

# Reactions of Molecular Crystals with Gases. III. The Relationship of Anisotropy to Crystal Structure in Reactions of Carboxylic Acids and Anhydrides with Ammonia Gas<sup>1,2</sup>

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**Abstract:** The reactions of crystals of benzoic, 4-bromobenzoic, 4-nitrobenzoic, phthalic, and adipic acid as well as of 4-chlorobenzoic and 4-bromobenzoic anhydrides have been shown to proceed anisotropically to form the ammonium salts or, with anhydride molecules, amide from one carboxyl group and ammonium salt from the other. The reactivities along the principal directions through the crystals have been correlated with the crystal structures of these substances. 7-Cyclohexylidenenorborn-2-ene-5,6-dicarboxylic anhydride, which had been shown by Kohler and Kable to undergo a reversal of the Diels-Alder reaction in solution too fast to permit its hydrolysis to the acid, has been found to react in the crystalline state with ammonia vapor to give the amide-ammonium salt with no detectable accompanying reverse Diels-Alder reaction. Relationships between the crystal structures of the substances studied and also comparisons with the crystal structures of the 4-substituted benzamides are discussed.

In previous papers<sup>3,4</sup> the reactions of crystalline carboxylic acids with gaseous ammonia and amines were discussed, and the relationship of the reaction anisotropy to the arrangement of molecules in crystalline 4-chlorobenzoic acid was analyzed. In the present paper, the anisotropic behavior of representatives of two other major types of crystal structures for 4-substituted benzoic acids is examined and the reaction of gaseous ammonia with certain solid dibasic acids is reported. In addition the reaction is extended to certain carboxylic anhydrides, substances whose reactions in solution are many orders of magnitude slower than the reactions of the corresponding acids in the same medium.<sup>1b</sup>

## Experimental Section<sup>5</sup>

**Preparation and Characterization of Single Crystals for Gas-Solid Reactions.** Benzoic acid, after preliminary recrystallization from 95% ethanol and sublimation, was recrystallized from ethyl ether-ethanol (9/1) by slow evaporation over a period of several days. Tablets were obtained with {001} as the major faces and bounded by {101} and  $\{\bar{1}01\}$  in agreement with earlier work;<sup>6a,7</sup>

(1) (a) Taken in part from the Ph.D. Thesis of Rodger S. Miller, submitted to the University of Illinois, Urbana, 1973. (b) For preliminary reports of a part of this work, see R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 2784 (1971); *ibid.*, **94**, 5117 (1972).

(2) We are indebted to the National Science Foundation Grant GH 33634 and to the Advanced Research Projects Agency of the Department of Defense (Contract HC 15-67-C-0221) for support of this work.

(3) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **96**, 6329 (1974).

(4) R. S. Miller, I. C. Paul, and D. Y. Curtin, *ibid.*, **96**, 6334 (1974).

(5) Melting points were determined with a Thomas-Hoover capillary melting point apparatus and were corrected. Infrared spectra of Fluorolube mulls were determined with a Perkin-Elmer Model 237b or 521 spectrometer calibrated to the 1601-cm<sup>-1</sup> band of polystyrene. Nmr spectra were measured in 10% solutions in CDCl<sub>3</sub> or CCl<sub>4</sub> with tetramethylsilane as an internal standard. Optical goniometry was carried out with a Tecam two-circle goniometer. X-Ray powder photographs were made with a Debye-Scherrer powder camera with nickel-filtered Cu K $\alpha$  radiation. Photographs were taken with a Beseler Topcon Super D 35-mm camera mounted on a Bausch and Lomb Model LS dynoptic polarizing microscope chiefly with High Speed Ektachrome Type B. We are indebted to Mr. J. Nemeth and his associates for microanalyses.

(6) P. Groth, "Chemisches Krystallographie," Vol. 4, Verlag von W. Engelmann, Leipzig, 1919: (a) p 456, (b) p 468, (c) p 478, (d) p 722, (e) *ibid.*, Vol. 3, p 465.

interfacial angles (calcd value) (101):(001) 69° (69.4°), (101):(001) 83° (82.5°).

**4-Bromobenzoic acid** was crystallized from acetone by evaporation. The choice of axes here is that employed in the X-ray structure determination<sup>8</sup> (*a* and *c* reversed from the usage in Groth).<sup>6b</sup> (Groth in addition gives *a* twice the correct length.) There were obtained rectangular tablets somewhat elongated along *c* with {100} as the major faces: interfacial angles (calcd) (100):(001) 85° (84.5°), (100):(110) 78° (78.2°).

**4-Nitrobenzoic acid**, after purification by reprecipitation from aqueous alkaline solution with dilute HCl, was crystallized from a hot solution in ethyl acetate by slow cooling to give plates with {001} as the prominent faces:<sup>6c,9</sup> interfacial angles (calcd), (001):(101) 54° (54.2°), (001):(100) 84° (83.6°), (001):(011) 79° (76.6°).

**Phthalic acid**, after preliminary crystallizations from 95% ethanol, was recrystallized from a hot concentrated aqueous solution by slow cooling to give colorless, nearly square tablets with {010} as the prominent faces:<sup>6d,10</sup> (010):(001) 90° (90.0°), (010):(110) 71° (70.6°), (001):(110) 88° (87.0°).

**Adipic acid**, after preliminary crystallization from 95% ethanol (decolorization with activated charcoal), was crystallized from a solution in hot ethyl ether to give thin plates (*P*<sub>21</sub>/*c* setting) with {100} as the prominent faces:<sup>6e,11</sup> (100):(010) 89° (90.0°), (100):(102) 73° (71.8°), (100):(10 $\bar{1}$ ) 64° (68.0°), (102):(101) 137° (140.0°).

**4-Chlorobenzoic anhydride**, crystallized from acetone, gave rods elongated on *a* with {001} as the most prominent faces:<sup>12</sup> (001):(012) 67° (66.4°), (001):(011) 78° (77.7°), (001):(010) 91° (90.0°).

**4-Bromobenzoic anhydride**, after three crystallizations from dry benzene, was allowed to crystallize from a warm concentrated benzene solution by cooling to room temperature. There resulted small, colorless tablets<sup>13</sup>: (100):(1 $\bar{1}0$ ) 78° (78.1°), (100):(201) 70° (69.8°), (100):(001) 86° (85.2°).

**7-Cyclohexylidenenorborn-2-ene-5,6-dicarboxylic anhydride** was prepared by the method of Kohler and Kable<sup>14</sup> from 14.6 g of cyclohexylidene-fulvene (bp 88°, 6 Torr) and a suspension of an

(7) G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Crystallogr.*, **8**, 157 (1955).

(8) K. Ohkura, S. Kashino, and M. Haisa, *Bull. Chem. Soc. Jap.*, **45**, 2651 (1972).

(9) T. D. Sakore and L. M. Pant, *Acta Crystallogr.*, **21**, 715 (1966); S. S. Tavale and L. M. Pant, *Acta Crystallogr., Sect. B*, **27**, 1479 (1971).

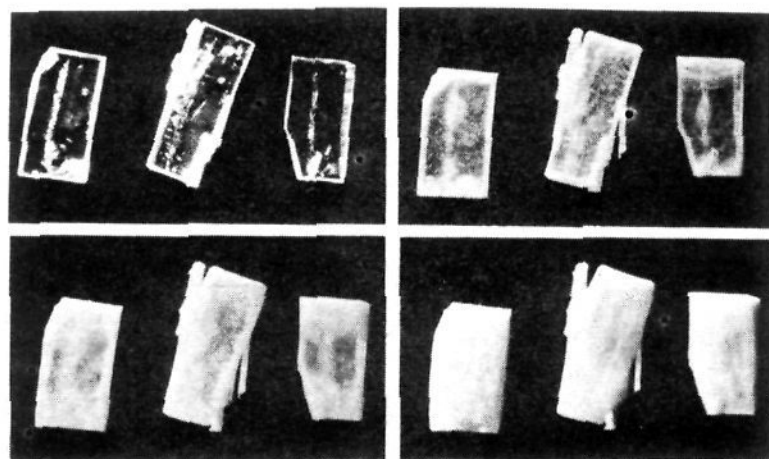
(10) W. Nowacki and H. Jaggi, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **109**, 272 (1957). (Groth<sup>6d</sup> gives a value for relative *b* which is one-half the correct value.)

(11) J. Housty and M. Hospital, *Acta Crystallogr.*, **18**, 693 (1965). Here, as in the present discussion, the space group is taken as *P*<sub>21</sub>/*c* rather than *P*<sub>21</sub>/*a* as in earlier structure determinations.

(12) M. Calleri, C. Ferraris, and D. Viterbo, *Atti Acad. Sci. Torino, Cl. Sci. Fis. Mat. Natur.*, **100**, 145 (1966).

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

(14) E. P. Kohler and J. Kable, *J. Amer. Chem. Soc.*, **57**, 917 (1935).



**Figure 1.** Reaction of three crystals of 4-nitrobenzoic acid with ammonia vapor: upper left, after 7 min; upper right, after 3 hr; lower left, after 12 hr; lower right, after 41 hr. The migration of the reaction front in the long direction of the crystal (parallel to the *b* axis) is more rapid than that perpendicular to the long axis.

excess of maleic anhydride in 1,4-dioxane. Filtration of the colorless precipitate which had formed after 2 hr and washing of the precipitate several times with anhydrous ether gave 20% of analytically pure white crystalline cycloadduct: mp 133–134° (lit.<sup>14</sup> 132°); ir 2940, 1850, and 1760  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ ) 1.50 (s, 6), 2.20 (bd s, 4), 3.58 (m, 2), 4.0 (m, 2), 6.40 (m, 2).

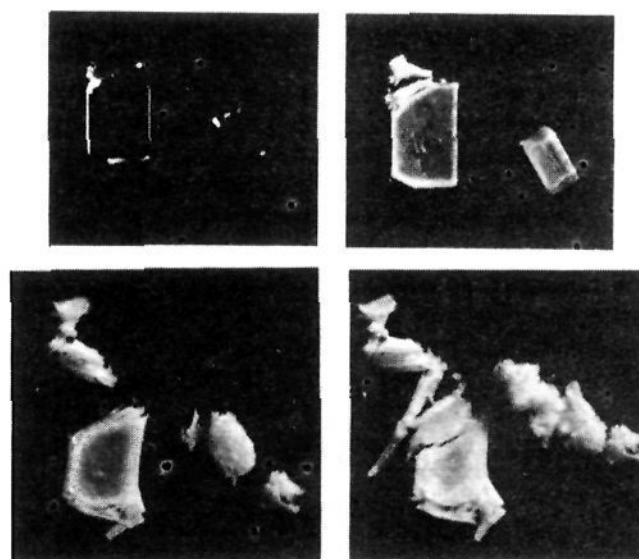
**Anisotropic Reactions of Crystalline Benzoic Acid, 4-Bromobenzoic Acid, 4-Nitrobenzoic Acid, Phthalic Acid, and Adipic Acid with Ammonia Gas.** The stoichiometry of these reactions was discussed previously.<sup>3</sup> When single crystals of the monocarboxylic acids in a glass enclosure on a microscope stage were observed during reaction, it was found that the top surface (major face) of each crystal remained clear during early stages of reaction. However, a reaction front proceeding at the other faces could be observed visually and photographed since as reaction occurred there was produced disorder and consequent light scattering. Plots made of the advance of the front along each of the two longer dimensions of the macroscopic crystal (tenths of a millimeter per minute) showed that the differences in frontal advance in these two directions were too small to be significant in the cases of benzoic and 4-bromobenzoic acids, as was also found for 4-chlorobenzoic acid.<sup>4</sup> 4-Nitrobenzoic acid crystals showed a clear differentiation in rate of frontal advance along the two axes of faster reaction; measurements of three different crystals gave limiting ratios of 5.4, 2.6, and 2.0, the reaction being faster in the direction parallel to the long crystal direction (*b* crystallographic axis). This difference is readily seen in the photographs of three reacting crystals shown in Figure 1.

The dicarboxylic acids, phthalic and adipic, showed similar preferential reaction from the lateral faces of the crystal, but the course of the reaction was markedly altered by the development of cracks, presumably by reaction at defects in the top surface, which ultimately led to fragmentation of the crystal. The sequences of events for these two substances are shown in Figure 2 and Figure 3.

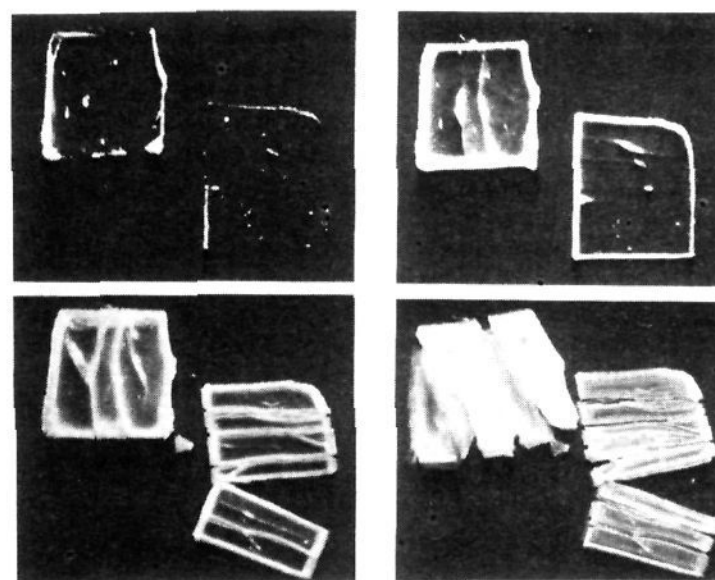
**Reactions of Crystalline 4-Chloro- and 4-Bromobenzoic Anhydrides with Ammonia Gas.** Analytically pure crystals of the anhydride in a small flask were exposed to ammonia gas until there was no further gain in weight. Carbon, hydrogen, and nitrogen analyses of the product agreed to within 0.3% with the values expected for a 1:1 mixture of ammonium 4-halobenzoate and 4-halobenzamide.

*Anal.* Calcd for  $\text{C}_7\text{H}_5\text{ClNO}_2 \cdot \text{C}_7\text{H}_6\text{ClNO}$ : C, 51.1; H, 4.3; N, 8.6. Found: C, 51.3; H, 4.6; N, 8.5. Calcd for  $\text{C}_7\text{H}_5\text{BrNO}_2 \cdot \text{C}_7\text{H}_6\text{BrNO}$ : C, 40.2; H, 3.4; N, 6.7. Found: C, 40.1; H, 3.3; N, 6.5.

Single crystals in a glass enclosure on a microscope stage were observed and photographed during reaction with ammonia gas. At the end of the reaction the product had become somewhat opaque and there was no extinction when the crystal was rotated between crossed polarizing filters. A "single crystal" from reaction of 4-chlorobenzoic anhydride was mounted in a capillary (without grinding) and an X-ray powder photograph showed that the product solid was composed of microcrystallites randomly ordered. Attempts to gain evidence of a solid compound of the benzamide and ammonium benzoate were partially successful. The ir spectrum of a Fluorolube mull of the product from the ammonia reaction was not significantly different from the superposition of



**Figure 2.** Reaction of two crystals of phthalic acid with ammonia vapor: upper left, before reaction; upper right, after 15 min; lower left, 41 min; lower right, 240 min.



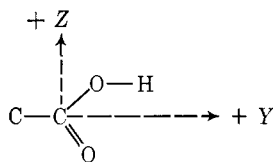
**Figure 3.** Reaction of three adipic acid crystals with ammonia vapor: upper left, before reaction; upper right, 491 min; lower left, 1267 min; lower right, 4237 min.

the spectra of 4-chlorobenzamide and ammonium 4-chlorobenzoate measured independently and also resembled the spectrum of a mull of the mixture. However, comparison of X-ray powder photographs of the product of the ammonia reaction with powder photographs of the pure components showed differences which suggested that the reaction product was not simply a mixture of amide and salt. This was confirmed by melting points of mixtures of 4-chlorobenzamide and ammonium 4-chlorobenzoate which showed a maximum at a composition of about 1:1.4 ammonium salt to amide. Similar results were obtained with fused samples in capillary tubes (heating rate 1–2°/min) and with melting points determined by differential thermal analysis (20°/min). Attempts to obtain single crystals of a compound of 4-bromobenzamide and ammonium 4-bromobenzoate by evaporation of a 1:1 solution of the components in ether over a period of several weeks gave a white flocculent precipitate whose infrared spectrum was similar to the sum of the spectra of the components.

Single crystals of the anhydrides observed on a microscope stage while they reacted with gaseous ammonia showed anisotropic behavior rather similar to that of the benzoic acids. Photographs of the reaction of 4-chlorobenzoic anhydride have been published in a preliminary communication.<sup>1b</sup>

**Reaction of Crystalline 7-Cyclohexylidenenorborn-2-ene-5,6-dicarboxylic Anhydride with Ammonia Gas.** Solid anhydride in a flask was maintained under a stream of ammonia gas for 14 days at which time the increase in weight showed that more than the stoichiometric amount of ammonia had been absorbed. On standing at room temperature ammonia was given off, and after 12 hr under 1 mm pressure, microanalysis without further purification gave the correct values for the amide ammonium salt, opaque crystals: mp 169–171° dec; ir (mull) 1655, 1540, 1390  $\text{cm}^{-1}$ .

*Anal.* Calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3\text{N}_2$ : C, 64.7; H, 8.0; N, 10.1. Found: C, 64.5, 64.2; H, 8.0, 8.1; N, 9.3, 9.7.

Table I. Comparison of Stacking among Benzoic Acid Dimers<sup>a</sup>

	C—O lengths (Å)	Space Group (Z)	Shortest crystallographic axis Å	$D_c$ (g/cm <sup>-3</sup> )	No. of types of stacks	Y (Å)	Z (Å)	Angle (deg) between planes of CO <sub>2</sub> H and phenyl ring
Benzoic <sup>a</sup>	1.24; 1.29	$P2_1/c$ (4)	4.14	1.32	2	-3.63	-1.22	1.9
4-Cl <sup>b</sup>	1.253 (6); 1.273 (6)	$P\bar{1}$ (2)	3.861	1.53	1	+1.12	-1.61	5.7
4-Br <sup>c</sup>	1.225 (14); 1.307 (13)	$P2_1/a$ (4)	3.98	1.85	2	+1.10	-1.74	5.8
4-CH <sub>3</sub> <sup>d</sup>	1.292; 1.292	$P\bar{1}$ (2)	7.59	1.26	1	+8.09	-0.45	2.9
4-NO <sub>2</sub> <sup>e</sup>	1.242 (5); 1.306 (5)	$C2/c$ (8)	5.07	1.59	2	-3.64	-1.11	2.1
4-NH <sub>2</sub> <sup>f</sup>	1.236 (6); 1.315 (5)	$P2_1/n$ (8)	3.86	1.37	4	+1.06	-1.62	2.8
	1.248 (6); 1.293 (6)					+1.13	-1.37	3.4

<sup>a</sup> Reference 7. <sup>b</sup> This work. <sup>c</sup> Reference 8. <sup>d</sup> Reference 15. <sup>e</sup> Reference 9. <sup>f</sup> Reference 16. <sup>g</sup> Definition of X, Y, and Z axes: X is normal to the plane of the carboxyl group.

The anhydride was stirred for 2 hr in a mixture of concentrated ammonium hydroxide and ethanol (20:75). The resultant slightly yellow solid after filtration and drying was stirred in 1 N HCl for 1 hr. As the solid dissolved, additional material crystallized from the solution. When collected, dried, and subjected to nmr and ir analysis, the product was shown to be largely the amide-acid below although it was somewhat impure as shown by the yellowish color.

**5-Carboxy-7-cyclohexylidenenorborn-2-ene-6-carboxamide**, obtained by neutralization of the amide ammonium salt above in ethanol-water (1:10), was dried in a vacuum desiccator for 24 hr as a white precipitate: mp 158–158.5° dec; ir (mull) 1635, 1740, 3380–3500 cm<sup>-1</sup>; nmr (DMSO-*d*<sub>6</sub>) 1.30 (bd s, 6), 1.90 (bd s, 4), 2.90 (m, 2), 3.30 (bd s, 2), 5.90 (m, 2) 6.30 (bd s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 26.0 (59.27), 39.2 (28.48), 54.0 (45.00), 77.1 (26.13), 78.1 (75.68), 79.1 (26.95), 91.1 (52.25), 92.1 (56.95), 104.1 (37.52), 105.1 (37.99), 115.1 (25.01), 117.1 (80.06), 118.1 (30.52), 131.2 (34.72), 146.2 (100.00).

Anal. Calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>5</sub>: C, 68.9; H, 7.3 Found: C, 69.0; H, 7.3.

## Discussion

An understanding of the reactions of crystalline benzoic acid and related compounds with gases such as ammonia surely requires consideration of the crystal structures of these compounds.

We have examined several aspects of the crystal structures of a number of singly 4-substituted benzoic acids<sup>7-9,15,16</sup> (Table I). In all cases the molecules in the crystal form hydrogen-bonded dimers. These dimers are arranged in stacks in a direction nearly normal to the planes of the phenyl rings. It will be convenient to describe the relative arrangement of adjacent molecules in the stacks in the benzoic acid crystals with reference to three axes. One of the axes (*X*) is perpendicular to the plane of the carboxyl groups of the dimer (very close to the plane of the phenyl rings), and the other two are in this plane (see Table I). One of these axes (*Y*) is defined by the direction of the C(1)–C (carboxyl) bond and the other (*Z*) is normal to that direction and to the perpendicular to the plane of the carboxyl group. In Table I are given some details of the crystal structures and relative overlaps of adjacent dimers in a stack for various 4-substituted benzoic acids. The overlaps are shown in Figure 4. Among the acids surveyed, there are three distinct types

of relative overlap. First that exhibited by 4-chloro-, 4-bromo-, and both stacks of 4-aminobenzoic acid has a slightly greater displacement in the *Z* direction than in the *Y* direction. This overlap has the effect of placing the carboxyl carbon over the carbonyl oxygen atom (insofar as this oxygen can be distinguished from the hydroxyl one). Second, that typified by benzoic and 4-nitrobenzoic acid has a displacement of over 3.5 Å in the *Y* direction and relatively little in the *Z* direction. This has the effect of placing the carboxyl carbon over one of the meta carbons of the ring. This overlap is associated with very small angles of rotation of the carboxyl group. Finally, in the case of 4-methylbenzoic acid, there is a very large displacement in the *Y* direction, probably due to the presence of the bulky 4-methyl group.

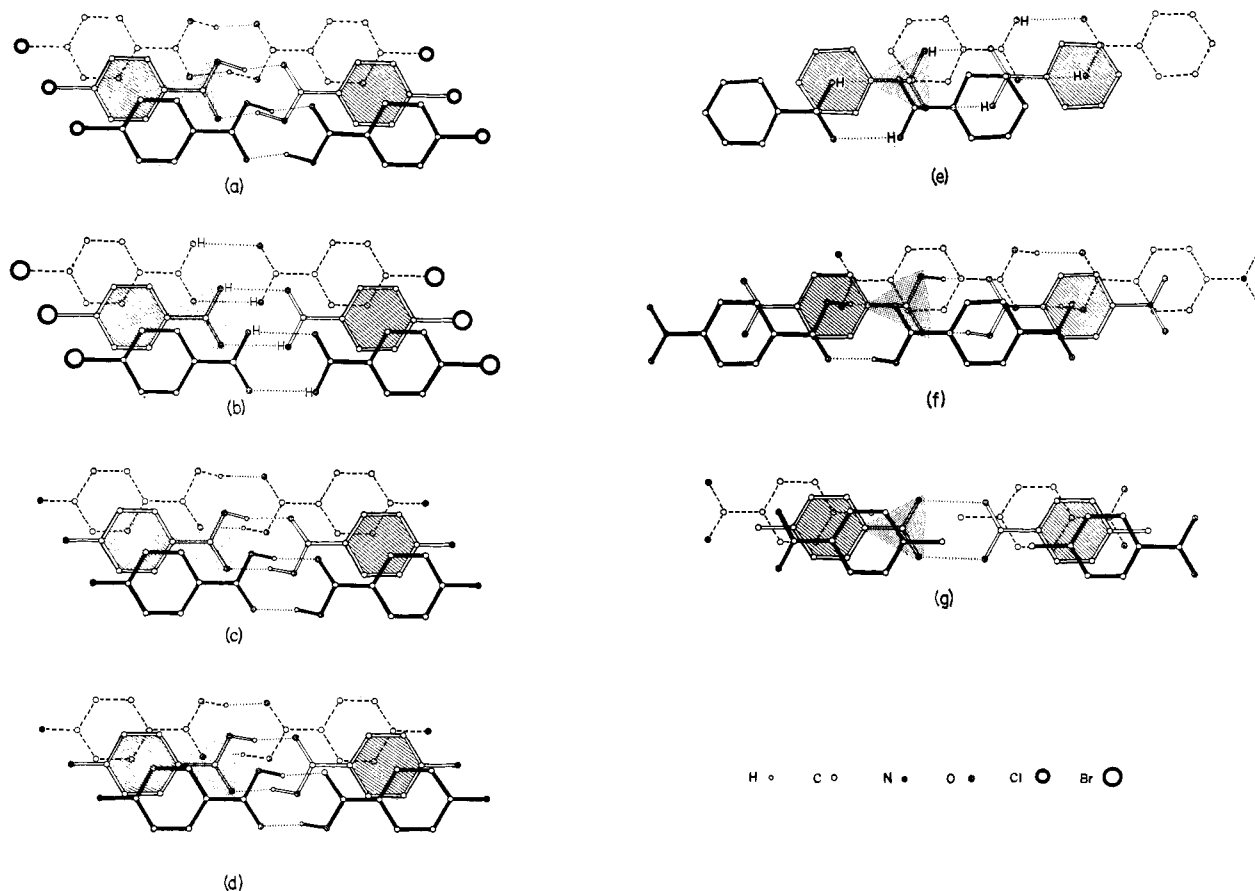
These differences in molecular overlap result in differences in the inclination of the axis of the stack of dimer to the perpendicular to the plane of the rings in the crystal. Such differences are partly responsible for the variety of space groups found among these acids. However, both the nature and size of the 4-substituted groups will also have important effects upon the overall crystal packing adopted. The chloro,<sup>4</sup> amino (*via* hydrogen bonding), and nitro<sup>17</sup> groups all appear to have the capability to participate in intermolecular interactions.

However, despite these complications, there are many common basic features in the three-dimensional arrangements of molecules of benzoic acids in the crystal. Some of these relationships may be obscured by differences in crystal symmetry. In Table I is shown the variation in space group encountered among these benzoic acids. Further the choice of unit cell is often dictated by conventions developed for ease in X-ray structure determination and is not that which would be chosen in order to bring out most clearly the structural relationships in which we are here interested. In Figure 5 are shown representatives of three of the most common types of packing in such crystals with one molecule in the crystal asymmetric unit; 4-aminobenzoic acid has two molecules in the asymmetric unit. In each case

(15) M. G. Takwale and L. M. Pant, *Acta Crystallogr., Sect. B*, **27**, 1152 (1971).

(16) T. F. Lai and R. E. Marsh, *Acta Crystallogr.*, **22**, 885 (1967).

(17) J. D. McCullough, Jr., I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **94**, 883 (1972).



**Figure 4.** Overlap of dimers of several benzoic acid derivatives in the crystalline state. The atoms of three adjacent dimers are projected onto the best plane defined by the carbon and two oxygen atoms of a carboxyl group and the attached ring carbon in one of the molecules of the central dimer; this plane is shown in the figure by a dotted shading. The central dimer is shown by line shading, the dimer above that plane by heavy lines, the dimer below by dashed lines. The structures shown are (a) 4-chlorobenzoic acid, (b) 4-bromobenzoic acid, (c) and (d) the two independent molecules of 4-aminobenzoic acid, (e) benzoic acid, (f) 4-nitrobenzoic acid, and (g) 4-methylbenzoic acid.

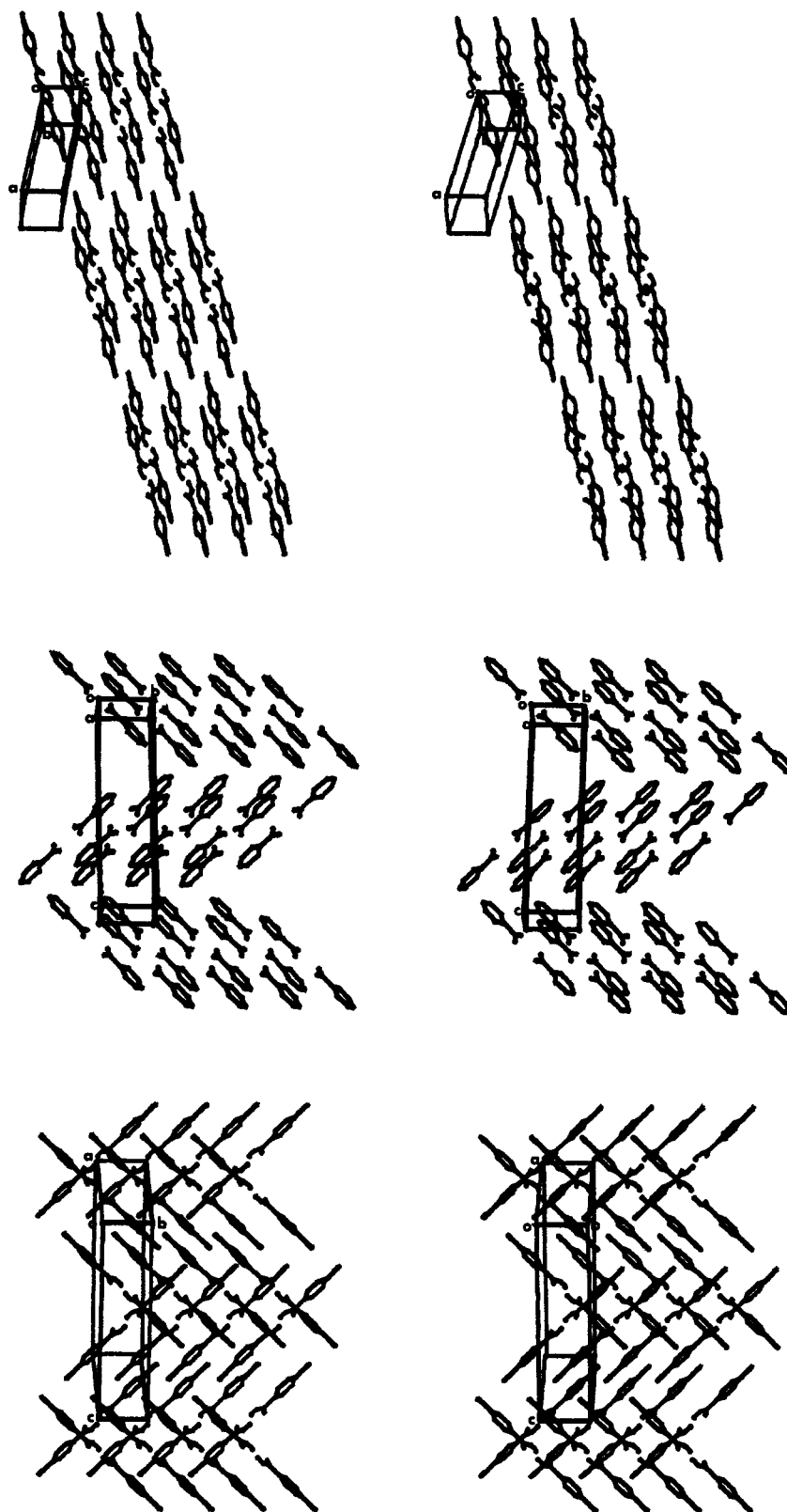
the hydrogen-bonded cyclic dimers are nearly planar. Molecules may be considered as being arranged in chains connected by contacts through the 4-substituted groups of the benzene ring, the chains being nearly linear in 4-chlorobenzoic acid but zig-zag in the other two structures shown in Figure 5. A group of parallel chains combine to form a layer plane; in each example in Figure 5 the layer plane is taken as parallel to the plane of the paper. The axis from left to right in the layer plane is the twofold screw axis or, in the triclinic space group where no such symmetry element is present, the shortest crystallographic axis. The conventional choice of the unit cell is indicated in each example in Figure 5. It should be noted that the angles between the molecular axis (through the 4 and 4'-carbon atoms in the benzene rings of a dimer unit) and the layer plane is less than  $3^\circ$  in each case. The axis of the previously described stacks always lies in the layer plane. Adjacent layer planes may consist of molecules with identical orientations (as in the cases of 4-chlorobenzoic and benzoic acid) or of molecules with different orientations, related by a symmetry operation (the case of 4-nitrobenzoic acid). Presumably, whether the crystals have linear or zig-zag chains, or whether the layer planes are simply related by translation or not, is determined by the nature of the intermolecular contacts, particularly those involving the para-substituted group. Schmidt<sup>18</sup>

(18) G. M. J. Schmidt, *J. Chem. Soc.*, 2014 (1964).

classified a number of cinnamic acid derivatives on the basis of their shortest crystallographic axis. Under this classification, 4-chlorobenzoic acid with a  $c$  axis of 3.86 Å belongs to the  $\beta$ -type, while benzoic acid with a short axis of 5.14 Å is of the  $\alpha$  type, whereas 4-nitrobenzoic acid (5.07 Å) would be of the  $\gamma$  type. This system was found extremely valuable in the prediction of photochemical products of cinnamic acids.

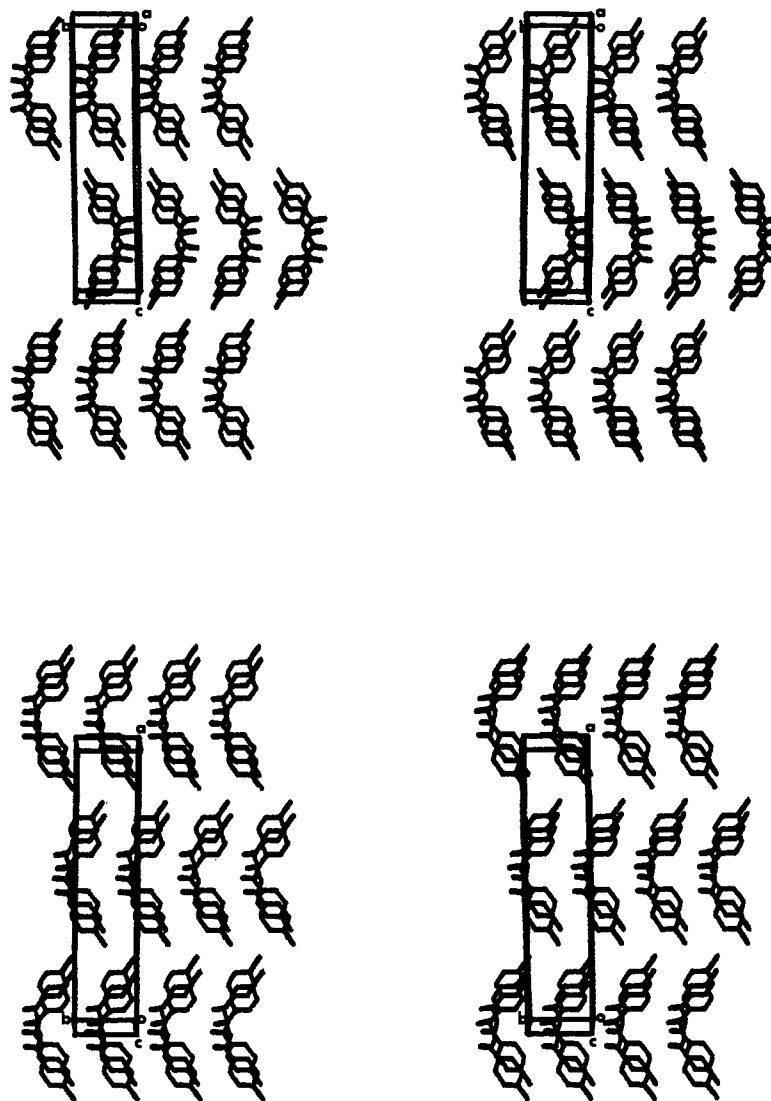
Many of the basic features of packing just described are applicable also to related types of structure. The crystal structures of 4-chlorobenzoic anhydride<sup>12</sup> and 4-bromobenzoic anhydride<sup>13</sup> are strikingly similar to the structures of the 4-substituted benzoic acids as is shown in Figure 6. The molecules are stacked and chains of molecules again form a layer plane containing the  $b$  axis (a twofold axis which relates the two halves of each molecule is parallel to  $b$  in each case). Alternate layers are related by centers of symmetry in the chloro anhydride and by the centering operation for the bromo anhydride. The individual molecules depart substantially from the coplanarity characteristic of the acids. In spite of the differences, the overall layered structure with alternating polar (carbonyl) and nonpolar regions characteristic of the acids is preserved. For the sake of completeness it should be noted that the 4-substituted benzamides have similar structural features. In Figure 7 are shown the structures of benzamide,<sup>19</sup> 4-bromo-

(19) C. C. F. Blake and R. W. H. Small, *Acta Crystallogr., Sect. B*, 28, 2201 (1972).



**Figure 5.** Molecular arrangements of three aromatic carboxylic acids. (a) 4-Chlorobenzoic acid ( $P1$ ).<sup>4</sup> Note that the major (least reactive) face of the crystal is defined by the eight chlorine atoms pointing downward at the bottom of the drawing. The view here is down the normal to  $(\bar{2}10)$ , the layer plane. The chain axis (see text) is parallel to  $[122]$ . (b) Benzoic acid ( $P2_1/c$ ).<sup>7</sup> This view is onto the layer plane  $(10\bar{2})$ . The predominant (and least reactive) crystal face is defined by the 4 carbon atoms of the eight benzene rings at the bottom of the drawing. The chain axis (vertical) is parallel to  $[201]$ . (c) 4-Nitrobenzoic acid ( $A2/a$ ).<sup>9</sup> A vertical slice parallel to the page and one molecule thick is similar to a similar slice of the benzoic acid crystal in (b). However, alternate slices have been shifted relative to one another by the centering operation to give a criss-crossed effect. The layer plane is  $(10\bar{1})$  and the (vertical) chain axis is parallel to  $[\bar{1}01]$ . (The drawing may be misleading unless it is viewed in stereo.)





**Figure 6.** Molecular arrangements in two crystalline anhydrides. Upper picture 4-chlorobenzoic anhydride,<sup>12</sup>  $P2/c$ . The view into the layer plane (102). The unreactive face of the crystal is parallel to the plane outlined by the eight chlorine atoms at the bottom of the drawing. Lower picture, *p*-bromobenzoic anhydride,<sup>13</sup>  $C2$ . View onto the layer plane (201). The unreactive face of the crystal is parallel to the plane outlined by the eight bromine atoms at the bottom of the drawing.

benzamide,<sup>20</sup> and 4-iodobenzamide.<sup>21</sup> The extra H(N) in these structures not only induces nonplanarity in individual molecules but introduces cross-linking by hydrogen bonding of adjacent molecules to form chains. In spite of these complications, the basic layered structure of the benzoic acids is present here also.<sup>22</sup> Although quantitative correlation of melting points of organic compounds has been attempted, it has been carried out successfully in relatively few instances.<sup>23</sup> It is interesting to note that a plot of the melting points of a number of anhydrides *vs.* those of the corresponding benzoic acids is reasonably linear as shown in Figure 8. A

(20) Y. Harada, T. Taniguchi, Y. Takaki, and K. Sakurai, *Mem. Osaka Kyoiku Univ.*, **16**, Ser. 3, 37 (1967).

(21) K. Nakata, Y. Kato, Y. Takaki, and K. Sakurai, *Mem. Osaka Kyoiku Univ.*, **20**, Ser. 3, 93 (1971).

(22) The molecular packing modes of some primary amides have been analyzed by L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc. A*, 2372 (1969). They have designated the packing of the amides considered here as having "translation packing."

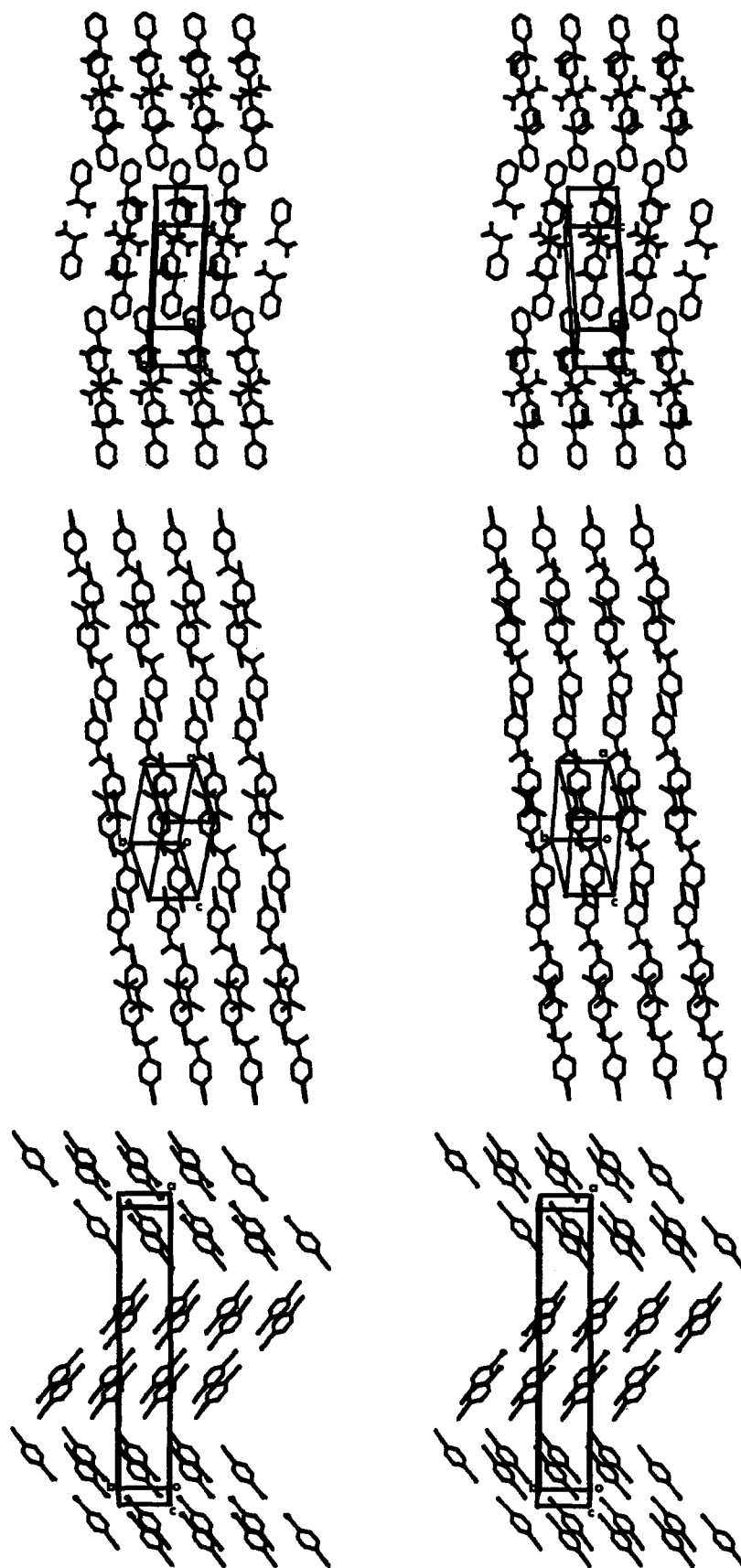
(23) See for example H. F. Herbrandson and F. C. Nachod, "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, pp 3-16.

similar plot but with a smaller slope relating the melting points of 4-substituted benzamides with those of the corresponding acids (Figure 8) can be obtained.<sup>24</sup>

The anisotropy of the reaction of ammonia with the benzoic acids and anhydrides described in the experimental section can now be discussed in terms of the crystal structures shown in Figures 5 and 6. Each of the acids and anhydrides shown in Figures 5 and 6 and also 4-bromobenzoic acid has a common crystal morphology, that in which the crystals are plates with the major faces parallel to the planes that separate adjacent 4-substituted groups. Although there are differences from case to case in the exact faces which are developed, it is striking that the two major zone axes of the crystal are also the conventional crystallographic axes. The relationships are summarized in Table II.

As was described earlier<sup>4</sup> reaction with ammonia gas

(24) Melting points are taken where possible from the "Handbook of Chemistry and Physics," 52nd ed, R. C. Weast, Ed., Chemical Rubber Company, Cleveland, Ohio, 1972, or otherwise from Beilstein's *Handbuch der Organischen Chemie*. For a discussion of the relationship of molecular shape to the dependence of heat of fusion on melting point see J. Pirsch, *Monatsh. Chem.*, **97**, 249 (1966).



**Figure 7.** Arrangement of molecules in crystals of three amides: upper drawing, benzamide,<sup>19</sup>  $P2_1/c$ , looking down on the layer plane (104); middle drawing, 4-bromobenzamide,<sup>20</sup>  $P\bar{1}$ , looking down on the layer plane (201); lower drawing, 4-iodobenzamide,<sup>21</sup>  $P2_1/a$ , looking down on the layer plane (001). Only in the benzamide structure are the amide hydrogens shown. In the bottom structure the amide group is almost perpendicular to the plane of the paper and is partly obscured.

**Table II.** Relationship between the Crystal Morphologies of Benzoic Acids and Anhydrides

	Crystal plane parallel to major face	Zone axes <sup>a</sup>	
		Long	Short
Benzoic acid	(001)	[010]	[100]
4-Chlorobenzoic acid	(100)	[010]	[001]
4-Bromobenzoic acid	(100)	[001]	[010]
4-Nitrobenzoic acid	(001)	[010]	[100]
Phthalic acid	(010)	[100]	[001]
Adipic acid	(100)	[100]	[001]
4-Chlorobenzoic anhydride	(001)	[100]	[010]
4-Bromobenzoic anhydride	(100)	[001]	[010]

<sup>a</sup> The ratios of the lengths of the zone axes of course vary from crystal to crystal and may sometimes approach unity. The assignment of designations "long" and "short" is therefore not always meaningful.

of single crystals of 4-chlorobenzoic acid, analyzed in terms of the rate of migration of the reaction front with respect to the *a* (more rigorously *a*\*), *b*, and *c* directions, is found to proceed very slowly along *a* and rapidly and with nearly the same velocity parallel to *b* or to *c*. Examination of the crystal structure in Figure 5 suggests that once an ammonia molecule has arrived at and reacted with a particular carboxyl group, adjacent carboxyl groups along the *b* and *c* directions are accessible to other ammonia molecules which may diffuse into the region. On the other hand diffusion along the *a* (or *a*\*) direction requires crossing the nonpolar layer of the crystal to get from one carboxyl group to the next. It is therefore reasonable that migration in this direction should be slow. Precisely similar observations and explanations apply to the reaction with benzoic acid (reaction slow along *c* and approximately equally rapid along *a* and *b*), 4-bromobenzoic acid, and 4-chlorobenzoic anhydride. We have proposed that such reactions be called ditropic (two directions).<sup>25</sup>

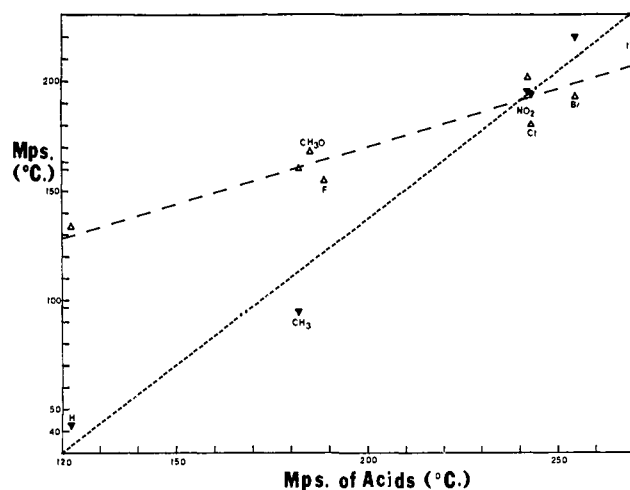
4-Nitrobenzoic acid, however, as shown in Figure 1, although it underwent reaction very slowly in the direction parallel to *c* which crosses the noncarboxylic layer of the crystal, differed from the cases above in that frontal migration was from two to five times as rapid parallel to *b* as it was parallel to *a*. It is not clear what factors are responsible for this effect, but it is tempting to speculate that it may be associated with the criss-cross crystal packing. This reaction approaches but does not attain ideal unitropic behavior (reaction along just one axis). A more nearly ideal example is the reaction of (*R*)-(+)-2,2-diphenyl-1-methylcyclopropanecarboxylic acid with ammonia gas.<sup>25</sup> Another example of an acid which has packing behavior similar to benzoic acid but which shows different rates of frontal migration in each of the crystal directions is acenaphthalene-1-carboxylic acid which has been studied by Desvergne and Thomas<sup>26</sup> and the crystal structure reported by Bouas-Laurent, Desvergne, Gaultier and Hauw.<sup>27</sup>

The rates of the reactions of ammonia gas with crystalline 4-chloro- and 4-bromobenzoic anhydride when followed quantitatively by the method previously

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

(26) J. P. Desvergne and J. M. Thomas, *Chem. Phys. Lett.*, **23**, 343 (1973).

(27) H. Bouas-Laurent, J. P. Desvergne, J. Gaultier, and C. Hauw, *Cryst. Struct. Commun.*, **2**, 547 (1973).



**Figure 8.** Plots of (▼) melting points of para-substituted benzoic anhydrides and (△) para-substituted benzamides vs. the melting points of the corresponding acids. The equation relating the melting points of anhydrides and acids is  $Y = 1.34X - 131$ ; the correlation coefficient, *r*, is 0.99. The equation relating the melting points of the amides and acids is  $Y = 0.524X + 65.4$  with  $r = 0.95$ .

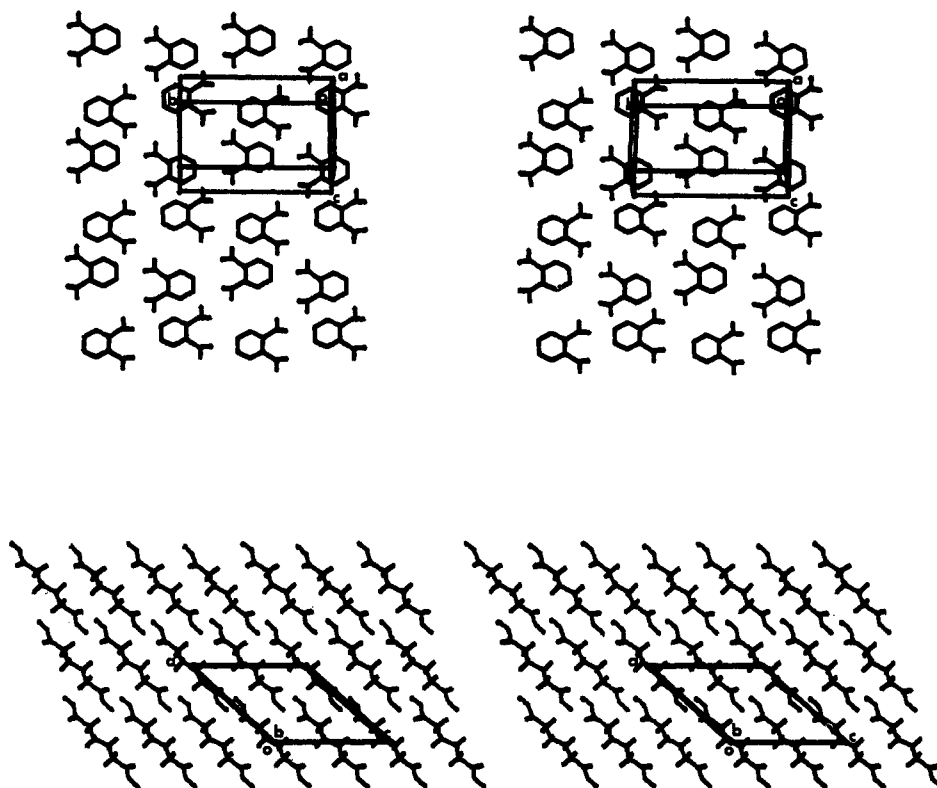
reported<sup>3</sup> were shown to proceed at rates comparable to those of the benzoic acids. The product was a quantitative yield of a mixture of the ammonium benzoate and the benzamide which seem to coexist as a solid compound whose structure, however, has not been determined in detail. Unique among the crystalline compounds discussed here is 4-bromobenzoic anhydride in space group *C*2 because it alone has in a perfect single crystal all molecules identically oriented. Thus the *b* axis is a polar axis and it is to be expected that reaction might proceed at a rate in the positive direction different from the rate in the negative direction along the *b* axis. Further work has confirmed that reaction is initiated at a single {010} face and proceeds most rapidly in only one direction parallel to the *b* axis.<sup>28</sup> It is to be hoped that further study of polar unitropic reactions may lead to more insight into solid-gas reactions.

The study by Kohler and Kable<sup>14</sup> of the preparation and properties of 7-cyclohexylidenenorborn-2-ene-5,6-dicarboxylic anhydride (**1**) suggested a possible example of the practical utility of the solid anhydride-gaseous ammonia reaction. Attempts<sup>14</sup> to convert the anhydride to its parent acid had been unsuccessful because the anhydride, although stable in the crystalline state, underwent a ready fragmentation to the fulvene and maleic anhydride when hydrolysis in solution was attempted. When the crystalline anhydride was exposed to gaseous ammonia, it was found to react to give the ammonium salt of the amide, **2**, in quantitative yield with no yellow color due to the fulvene observable.

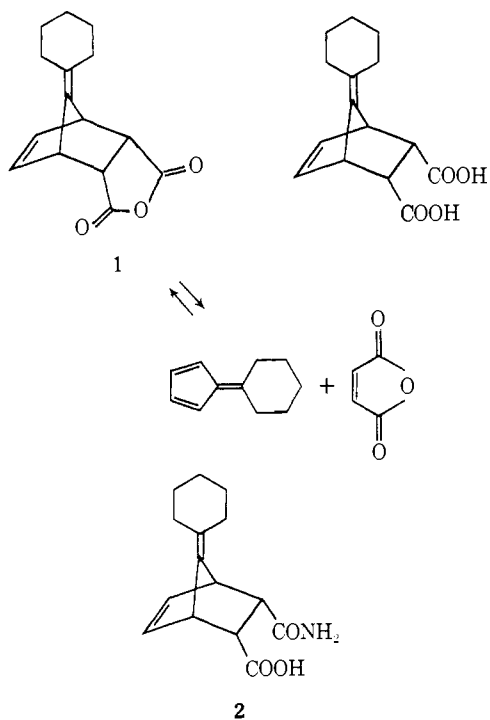
A final class of acids whose reaction with ammonia will be discussed here is that of the dibasic acids. The structure of phthalic acid is shown in Figure 9.<sup>10</sup> The structure is made up of infinite parallel chains of phthalic acid molecules linked by H-bonded carboxyl dimer units. These chains together with a vector parallel to the *b* axis may be taken to define the layer plane here oriented in the plane of the paper to emphasize the similarity of the crystal structure with that of the monobasic acids described previously. As with most other acids discussed

(28) Dr. C.-T. Lin is continuing work on this reaction.





**Figure 9.** Arrangement of the molecules in crystals of two dibasic acids. Upper picture, phthalic acid,<sup>10</sup>  $C2/c$ , looking down on the layer plane (101). Infinite chains joined by carboxyl H-bonded dimer units are parallel to  $[\bar{1}01]$ . The top face of the reacting crystal in Figure 2 is parallel to (010). Lower picture, adipic acid<sup>11</sup> looking down on (010).



here, reaction of ammonia was found to occur most rapidly (and at essentially equal rates) from the sides of the crystal, the best-developed  $\{010\}$  faces, although clouding somewhat, remaining sufficiently clear to permit observation of the advancing fronts along the  $a$  and  $c$  directions until quite late in the reaction. Inspection of the crystal structure leads to a ready explanation of

the observed behavior. The reactive carboxyl groups lie in layers parallel to the  $ac$  plane so that as reaction occurs adjacent carboxyl groups are accessible to ammonia molecules as they diffuse in through regions of disorder created by prior reaction. To advance in the  $b$  direction, however, ammonia molecules must penetrate nonpolar hydrocarbon layers composed of benzene rings. The most striking difference between the reaction of phthalic acid and those of the monocarboxylic acids is that in regions where reaction has occurred the "crystal" undergoes fragmentation or shattering. This behavior may be related to the degree of brittleness of the parent acid crystal as well as to the twofold increase in the amount of ammonia reacting per substrate molecule.

Adipic acid, whose structure<sup>11</sup> is also shown in Figure 9, showed even more extraordinary behavior. Reaction seemed to penetrate the major face at defects and once initiated spread along a direction parallel to a crystallographic axis. After a short time, sufficient stress had developed to cause the crystal to fragment. The mechanism of the development of the fracture lines is of interest and clearly requires further investigation.

These studies suggest that reactions of crystalline solids with gases of the type examined here require not only a chemical reaction of sufficient speed but also that the initial reaction leads to disorder of a sort which permits penetration of the gaseous reactant into the interior of the crystal. Although this process is extremely complicated it is most encouraging that reactivity can be correlated with crystal structure to as great a degree as has been possible. It is hoped that such work

may lead to more interest in the analysis and prediction of the crystal packing of molecular crystals and it should most certainly serve as a warning to those tempted to

study the kinetics of solid-gas reactions without due regard to differences in reactivity at different crystal faces and in different directions within the crystal.

## Spectroscopic Studies of Formation and Decay of Triplet Exciplexes. Evidence for a Limited Role of Charge-Transfer Interactions in a Nonpolar Solvent<sup>1</sup>

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Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received March 23, 1974

**Abstract:** Triplet states of anthracene and metalloporphyrins such as zinc etioporphyrin I in benzene solution are quenched by low concentrations of nitro aromatics and organic chloro compounds. At high quencher concentrations, new transients are observed which are exciplexes intermediate in the quenching process. Although there is some correlation of triplet quenching rates with ease of quencher reduction, the results are not consistent with a purely charge-transfer model. The exciplexes are probably best described as weak complexes of a slightly perturbed excited state similar to ground-state donor-acceptor complexes.

Interaction of electronically excited states with ground-state molecules in processes not involving electronic energy transfer has come to be recognized as a common phenomenon in photochemistry.<sup>3</sup> Among the frequently encountered consequences of such interaction are enhanced radiationless decay, chemical reaction from quencher or substrate or between them, electron transfer resulting in ion formation, and appearance of new emission. The term "exciplex" or excited-state complex, first applied by Lumry,<sup>4</sup> has been used by numerous workers to describe the intermediates involved in these diverse phenomena. Some workers have used the term exciplex to describe photochemical reactions, even in the absence of conclusive evidence that an excited-state complex is intermediate in the chemical reaction,<sup>5</sup> and many photochemists have used the term when otherwise unexplained energy-wasting processes (such as fluorescence quenching) occur, whether or not there is direct evidence for the existence of an excited-state complex. This broad usage of the term exciplex has led to the development of some controversy over exactly what an exciplex is and what factors govern true exciplex formation.

Excited-state quenching phenomena have invited a great range of descriptions. Although the observation of exciplex emission provides strong evidence for the existence of an excited complex, exciplex occurrence has been demonstrated in several cases where no emission occurs. Several workers have attempted to fit all exciplexes and excited-state quenching interactions into one theoretical framework, while others have argued for

more vague descriptions. In particular, there has been much debate about the extent of charge-transfer character in excited-state complexes. Weller<sup>6-9</sup> has pointed out that excitation of an electron from a bonding to an antibonding orbital produces a state which should have both a lower ionization potential and a greater electron affinity than the ground electronic state. Thus, an electronically excited molecule could form charge-transfer complexes in which it is the electron donor in some cases and the acceptor in others. In support of this, Weller and coworkers have found excellent correlation of exciplex energy with donor oxidation potentials and acceptor reduction potentials for the systems they have studied. Although it seems clear that formation of ions or ion pairs may be an important decay pathway for certain types of exciplexes in polar solvents, there is still considerable uncertainty over what factors govern exciplex decay in nonpolar solvents and even as to what paths for decay are available.<sup>10</sup> Hammond and coworkers<sup>11</sup> as well as Mataga<sup>12</sup> have argued that an exciplex is a new chemical species and should have a new wave function which is some combination of various excitation resonance and charge-transfer terms (eq 1).

$$\Psi_{\text{exciplex}} = \Psi_{S^*Q} \leftrightarrow \Psi_{SQ^*} \leftrightarrow \Psi_{S^+Q^-} \leftrightarrow \Psi_{S^-Q^+} \quad (1)$$

We have previously found that exciplexes formed between excited triplets of metalloporphyrins and nitroaromatics in benzene solution can be detected by flash spectroscopy.<sup>1,13</sup> Even though they do not emit, these

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(9) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

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(1) A preliminary account of a portion of this work has appeared: J. K. Roy and D. G. Whitten, *J. Amer. Chem. Soc.*, **94**, 7162 (1972).

(2) (a) University of North Carolina; (b) Davidson College, Davidson, N. C. 28036.

(3) See, for example, J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, pp 301-491, and references therein; or B. Stevens, *Advan. Photochem.*, **8**, 161 (1971).

(4) (a) M. S. Walker, T. W. Bednar, and R. Lumry, *J. Chem. Phys.*, **45**, 3455 (1966); (b) *ibid.*, **47**, 1020 (1967).

(5) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **95**, 5783 (1973).