

tion with changes in the amide structure. The Co^{II} complexes of bis-salicylaldehyde imines exist in a variety of crystalline forms some of which have reacted rapidly and reversibly with oxygen gas while others are inert.^{35,40} An example of biochemical interest is the reported^{4f} ready dehydrogenation by oxygen of the crystalline hydrate of L-1,4-cyclohexadienyl-L-alanine whereas the unhydrated L, D, and DL forms of the substance are stable under the same conditions. It has been recognized in these cases that there was involved initially a surface reaction and that the subsequent rate depends on the ability

(40) W. P. Schaeffer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 1575 (1969).

of the gas to gain access to the interior of the crystal. Unfortunately, there has been a paucity of crystallographic structural data in most of these cases. When direct microscopic examination of single crystals has been carried out no anisotropy has been reported. In contrast, the reactions of ammonia with acids almost always show much more rapid reaction at some crystal faces than at others (Figure 1).³ An understanding of this phenomenon in terms of the crystal structure seems to be a prerequisite to a further understanding of the mechanisms of such reactions. This subject will be developed further in the following papers.³⁰

Reactions of Molecular Crystals with Gases. II. The X-Ray Structure of Crystalline 4-Chlorobenzoic Acid and the Anisotropy of Its Reaction with Ammonia Gas^{1,2}

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Abstract: The crystal structure of 4-chlorobenzoic acid (**1**) has been determined from three-dimensional reflection data collected on a diffractometer. The crystals are triclinic with $a = 14.392(2) \text{ \AA}$, $b = 6.227(1) \text{ \AA}$, $c = 3.861(1) \text{ \AA}$, $\alpha = 88.68(3)^\circ$, $\beta = 100.12(4)^\circ$, and $\gamma = 93.31(3)^\circ$; the space group is $P\bar{1}$. The structure was refined to an R factor of 0.071 on 924 independent reflections. The crystal is comprised of stacks of hydrogen-bonded dimers as are many other substituted benzoic acid crystals. The dimers are so arranged that there is a nearly linear $\text{C}-\text{Cl} \cdots \text{Cl}-\text{C}$ interaction ($\text{C}-\text{Cl} \cdots \text{Cl}$ angle of 167°) with a $\text{Cl} \cdots \text{Cl}$ contact of 3.44 \AA . The progress of the reaction of single crystals of **1** with ammonia gas was followed under the microscope. The crystals grow as plates with $\{100\}$ being the developed face of the plate. A highly anisotropic direction of attack was observed, with the rate of reaction being quite rapid from the sides of the plate while the top face remained clear. This behavior can be rationalized in that the faces where reaction is rapid have carboxyl functional groups completely exposed to attack from the surface, whereas the $\{100\}$ faces have a layer of closely packed 4-chlorophenyl groups (with the $\text{C}-\text{Cl}$ vector pointing toward the surface of the $\{100\}$ faces) shielding the carboxyl groups from attack. Should, nonetheless, a surface layer of molecules react, progress of the reaction toward the center of the crystal is hindered effectively by the large distances between neighboring carboxyl groups in a direction normal to the $\{100\}$ faces.

Microscopic examination of the reactions of crystalline carboxylic acids with ammonia gas suggested³ that such reactions are in general anisotropic. In order to examine possible correlation of reactivity with the structure of the crystal faces, it is necessary to know the crystal structures of the pertinent acids. Many of the desired crystal structures had been reported but that of 4-chlorobenzoic acid, one of the fastest reacting and highest melting acids, was not known in any detail. This paper describes the determination of the X-ray structure of 4-chlorobenzoic acid and discusses the correlation of chemical reactivity with crystal structure for this compound.

(1) Taken from the Ph.D. Thesis of Rodger S. Miller, submitted to the University of Illinois, 1973, available from University Microfilms, Ann Arbor, Mich.

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

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

A morphological study on 4-chlorobenzoic acid (**1**) was carried out by Steinmetz⁴ and is reported by Groth.⁵ Single-crystal cell data were presented by Toussaint⁶ with subsequent minor changes by Pollock and Woodward.⁷ Toussaint also published a picture of a projection of the structure but without further details.⁶ In the course of a study of some other aromatic acids, Schmidt⁸ commented in general terms upon the probable packing arrangement in the unit cell although no additional experimental data were gathered.

Experimental Section

A plate-like crystal ($0.10 \times 0.20 \times 0.045 \text{ mm}$) was obtained from a solution of the acid in a 2% mixture of ethyl acetate in carbon tetrachloride. Crystal data: for $\text{C}_7\text{H}_5\text{O}_2\text{Cl}$, $M = 156.6$; triclinic,

(4) H. Steinmetz, *Z. Kristallogr., Kristallgeometrie, Kristallphys. Kristallchem.*, **53**, 473 (1914).

(5) P. Groth, "Chemische Kristallographie," Vol. 4, Engelmann, Leipzig, 1917, pp 466-467.

(6) J. Toussaint, *Acta Crystallogr.*, **4**, 71 (1951).

(7) J. M. Pollock and I. Woodward, *Acta Crystallogr.*, **7**, 605 (1954).

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

$a = 14.392(2)$, $b = 6.227(1)$, $c = 3.861(1) \text{ \AA}$; $\alpha = 88.68(3)$, $\beta = 100.12(4)$, and $\gamma = 93.31(2)^\circ$; $V = 340.1 \times 10^{-24} \text{ cm}^3$; D_{measd} (floatation in carbon tetrachloride and pentane) = 1.54 g cm^{-3} ; $Z = 2$, $D_{\text{calcd}} = 1.53 \text{ g cm}^{-3}$; $F(000) = 160$, $\mu(\text{Cu K}\alpha) = 44.1 \text{ cm}^{-1}$; no systematic absences; space group either $P1$ or $P\bar{1}$.

The cell dimensions were determined from the crystal mounted about the c axis (0.20 mm) by a least-squares analysis on the settings for the four angles of 12 carefully centered reflections (Cu $K\alpha$, $\lambda 1.54184 \text{ \AA}$). Intensity data were collected on a Picker FACS-1 diffractometer (Cu $K\alpha$ radiation) using a moving crystal-moving counter (θ , 2θ) scan mode. The scan rate was $2^\circ/\text{min}$ and the base width of the scan was 2° with a factor being applied for the separation of the α_1 , α_2 components of the radiation. Backgrounds at both limits of the scan were measured for 10 sec. Approximately monochromatic radiation was obtained by use of a nickel filter and pulse height analysis. The intensities of the reflections were measured on a scintillation counter. Three reflections (041, 202, and $0\bar{3}1$) were employed as standards and were recorded after every 100 measurements. Their intensities were within $\pm 0.5\%$ throughout the period of data collection, although the crystal became slightly opaque during this period (4 days). The octants of data hkl , $\bar{h}\bar{k}l$, $\bar{h}kl$, and $h\bar{k}l$ were collected out to $2\theta = 130^\circ$. A total of 924 independent reflections was judged to be above zero at the 3σ level of significance. Corrections were applied for Lorentz and polarization effects but not for absorption.

Structure Solution and Refinement. Some difficulties were encountered in trying to solve this structure by the Patterson heavy atom method. As the position of the Cl-Cl vector was not immediately obvious from the Patterson map, although the orientation of the ring was fairly clear, a systematic examination of all peaks that could reasonably represent the Cl-Cl vector was undertaken. However, while such an examination was still in progress,⁹ the structure was solved by a method previously used by Fleischer^{10,11} and employed subsequently in this laboratory.¹² When the orientation and general structure, but not the position, of the molecule are known in the space group $P\bar{1}$, the problem can be treated in $P1$. A rigid fragment of the molecule in the correct orientation with respect to the axes is placed arbitrarily and used as a phasing model for the rest of that molecule and the entire symmetry related molecule. When the remainder of the contents of the unit cell are revealed, the origin is transformed to correspond to the space group $P\bar{1}$ and refinement then proceeds in $P\bar{1}$. When the six carbon atoms of one ring were used as such a phasing model, treating the space group as $P1$, the positions of the six atoms of the other benzene ring were readily apparent. Inclusion of the 12 ring atoms in another phasing calculation yielded the position of the rest of the non-hydrogen atoms in the structure. Full-matrix least-squares refinement of the structure in the space group $P1$ lowered the R factor to 0.19. Positional and isotropic temperature factors were varied for the atoms, all nonzero reflections were given unit weight, and the quantity minimized was $\sum w||F_{\text{obsd}}| - |F_{\text{calcd}}||^2$. At this point, the structure was transformed to the space group $P\bar{1}$.

Full-matrix least-squares refinement varying positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms gave an R factor of 0.080 and a value for R_2 of 0.106.¹³ In the refinement, the reflections were weighted using a program written by Dieterich¹² and following the method proposed by Corfield, Doedens, and Ibers.¹⁴

The hydrogen atoms, including OH(2) bonded to O(2), had been previously located from a difference Fourier map. While the position of OH(2) following the refinement was not unreasonable, the B_θ value was 24 \AA^2 , in contrast to values of $3\text{--}6 \text{ \AA}^2$ for the hydrogen atoms attached to carbon atoms. When this atom was omitted from a structure factor calculation and a difference map was computed, a single peak of $0.4 \text{ electron/\AA}^3$ appeared $\sim 1 \text{ \AA}$ from O(2), but the C(7)-O(2)-peak angle had the rather unreasonable value of 150° . The reflection 201 was removed from the data set at this point as its $|F_{\text{obsd}}|$ was less than one-half of $|F_{\text{calcd}}|$, and it was thus judged to suffer from the effects of absorption and extinction.

(9) After the structure had been solved, it became clear that the positions of the chlorine atoms derived from the correct Cl-Cl vector had not been tried for phasing.

(10) E. B. Fleischer, *Acta Crystallogr., Sect. A*, **26**, 575 (1970).

(11) This method was brought to our attention by Dr. S. R. Byrn.

(12) D. A. Dieterich, Ph.D. Thesis, University of Illinois, 1973.

(13) $R = \frac{\sum ||F_{\text{obsd}}| - |F_{\text{calcd}}||}{\sum |F_{\text{obsd}}|}$; $R_2 = \frac{[\sum w||F_{\text{obsd}}| - |F_{\text{calcd}}||^2]}{[\sum w|F_{\text{obsd}}|^2]}^{1/2}$.

(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

Further refinement with OH(2) included in the model gave values of R and R_2 of 0.071 and 0.081. Once again, the geometry of the C-O-H group was not unreasonable, but the temperature factor was very high, 18 \AA^2 . In the last cycle of this series of refinements, the largest ratio of shift/esd for any parameter was 0.5. The largest peak on a difference map was $\sim 1 \text{ \AA}$ from the chlorine atom in the x direction and had a height of $0.4 \text{ electron/\AA}^3$. There were no peaks above $0.1 \text{ electron/\AA}^3$ near O(1), but despite the fact that OH(2) had been included in the model, there was a peak of $0.3 \text{ electron/\AA}^3 \sim 1 \text{ \AA}$ from O(2) but with a C(7)-O(2)-peak angle of 156° . The atomic coordinates and thermal parameters obtained from this refinement are listed in Tables I and II. Through-

Table I. Final Atomic Coordinates (in fractions of the unit cell edge) with Esd in Parentheses^{a,b}

Atom	x	y	z
Cl	0.4263 (1)	0.7860 (2)	0.8311 (4)
C(1)	0.1845 (3)	0.3336 (7)	0.3680 (12)
C(2)	0.2763 (4)	0.2783 (8)	0.3778 (14)
C(3)	0.3516 (3)	0.4153 (9)	0.5216 (14)
C(4)	0.3319 (3)	0.6111 (8)	0.6529 (13)
C(5)	0.2414 (4)	0.6696 (9)	0.6444 (14)
C(6)	0.1668 (4)	0.5306 (8)	0.5016 (13)
C(7)	0.1034 (3)	0.1872 (8)	0.2087 (12)
O(1)	0.1191 (2)	0.0194 (5)	0.0606 (10)
O(2)	0.0205 (2)	0.2407 (6)	0.2296 (11)
H(2)	0.289 (3)	0.159 (8)	0.277 (13)
H(3)	0.424 (3)	0.401 (7)	0.542 (12)
H(5)	0.234 (5)	0.815 (11)	0.754 (16)
H(6)	0.103 (3)	0.557 (7)	0.495 (12)
OH	-0.026 (9)	0.129 (17)	0.043 (30)

^a Hydrogen atoms are given the number of the carbon atom to which they are bonded. ^b Atom OH is the hydrogen atom bonded to O(2).

out the analysis the scattering curves for chlorine, oxygen, and carbon tabulated by Cromer and Mann¹⁵ and that for hydrogen calculated by Stewart, *et al.*,¹⁶ were used. The curve for chlorine was corrected for the effects of anomalous dispersion.¹⁷⁻¹⁹

Identification of Crystal Faces. 4-Chlorobenzoic acid was recrystallized as described above. Measurement of angles of the major face with the other faces showed general agreement with the previous results reported by Groth.⁵ Because of a difference in the choice of crystallographic axes, the indices due to Steinmetz⁴ and

(15) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(16) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(17) "International Tables for X-Ray Crystallography," Vol. III, the Kynoch Press, Birmingham, England, 1962, pp 213-216.

(18) See paragraph at end of paper regarding supplementary material.

(19) As we were particularly interested in the location of hydrogen atoms, some additional refinements were tried on a set of data from which were removed seven other low order reflections whose $|F_{\text{obsd}}| < |F_{\text{calcd}}|$. After refinement of a model including OH(2), a difference map was calculated and showed two peaks in the region between the oxygen atoms: one of $0.2 \text{ electron/\AA}^3$ within bonding distance of O(1) and one, in addition to OH(2), of $0.35 \text{ electron/\AA}^3$ within bonding distance of O(2). After this refinement, R was 0.065 and R_2 was 0.072. Second, a model, including two hydrogen atoms with half-occupancy attached to O(1) and O(2), respectively, was then refined; the values of R and R_2 were 0.066 and 0.075. However, the half-atom OH(1) was found to be moving toward OH(2) and the model was converging toward the single hydrogen model. Utilizing an approach previously employed by Leiserowitz and coworkers,²⁰ we then omitted both hydrogen atoms from a structure factor calculation, but found that there were two peaks $> 0.25 \text{ electron/\AA}^3$ at positions reasonable for hydrogen atoms to be covalently bonded to both O(1) and O(2) on a subsequent difference map. We therefore conclude that there is considerable evidence from the difference electron density maps for disorder in the region of the carboxyl group. However, it does not appear to be completely random and there is definite evidence from the difference maps that the hydrogen is more often attached to O(2) and that C(7)-O(2) is the hydroxyl bond than the reverse.

(20) S. E. Filippakis, L. Leiserowitz, D. Rabinovich, and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 1750 (1972), and subsequent papers in their series.

Table II. Final Thermal Parameters with Standard Deviations in Parentheses^{a,b}

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.00573 (9)	0.0328 (5)	0.112 (1)	-0.0038 (2)	-0.0004 (3)	-0.0170 (6)
C(1)	0.00387 (26)	0.0191 (13)	0.052 (4)	-0.0011 (4)	0.0022 (7)	-0.0035 (16)
C(2)	0.00389 (27)	0.0208 (14)	0.072 (4)	0.0003 (5)	0.0026 (8)	-0.0064 (20)
C(3)	0.00328 (28)	0.0279 (16)	0.078 (5)	0.0005 (5)	0.0013 (9)	-0.0051 (21)
C(4)	0.00441 (29)	0.0221 (14)	0.063 (4)	-0.0023 (5)	0.0003 (8)	-0.0042 (19)
C(5)	0.00511 (31)	0.0220 (15)	0.072 (5)	-0.0005 (5)	0.0027 (9)	-0.0065 (20)
C(6)	0.00405 (28)	0.0212 (14)	0.073 (4)	0.0012 (5)	0.0029 (8)	-0.0056 (19)
C(7)	0.00353 (25)	0.0230 (14)	0.064 (4)	-0.0004 (5)	0.0015 (8)	-0.0004 (20)
O(1)	0.00473 (21)	0.0204 (10)	0.102 (4)	0.0005 (3)	0.0028 (6)	-0.0195 (15)
O(2)	0.00311 (19)	0.0309 (12)	0.135 (4)	-0.0003 (4)	0.0037 (7)	-0.0269 (18)

Atom	B_{θ}	Atom	B_{θ}
H(2)	5 (1)	H(6)	3 (1)
H(3)	4 (1)	OH	18 (4)
H(5)	7 (2)		

^a Anisotropic thermal parameters expressed as $\exp -[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. ^b Isotropic parameters expressed as $\exp -[B_{\theta} \sin^2 \theta/\lambda^2]$.

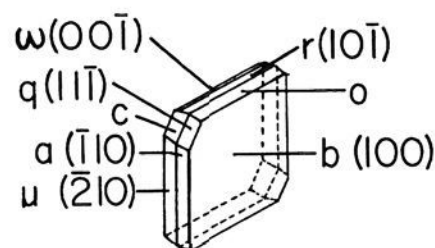


Figure 1. A crystal of 4-chlorobenzoic acid.⁵ Faces observed by Steinmetz⁴ are designated by the letters employed previously.⁵ Those faces observed in the present work are, in addition, designated with the indices based on the present assignment of axes.

employed by Groth⁵ were converted to their equivalent in the present coordinate system by means of the transformation matrix $[\bar{1}, 1, 0/1, 0, 1/0, 0, \bar{1}]$. A drawing of a crystal with the faces labeled with Groth's alphabetical designation together with the indices corresponding to the present coordinate system is shown in Figure 1.²¹

Reaction of Single Crystals of 4-Chlorobenzoic Acid with Ammonia Gas. Since the preliminary study of the reaction was described in the previous paper³ there remains to be discussed only the microscopic examination of the reaction of single crystals of the acid which were placed in an enclosed cell and observed on a microscope stage while a stream of ammonia was passed over them. The top (100) face remained clear whereas the disorder induced in the crystal by the formation of ammonium 4-chlorobenzoate was observed to begin quite uniformly at the other faces and to move toward the center of the crystal as shown in Figure 2.

Results and Discussion

Molecular Structure. The bond lengths and angles in **1** are shown in Figure 3. The results of our study appear to be generally consistent with the picture of the projection of the structure given by Toussaint.⁶ The average C-C bond length in the benzene ring is 1.384 Å with a root mean square deviation of 0.010 Å. A rigid body analysis was carried out on the entire molecule following the method of Schomaker and Trueblood.²² The rms difference between the atomic vibrations obtained from the results of the X-ray analysis

(21) Toussaint⁶ reported cell dimensions of $a = 14.39$ Å, $b = 6.29$ Å, $c = 3.86$ Å, $\alpha = 91.6^\circ$, $\beta = 95.3^\circ$, and $\gamma = 92.7^\circ$ and gave $[\bar{1}, 1, \bar{1}/1, 0, 1/0, 0, \bar{1}]$ for the transformation matrix from the Steinmetz⁴ to Toussaint orientations. However, this matrix corresponds to a change in the handedness of the axes. We find that the transformation from the cell data presented by us to those reported by Toussaint is $[1, 0, 1/0, 1, 0/0, 0, \bar{1}]$. Once again this matrix involves a reversal of the handedness of the axes. These results indicate that the axes reported by Toussaint correspond to a left-handed coordinate system. We thank Professor Jean Toussaint for his assistance on these points.

(22) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968).

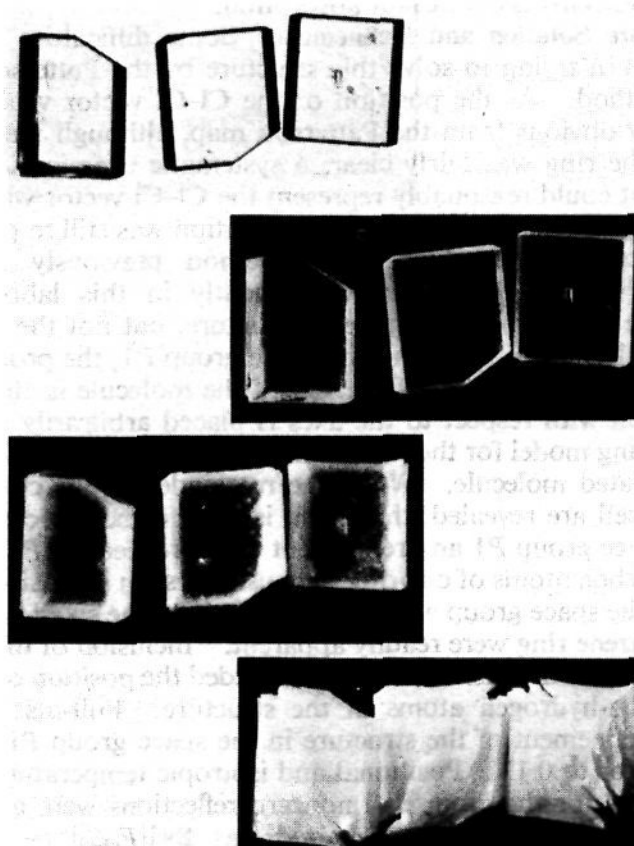


Figure 2. A group of three crystals of 4-chlorobenzoic acid photographed during their reaction with ammonia gas. Upper picture is before reaction, rear illumination. The two middle pictures show the crystals after reaction for 21 and 100 min, respectively, photographed with the crystals illuminated from the top. Bottom picture shows the same crystals after 1280 min with reaction essentially complete, illuminated from the top.

and those from the rigid body postulate is 0.003 Å². On the basis of this analysis, the bond lengths were adjusted for libration and the adjusted values are shown in Table III. Many of the bond lengths were in-

Table III. Bond Lengths (Å) before and after Adjustment for Libration by Rigid Body Analysis^a

Bond	Without correction	After correction	Bond	Without correction	After correction
C(1)-C(2)	1.378 (7)	1.388	C(4)-Cl	1.744 (5)	1.747
C(2)-C(3)	1.384 (7)	1.388	C(1)-C(7)	1.491 (7)	1.495
C(3)-C(4)	1.394 (7)	1.402	C(7)-O(1)	1.253 (6)	1.261
C(4)-C(5)	1.366 (7)	1.377	C(7)-O(2)	1.273 (6)	1.281
C(5)-C(6)	1.384 (7)	1.389			
C(1)-C(6)	1.396 (7)	1.405			

^a Using method described in ref 21.

creased by 0.008–0.011 Å after this correction. Because of the uncertain validity of the adjustment in this structure, the original values will be used in the subsequent discussion.

The length of 1.744 (5) Å found for the C–Cl bond in the present study is in good agreement with the values found for such bonds in other molecules,²³ with the exception of the cases, pointed out by Rudman,²⁴ where there are two C–Cl bonds attached to adjacent carbon atoms in the benzene ring. For example, the C–Cl lengths in 2-chlorobenzoic acid,²⁵ in the potassium acid salt of 4-chlorobenzoic acid,²⁶ and in the piperidinium salt of 4-chlorobenzoic acid²⁷ are 1.737 (7), 1.741 (10), and 1.735 (11) Å, respectively.

The two C–O bonds in the carboxylic acid group are quite similar in length, 1.253 (6) and 1.273 (6) Å, a fact that suggests disorder of two positions related by a 180° rotation about the C(aromatic)–C(carboxyl) bond.^{28, 29}

The molecule of 4-chlorobenzoic acid is significantly nonplanar. The six carbon atoms in the benzene ring are coplanar (maximum deviation 0.003 Å), and the best plane through the four atoms of the carboxyl group (C(1), C(7), O(1), and O(2)) makes an angle of 5.7° with the plane of the benzene ring. The atoms C(1), C(7), O(1), and O(2) lie 0.015, 0.016, 0.138, and –0.076 Å from the plane of the ring. Small angles of rotation of carboxyl groups from the planes of the benzene rings are quite typical in aromatic acids and salts, e.g., benzoic acid (2°),³⁰ 4-bromobenzoic acid (5.8°),³¹ 4-chlorobenzoate in the piperidinium salt (7°),²⁷ in the potassium acid salt of 4-chlorobenzoic acid (9°),²⁶ whereas in 2-chloro-²⁵ and 2-bromobenzoic acids,³² the angles are 14 and 18.3°, respectively.

Crystal Packing. A stereoscopic view of the crystal structure is shown in Figure 4. As is invariably the case for aromatic monocarboxylic acids in achiral molecules, the 4-chlorobenzoic acid molecules form centrosymmetric dimers by hydrogen bonding. The O(2)···O(1^V) distance is 2.615 (5) Å (see Table IV for definition of Roman numerals). This O···O distance is too long for a symmetrical O···H···O hydrogen bond³³ and is thus further evidence that the –CO₂H groups are disordered. The O(2)–OH length is 1.11 (12) Å, the OH···O(1^V) distance is 1.58 (13) Å, and the O(2)–OH···O(1^V) angle is 151 (2)°. The dimers are arranged in stacks. The overlap of the aromatic rings within the stacks of the molecules along the z

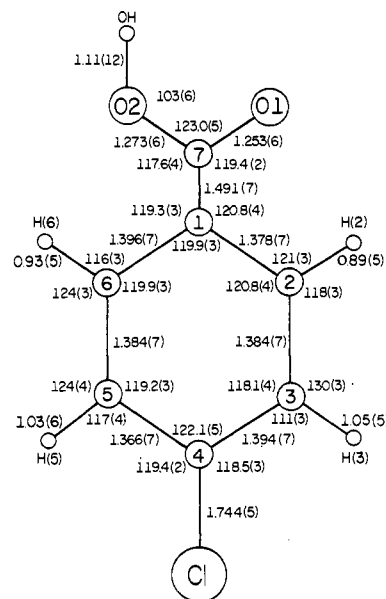


Figure 3. Drawing of 4-chlorobenzoic acid with bond lengths (Å) and angles (deg); standard deviations in parentheses.

Table IV. Intermolecular Contacts (≤ 3.6 Å) in 4-Chlorobenzoic Acid

O(1)···C(5 ^I)	3.47	C(6)···O(1 ^V)	3.50
O(1)···C(5 ^{II})	3.43	C(7)···O(1 ^V)	3.38
O(1)···C(6 ^{II})	3.50	C(7)···O(2 ^V)	3.43
C(1)···C(6 ^{III})	3.51	O(1)···O(1 ^V)	3.37
C(3)···C(4 ^{III})	3.51	O(1)···O(2 ^V)	2.61
O(1)···C(1 ^{III})	3.51	O(2)···O(2 ^V)	3.49
O(1)···C(7 ^{III})	3.40	O(1)···OH ^V	1.58
O(1)···O(2 ^{III})	3.55	C(6)···O(2 ^V)	3.44
C(5)···O(1 ^V)	3.43	Cl···Cl ^{VII}	3.44
I refers to x, –1 + y, –1 + z		V refers to –x, –y, –z	
II refers to x, –1 + y, z		VI refers to –x, 1 – y, 1 – z	
III refers to x, y, –1 + z		VII refers to 1 – x, 2 – y, 2 – z	
IV refers to x, 1 + y, z		VIII refers to x, y, 1 + z	

direction is shown in Figure 5. The C(5)–H and the C(2)–H bonds lie over the benzene rings in adjacent molecules in these stacks. The shortest interatomic distances between molecules in a stack are C(1)···C(6^{III}), C(3)···C(4^{III}), C(1)···O(1^{VIII}), C(7)···O(1^{VIII}), and O(1)···O(2^{III}) of 3.51, 3.51, 3.51, 3.40, and 3.55 Å, respectively. The mean interplanar distance between aromatic rings in the stack is 3.486 Å.

There is a short Cl···Cl^{VII} contact of 3.441 (3) Å between stacks of dimers of 4-chlorobenzoic acid; the C(4)–Cl···Cl^{VII} angle is 167.0 (2)°. Pauling³⁴ gives a value of 1.80 Å as the van der Waals radius for chlorine; however, Bondi³⁵ gives a value of 1.70 Å. There are several examples of Cl···Cl intermolecular contacts where one of the chlorine atoms lies almost along the axis of the covalent bond formed by the other chlorine atom. Sakurai, Sundaralingam, and Jeffrey³⁶ surveyed a number of short intermolecular Cl···Cl con-

(23) (a) G. J. Palenik, J. Donohue, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 1139 (1968); (b) H. Hope, *Acta Crystallogr., Sect. B*, **25**, 78 (1969); (c) H. Hope and D. Victor, *ibid.*, **25**, 1849 (1969).

(24) R. Rudman, *Chem. Commun.*, 536 (1970); *Acta Crystallogr., Sect. B*, **27**, 262 (1971).

(25) G. Ferguson and G. A. Sim, *Acta Crystallogr.*, **14**, 1262 (1961).

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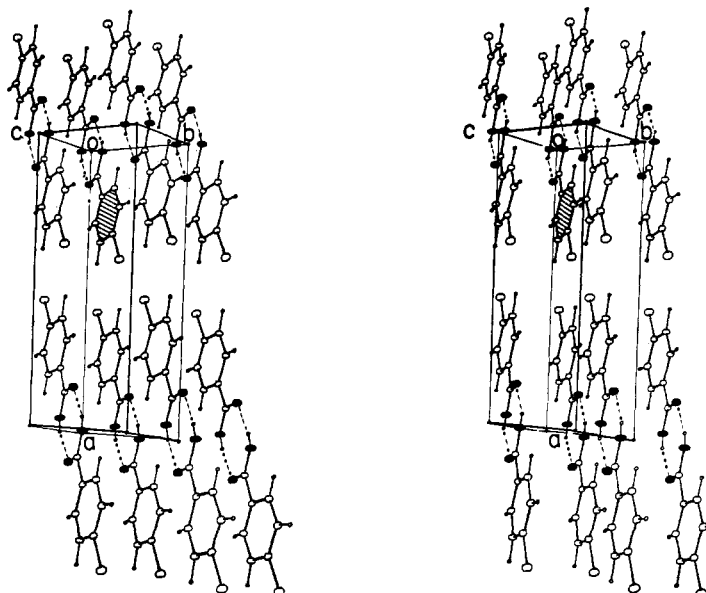


Figure 4. Stereoscopic view of the packing of 4-chlorobenzoic acid. The reference molecule is shaded.

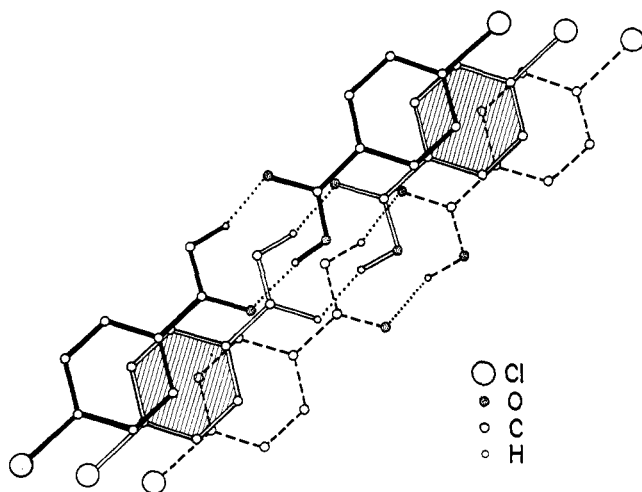


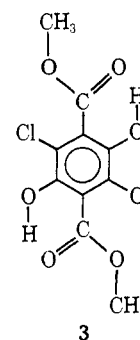
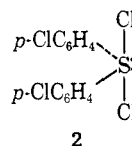
Figure 5. Overlap of dimers in a stack projected onto the plane defined by the six atoms of the phenyl ring.

tacts in the range 3.27–3.49 Å³⁷ that had been found in several structures. A very short Cl···Cl contact of 3.307 (3) Å was found in the structure of the chlorine complex of bis(4-chlorophenyl) sulfide (2),³⁸ where some Cl···Cl bonding interaction is involved. In this latter structure, the S–Cl···Cl angle is 162°. In a number of molecules with chloro-substituted aromatic rings, this type of Cl···Cl interaction may be quite important in determining crystal structure arrangements. For example, in the yellow form of the dimethyl ester of 3,6-dichloro-2,5-dihydroxyterephthalic acid (3), there is a Cl···Cl contact of 3.47 Å and a C–Cl···Cl angle of 146.7 (2)°,³⁹ between chlorine atoms in adjacent layers in the direction of slowest interconver-

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sion of the yellow form of 3 to the white. Intermolecular contacts involving chlorine atoms may also be important in the phase transitions between the monoclinic and triclinic forms of 1,4-dichlorobenzene. In the monoclinic form of 1,4-dichlorobenzene⁴⁰ there are two Cl···Cl contacts of 3.684 Å, with C–Cl···Cl angles of 165.8 and 92.5°, whereas in the triclinic form⁴¹ there is one Cl···Cl contact of 3.456 Å with a C–Cl···Cl angle of 169.2°. Short Cl···Cl contacts which may be important in packing have also been noted in 4-chlorobenzoic anhydride⁴² and in 4,4'-dichloroazobenzene.^{23c} Br···Br contacts significantly less than twice the van der Waals radius have also been noted when the C–Br···Br angle approaches linearity.⁴³ These types of halogen–halogen contacts appear to play a significant role in determining the crystal structure of a range of 4-halo-substituted benzene derivatives as will be described in the following paper.⁴⁴

Relationship of Crystal Packing to Anisotropic Behavior in the Reaction of Crystalline 4-Chlorobenzoic Acid with Ammonia Gas. Comparison of photographs of reacting crystals (Figure 2) with the identification of

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crystal faces from optical goniometry (Figure 1) shows that while the (100) crystal face remains quite free from attack by the ammonia gas, the other faces, $(\bar{1}10)$, $(\bar{2}10)$, (001), $(10\bar{1})$, $(11\bar{1})$, and their five centrosymmetric counterparts, react at nearly equal rates as shown by the nearly uniform advance of the reaction fronts at these faces toward the center of the crystal. In order to address the fundamental question of how the rate of advance of a reaction front through the crystal depends on the crystal packing, it is necessary to have a clear visualization of the orientation of the internal structure in the macroscopic crystal. In Figure 6 are shown schematic views along the two major zone axes depicting the relationship of the principal crystal faces to the arrangement of molecules in the structure. It is striking that each of the faces has the carboxyl dimer functional groups completely exposed to attack from the surface *except* for the {100} which have a layer of closely packed 4-chlorophenyl groups shielding the carboxyl groups from attack. Penetration of ammonia molecules through such a nonpolar layer in a perfect crystal should indeed be difficult. However, crystals employed in this study were grown from solution with no special preparation of the surfaces, and it would seem likely that the crystal faces only crudely approximate the completely planar ideal surfaces shown in Figure 6. Even if ammonia molecules should penetrate {100} (at a surface defect) and react with carboxyl groups below the hydrophobic layer, the same kind of barrier of 4-chlorophenyl rings to further inward penetration will be encountered in the next layer of dimers and it could be expected that progress of a reaction front in such a direction should be quickly attenuated. On the other hand, as Figure 6 shows, as reaction proceeds inward from the other crystal faces, each reaction of ammonia with a carboxyl group can be expected to lead to disorder in the vicinity of the reaction site which will, in turn, expose another carboxyl group to new ammonia molecules. The existence of the carboxyl groups in columns leads the ammonia to the center of the crystal. It may be noted that while the orientations of carboxyl groups in the various columns leading in

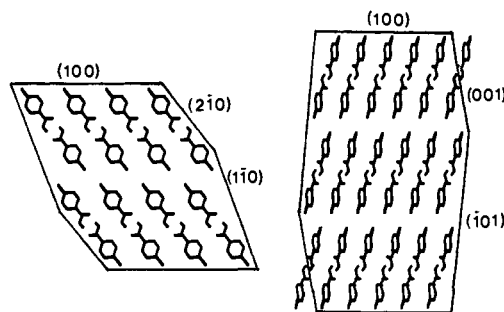


Figure 6. Drawings of 4-chlorobenzoic acid crystals showing the idealized molecular arrangement at the major faces: (a) view along the c axis (a major zone axis of the crystal); (b) view looking along b , the other major zone axis. The relative sizes of the various faces are arbitrary in this drawing.

from the crystal faces shown in Figure 6 differ markedly, the rates of travel of the reaction fronts other than that from (100) do not differ sufficiently (Figure 2) for a clear distinction to be made in our work thus far. This analysis of the reaction suggests the generalization that the presence of carboxyl groups at a crystal surface is a necessary but not a sufficient condition for a solid gas reaction of the type under discussion. In addition there is the requirement that the carboxyl groups be so arranged that reaction of one exposes the next to another ammonia molecule. More evidence bearing on this point will be discussed in the following paper in which the reaction of ammonia gas is extended to other carboxylic acids and to carboxylic acid anhydrides.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6334.