporation of a dry benzene solution of the anhydride led to rectangular plates (type A in Figure 1) whose morphology was described earlier.[1a] A second investigator (C.-T.L.) working sometime later in an adjoining laboratory obtained similar tiny well-formed crystals. They could not, at that time, be induced to grow larger. A third investigator (E.N.D.) working in another building in our department obtained from benzene large, very thin crystals (type B in Figure 1) with an arrow shape. Later investigators (W.-I.S. and R.B.K.) (working in the same laboratory which had been occupied by C.-T.L) obtained larger bars (Figure 1, type C) with the same orientation observed in the original investigation but with small corner faces which revealed the direction of the polar axis. The crystals (type C) whose interfacial angles are reported below were obtained by slow cooling of a hot benzene solution of the anhydride.

Determination of Crystal Faces and Internal Orientation of the Three Types of Crystals of *p*-Bromobenzoic Anhydride. All three types of crystals showed {100} as the major faces. As reported earlier[1a] type A crystals (Figure 1) were shown by optical goniometry and orientation in the X-ray camera to have [001] as the long morphological direction. Crystals of type B were too thin and had faces too ill formed to give good measurements with an optical goniometer. Orientation in an X-ray camera confirmed that the long morphological axis was *b* [010] with the major faces {100}. The angle between the zone axis formed by the oblique faces of the "arrowhead" and (100) on the one hand and that formed by the side faces and (100) on the other was found to be about 32°, in approximate agreement with the observation of type C crystals discussed below.

Optical goniometric measurements with crystals of type C gave the following angles (deg) between faces (angle obsd (angle calcd)): $(100)-(001)$, 85 (85.2); $(100)-(20\bar{1})$, 78 (78.7); $(100)-(00\bar{1})$, 94 (94.8); $(100)-(\bar{2}01)$, 100 (101.3); $(100)-(1\bar{1}0)$, 78 (78.1); $(100)-(110)$, 78 (78.1); $(100)-(\bar{1}10)$, 103 (101.9); $(100)-(\bar{1}\bar{1}0)$, 101 (101.9); $(1\bar{1}0)-(001)$, 88 (89.0); $(001)-(110)$, 90 (89.0); $(110)-(20\bar{1})$, 88 (87.6). The oblique faces gave poor reflections in the optical goniometer. Since these are the faces which label the direction of the polar axis in crystals of types B as well as C, they were examined particularly carefully. The zone axis relating them to the major face (100) was found in measurements with two crystals to be inclined at an angle of 34 ± 1° from the [010] axis; the zone axis of the zone containing faces with the general formula $(1nn)$ (as well as those containing $(1\bar{n}n)$ and the two corresponding sets produced by the operation of the twofold symmetry axis) is at an angle of 33.9° from [010] as calculated from the cell constants. The calculated angles between the principal face (100) and oblique faces suggest that they are $(\bar{1}11)$ and the symmetry-related counterparts but the agreement of the calculated (92.8°) and measured angles (90 + 3°) is not sufficiently good to make such an assignment firm, particularly since these faces failed to give good reflections and showed signs of some curvature. These assignments are tentatively $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ for crystals with the *R* absolute configuration and $(\bar{1}11)$ and $(11\bar{1})$ for crystals with the *S* configuration (see Discussion section). The type C crystal used for determination of the absolute direction of the polar axis was removed from the X-ray diffractometer and examined in an optical goniometer. The angle between the faces predicted from the X-ray results to be (100) and $(20\bar{1})$ was found to be 79.5° (calcd 78.5°) in agreement with the X-ray assignment of absolute configuration.

Microscopic observation[6] of the reaction of crystals of the bromo anhydride with ammonia gas was carried out in a small compartment formed by separation of two microscope slides with a brass ring provided with tiny entrance and exit tubes through which the ammonia gas was passed. The reaction was observed and photographed without opening the ammonia-filled compartment through a microscope equipped with polarizing filters. The crystal of type B which had been employed for determination of the absolute direction of the polar axis was removed from the X-ray diffractometer and its reaction with ammonia gas photographed. Attack of the ammonia occurred preferentially at the pointed end of the crystal (reaction of a similar crystal is shown in Figure 2).

X-ray Determination of the Absolute Direction of the Polar Axis of Crystals of Types B and C. A crystal of type C (0.5 × 0.3 × 0.15 mm) was placed on a Syntex P2$_1$ diffractometer (Mo Kα), and cell and intensity data were measured.

Crystal data: $C_{14}H_8O_3Br_2$, $M_r = 384$, monoclinic, $a = 28.138$ (8) Å, $b = 5.921$ (1) Å, $c = 3.975$ (2) Å, $\beta = 94.77$ (2)°, $V = 660.0$ Å^3, ρ_{calcd}

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[1] (a) I. C. Paul and D. Y. Curtin, *Science* (*Washington, D.C.*), **187**, 19 (1975); (b) R. Lamartine, G. Bertholon, M.-F. Vincent-Falquet, and R. Perrin, *Justus Liebigs Ann. Chem.*, 131 (1976); (c) J. M. Thomas, S. E. Morsi, and J. P. Desvergne, *Adv. Phys. Org. Chem.*, **15**, 64 (1977).

[2] C.-T. Lin, I. C. Paul, and D. Y. Curtin, *J. Am. Chem. Soc.*, **96**, 3699 (1974); C. C. Chiang, C.-T. Lin, A. H.-J. Wang, D. Y. Curtin, and I. C. Paul, *Ibid.* 99, 6303 (1977).

[3] M. Calleri, C. Ferraris, and D. Viterbo, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.*, **100**, 145 (1966).

[4] C. S. McCammon and J. Trotter, *Acta Crystallogr.*, **17**, 1333 (1964).

[5] R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, **96**, 6340 (1974).

[6] See ref 1a for a preliminary account of this work including a series of photographs of a crystal of *p*-bromobenzoic anhydride reacting with ammonia vapor showing the polar unitropic nature of the reation and also stereopair drawings showing the polar nature of the crystal structure.

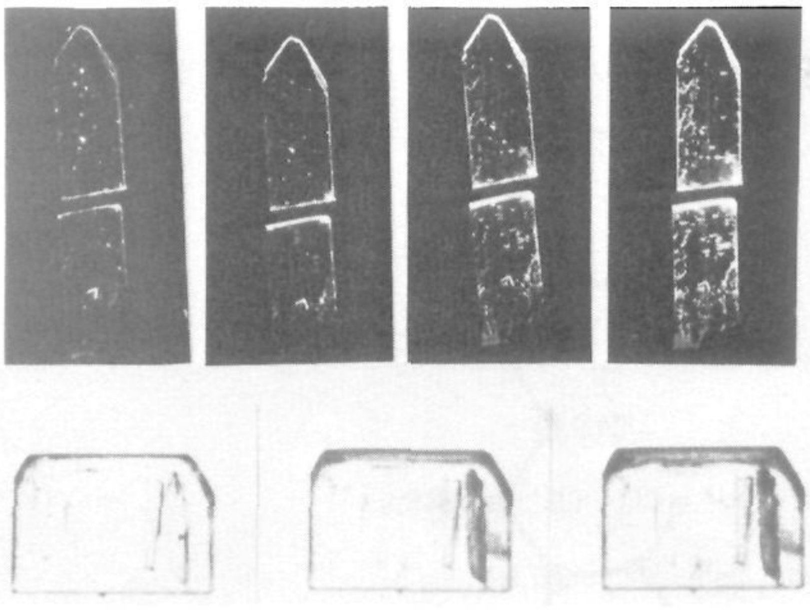

Figure 2. Reaction of *p*-bromobenzoic anhydride crystals with ammonia gas. Crystal of type B is fractured across the middle and both halves are exposed to ammonia vapor. Top (left to right) crystal in the extinction position between crossed polarizing filters before exposure to ammonia, reaction time: 1.2, 1.7, 2.2, top right 3.2 h. Bottom series, a crystal of type C: left, before reaction; middle, 3.3 h; right, 4.3 h.

Table I. Agreement Factors after Refinement of Images (Including Unobserved) of Both Chiralities

	R^a	wR^b	R	wR	ERF^c
model with C=O in $-b$ direction	0.057	0.072	0.078	0.078	1.35
model with C=O in b direction	0.062	0.080	0.084	0.086	1.50

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR = [\Sigma w ||F_o| - |F_c||^2 / \Sigma w |F_o|^2]^{1/2}$. [c] These factors include the unobserved reflections. [d] $\text{ERF} = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Where m is the number of observations and n is the number of parameters.

$= 1.93$ g cm^{-3}, $Z = 2$, $F(000) = 372$, space group $C2$, μ(Mo Kα) = 65.0 cm^{-1} (λ(Mo Kα) = 0.710 69 Å).

Intensity data in the octants hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ were collected out to $2\theta = 65°$ (Mo Kα). Out of a possible 2375 symmetry-independent reflections, a total of 1683 were considered significant at the 1.96σ level. The data were corrected for Lorentz and polarization factors, and an empirical absorption correction (transmission factors 0.15–0.38) was also applied.

The initial model corresponded to the enantiomorph of the coordinates of McCammon and Trotter.[4] Positional and anisotropic thermal parameters for the nonhydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms were varied in a full-matrix least-squares refinement. The image presented by McCammon and Trotter[4] had the carbonyl groups pointing in the $+b$ direction of our laboratory crystal. The model with the carbonyl groups pointing in the $-b$ direction gave very significantly better agreement than the one of opposite chirality (Table I). In addition, 24 reflections were chosen where both Friedel pairs had been measured and were found to give significant differences. The structure factors for both members of each pair were calculated from the preferred model, and in every case the calculated differences were in the same direction as those observed.[9]

The reflections were weighted as $(\sigma(F_0)^2 + (0.04F_0)^2)^{-1}$, and the scattering curves were taken from ref 7 and included the anomalous dispersion corrections.[8] A final difference map was relatively clear except for peaks within 0.1 Å of the bromine atom of 0.5–0.7 e/Å^3. The final atomic coordinates are given in Table II.[9]

Earlier work in our laboratory on a type B crystal was in agreement with the assignment of the type C crystals. The available crystals of type B were poorly defined. Cell and intensity data were collected on a Picker FACS-1 diffractometer (Mo Kα).

Crystal data: $a = 28.148$ (13) Å, $b = 5.916$ (2) Å, $c = 3.990$ (4) Å, $\beta = 94.76$ (3)°, $V = 662.1$ Å^3 (λ(Mo Kα) = 0.710 69 Å).

Table II. Final Atomic Coordinates Obtained from the Chiral Crystal of Type C Examined

atom	x	y	z
Br	−0.20909 (2)	0.00000 (0)^a	−0.58577 (15)
C2	−0.1572 (2)	−0.1778 (11)	−0.7165 (15)
C3	−0.1664 (2)	−0.3857 (11)	−0.8685 (17)
C4	−0.1284 (2)	−0.5084 (15)	−0.9683 (14)
C5	−0.0819 (2)	−0.4256 (9)	−0.9180 (15)
C6	−0.0741 (2)	−0.2151 (10)	−0.7637 (17)
C7	−0.1113 (2)	−0.0916 (12)	−0.6627 (18)
C8	−0.0429 (2)	−0.5625 (9)	−1.0393 (17)
O9	−0.0466 (2)	−0.7446 (9)	−1.1652 (16)
O10	0.0000 (0)^b	−0.4480 (9)	−1.0000 (0)^b
H3	−0.203 (2)	−0.445 (11)	−0.885 (16)
H4	−0.129 (3)	−0.640 (12)	−1.093 (20)
H6	−0.041 (5)	−0.118 (22)	−0.785 (35)
H7	−0.106 (3)	0.041 (15)	−0.565 (19)

[a] This coordinate defined the origin in the b direction.
[b] These coordinates are on the twofold axis and were not refined.

Out of a possible 1943 reflections, a total of 1254 reflections were considered significant at the 2σ level. Lorentz and polarization corrections were applied, but no absorption correction was made. Prior to the final refinements, six low-order reflections which seemed to suffer badly from absorption or extinction effects were removed from the data set. Full-matrix least-squares refinement on the positional and ansiotropic thermal parameters for the nonhydrogen atoms, but holding the positional parameters of the hydrogen atoms at calculated positions and constraining the isotropic thermal parameter at 4.0 Å^2, gave values of R, wR, and ERF of 0.105, 0.138, and 1.74 for the image with the carbonyl pointing in the $-b$ direction and 0.115, 0.150, and 1.88 for the opposite image.

Reflections were weighted as $(\sigma(F_o)^2 + (0.06F_o)^2)^{-1}$. A final difference map showed a large number of residual peaks of ~1.0–2.0 e/Å^3 near the bromine atom and one or two other peaks outside any bonding distance to any atom. Undoubtedly the data set suffers significantly from absorption effects and as a result of poor crystal quality. Hence, the results from it, taken alone, would not be very convincing, but taken in conjunction with the results from the type C crystal, they offer strong confirmatory evidence.

Results and Discussion

A stereoscopic view of the *p*-bromobenzoic anhydride molecule is shown in Figure 3. From this figure, the twisted arrangement around the central anhydride group can be clearly seen. The C_2 axis runs horizontally in this figure. The calculated bond lengths and angles are consistent with generally accepted values.[9]

Recrystallization of *p*-bromobenzoic anhydride from benzene by slow evaporation gives, in contrast to the tiny crystals of type A obtained earlier, large, very thin arrow-shaped crystals elongated this time on b with, as before, the major faces parallel to $\{100\}$ (see Figure 1). We will refer to these crystals as type B. In another laboratory in our department we later obtained crystals similar to the tiny type A crystals elongated on c as described above but much larger. In addition some of them had pairs of faces unaccompanied by their centrosymmetric related counterparts (see Figure 1). These will be referred to as type C. The obvious advantage of these last two kinds of crystals is that both the direction of the polar axis and the absolute configuration can be revealed by the crystal morphology as will be discussed below.

X-ray determination of the absolute configuration of a crystal of type B showed that the carbonyl group $C \overset{\rightarrow}{=} O$ vectors point in the direction of the arrowhead as shown in Figure 4.

After the X-ray study the crystal was removed from the diffractometer and placed in a cell on a microscope stage, and ammonia gas was passed through the cell. Microscopic observation showed that there was a clear preference for attack of ammonia gas at the arrowhead end of the crystal. A similar preference was noted with other crystals studied. Since the ends opposite the arrowheads of these crystals did not have well-developed faces and might have been formed by fracture of a crystal, we deliberately fractured a crystal of type B and exposed both fragments to ammonia gas as before. Again the reaction began at the pointed end of the crystal preferentially with each of the fragments; the

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(7) The scattering curves are calculated from the analytical expression taken from "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974, pp 99–102.

(8) The anomalous dispersion factors were taken from "International Tables for X-Ray Crystallography", Vol. III, C. H. Macgillavry and G. D. Rieck, Eds., Kynoch Press, Birmingham, England, 1968, pp 213–216.

(9) See the paragraph at the end of the paper on supplementary material.

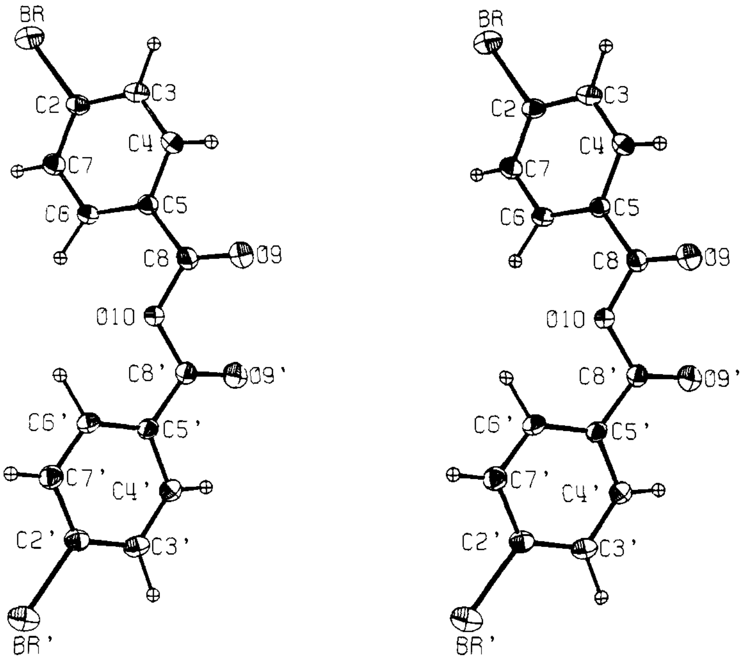

Figure 3. Stereoscopic view of a single molecule of *p*-bromobenzoic anhydride.

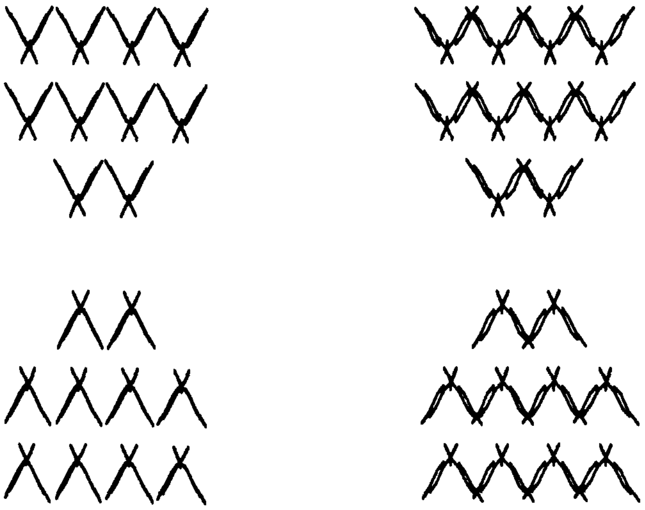

Figure 4. The relationship between absolute configuration and crystal morphology as determined by X-ray crystallography: upper drawing, an *R* crystal (coordinates with signs opposite to those reported by McCammon and Trotter[4]); lower drawing, an *S* crystal (coordinates with the signs as reported by McCammon and Trotter[4]). Note that in each case the carbonyl groups are pointed in the same direction as the arrowhead of the crystal. In each case the plane of the page is the *bc* plane with *c* to the left and *b* toward the top of the page.

directional preference was therefore independent of whether the crystal faces had been formed by fracturing the crystal (see Figure 2).

Examination of the molecular conformation of *p*-bromobenzoic anhydride in the crystalline state leads to a plausible explanation for the directional preference shown by ammonia gas in reacting from the carbonyl end of the crystal. When an ammonia molecule is hydrogen bonded to one of the two anhydride carbonyl groups, the nitrogen atom is in a reasonable position to attack the carbonyl carbon atom of the other acyl group. In Figure 5 is shown a stereopair drawing of such a possible cyclic hydrogen-bonded complex. Progression from there to the transition state for amide formation requires relatively little additional change of atomic positions. It appears reasonable, then, to postulate that the reaction is guided to progress from that end of the crystal where carbonyl oxygen atoms are accessible; as each layer reacts it becomes disordered to permit the further diffusion of ammonia to the next layer of carbonyl groups. Although we have no more direct evidence for this mechanism, it provides an interesting working hypothesis. The favorable geometry of the hydrogen-bonded complex in Figure 5 also has implications with regard to the mechanism of reaction of ammonia and amines with acid anhydrides in solution in nonhydrogen-bonding solvents since the mechanism proposed here is an example of bifunctional catalysis, a phenomenon important in physical organic and biochemistry.[10]

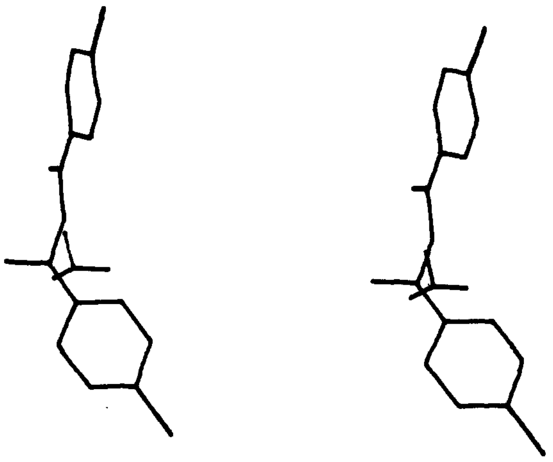

Figure 5. A schematic stereopair drawing showing a *p*-bromobenzoic anhydride molecule (plotted with the coordinates determined for the crystal by X-ray analysis) to which has been added an ammonia molecule in an orientation favorable for attack at the carbonyl carbon adjacent.

Although the *p*-bromobenzoic anhydride behaves in a fluid as an achiral molecule, in the crystal it is twisted into a chiral conformation and, in space group *C*2/*c*, an idealized single crystal contains only a single enantiomer and is therefore also chiral. When the absolute direction of the polar axis of such a crystal has been determined, so, also, has the absolute configuration of the molecules in the crystal. Furthermore, the absolute configuration of such a single crystal of *p*-bromobenzoic anhydride is revealed by its morphology as had been found for a few other crystalline substances.[11]

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[10] M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins", Wiley-Interscience, New York, 1972, p 330 ff.

[11] See, for example, T. M. Lowry, "Optical Rotatory Power", Dover Publications, New York, 1964, p 52 ff.

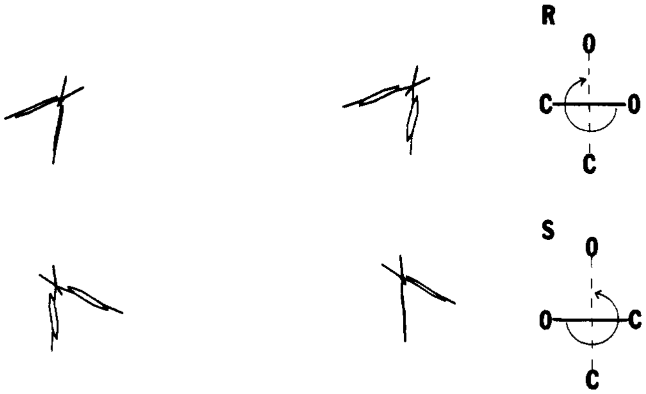

Figure 6. Assignment of *R* and *S* designations to molecules of *p*-bromobenzoic anhydride locked into the conformation observed in the crystal. The assignment is thus determined by the relationship between the carbonyl groups shown schematically on the right. Following the procedure employed with the biphenyls the molecule is turned with the lower priority C on the more remote carbonyl group point down. The order of the other three groups (with a near group taking precedence over a far group) then determines whether the molecule is *R* or *S*.

First it is necessary to discuss the nomenclature to be employed to designate absolute configuration of molecules such as *p*-bromobenzoic anhydride immobilized in a chiral conformation. The extension of the use of *R* and *S* as applied to chiral biphenyls can be applied with no major additional conventions needed to the present situation. When viewed along the axis joining the two carbonyl carbon atoms, the two isomers to be differentiated appear as shown in Figure 6. Application of the priority rules as for the biphenyls[12] leads to the assignments shown in the figure. It will be noted that the signs of the coordinates employed by McCammon and Trotter[4] correspond to the *S* configuration while those of the crystals examined in the present investigation (with all signs reversed) are *R*.

The relationship between the absolute configuration and crystal morphology is best seen by viewing the crystal down the long morphological (*b*) axis in the direction indicated by the arrowhead of the crystal itself. Figure 7 shows the *R* and *S* crystals viewed in this way. It can be seen that the *R* crystal has the (001) face inclined to the left from the top (100) face by an angle of 85° while to the right is the $(20\bar{1})$ face at an angle of 80°. The *S* crystal has the right and left sides reversed so that with careful visual inspection an assignment of absolute configuration can be made even without the aid of goniometric measurements.

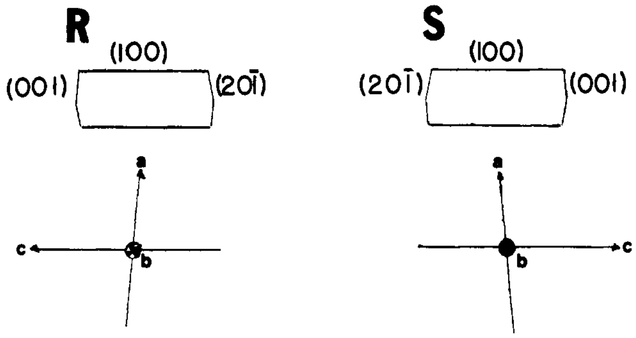

Figure 7. Drawing of *R* and *S* crystals of *p*-bromobenzoic anhydride viewed down the long crystallographic axis with the "arrowhead" of each crystal pointed into the page. The angles between (100) and (001) are 85.2° (calculated from unit cell constants) and between (100) and $(20\bar{1})$ are 78.8°. Notice that the axes are right-handed in each case so the $+b$ is into the page in the left drawing and out from the page in the right.

It has been shown previously[13] that chiral α-phenylethylamine vapor in a competition between reaction with a single *R* crystal of a chiral carboxylic acid and with a single *S* crystal was able to discriminate in its reactivity and reacted much faster with one enantiomer than with the other. It was therefore of interest to see if such selectivity is observed with chiral crystals of *p*-bromobenzoic anhydride. Single crystals were selected as *R* and *S* by observation of the interfacial angles as discussed above, and pairs of *R* and *S* crystals were exposed to (+)- or (−)-α-phenylethylamine vapor as had been done previously with chiral carboxylic acids. No marked differences could be observed in reaction with the *R* crystals as compared with the *S* crystals. However, it seems likely that other optically active gases may show significant differences in reactivity toward such pairs of enantiomers.

The existence of polar axes in organic crystals and their possible contribution to organic chemistry has been largely ignored by organic chemists. The work reported here suggests that such asymmetry may provide a useful tool in the elucidation of mechanisms of solid–gas reactions. While it is premature to forecast the future of the field of study of reactions of polar (and chiral) solids with gases, it seems likely, in view of the large number of organic substances which crystallize in non-centrosymmetric space groups, that there may be many interesting and even practical consequences of this kind of asymmetry awaiting discovery.

Acknowledgment. We would like to thank the National Science Foundation for support of this work.

Supplementary Material Available: Tables of thermal parameters and bond lengths and angles and listings of Friedel pairs and the structure factors for the type C crystal of *p*-bromobenzoic anhydride (21 pages). Ordering information is given on any current masthead page.

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(13) C.-T. Lin, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, 96, 3699 (1974).