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# The Crystal Structure of *p*-Aminobenzoic Acid*

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The crystal structure of a monoclinic modification of *p*-aminobenzoic acid has been determined from three-dimensional X-ray diffraction data. The unit-cell dimensions are: $a=18{\cdot}551$, $b=3{\cdot}860$, $c=18{\cdot}642$ Å, $\beta=93{\cdot}56°$; the space group is $P2_1/n$. There are 8 molecules in the unit cell, and hence two in the asymmetric unit. The structure was refined by least-squares methods to an $R$ index, for 1916 observed reflections, of 0·073 and a goodness of fit of 1·29; the resulting standard deviations in the bond distances are 0·006 Å. The dimensions of the two structurally distinct molecules are closely similar, and suggest a small amount of quinoid character. The amino and carboxyl groups are displaced slightly from the planes of the benzene rings, and the nitrogen atoms are non-planar. Pairs of molecules are linked together, to form dimers, through two O–H···O hydrogen bonds arranged about a center of symmetry; an additional N–H···O hydrogen bond is formed by one of the two kinds of molecule. Twinning and disorder are common for these crystals. In the disordered structure, which is based on an orthorhombic unit cell half as large as the monoclinic cell, the hydrogen-bonded dimers apparently remain intact but the arrangement of N–H···O bonds becomes random.

## Introduction

Preliminary X-ray diffraction photographs of crystals of *p*-aminobenzoic acid, $NH_2C_6H_4CO_2H$, indicated an interesting combination of twinning and disorder. Although the crystals are monoclinic, the $a$ and $c$ axes are very nearly equal in length, leading to an approximately orthogonal cell bounded by (101), (10$\bar{1}$), and (010). Zero-level Weissenberg photographs about **b** show almost exact *mm* symmetry, a reflection $h0l$ having essentially the same intensity (and spacing) as the corresponding reflection $l0h$. In addition, twinning about (101) or (10$\bar{1}$) is common, as evidenced by increased symmetry of upper-level photographs and by a slight splitting of the high-angle reflections. Finally, extensive streaking along alternate reciprocal lattice rows of upper-level Weissenberg photographs about **b** indicates severe disorder for many crystals; in the limiting case, when these lattice rows become continua, the intensities of the remaining spots show orthorhombic symmetry corresponding to the space group *Pnma* and a unit cell half as large as the monoclinic cell. In view of these interesting observations and because of the importance of *p*-aminobenzoic acid in certain biological processes, we have undertaken the present investigation.

During the course of this investigation, the work of Killean, Tollin, Watson & Young (1965; hereafter, KTWY) was reported. They have apparently observed the same sort of twinning and disorder; and after suitable transformation of axes, the two-dimensional structure they report is in satisfactory agreement with our results.

## Experimental

Our crystals of *p*-aminobenzoic acid were obtained by evaporation of aqueous ethanol and methanol solutions. They grow in the form of long, fibrous needles similar to modification I found by KTWY; we have not obtained the other forms reported by them, nor that reported by Prasad, Kapadia & Thakar (1937)

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and, more recently, by Alléaume, Salas-Ciminago & Decap (1966). Since the crystals shatter when cut with a razor blade, all photographs were taken with crystals mounted along the needle (*b*) axis.

A large number of crystals were examined. Most of them were badly twinned (as evidenced by the additional symmetry of upper-layer Weissenberg photographs); often the disorder streaks (see *Introduction*) were absent on fresh crystals but grew increasingly severe as the crystal aged. Eventually, a crystal about 0·2 mm in diameter was found which showed no significant amount of twinning or disorder; it was used to collect all the data.

Values of the cell dimensions $a$, $c$, and $\beta$ were obtained from a least-squares fit to measurements made on a zero-level Weissenberg photograph prepared in a special camera, of nominal radius 10 cm, which holds the film in the asymmetric position; the value of $b$ was obtained from $0kl$ and $hk0$ precession photographs calibrated with the known values of $c^*$ and $a^*$. The space group $P2_1/n$ was indicated by the absence of reflections $h0l$ with $(h+l)$ odd and $0k0$ with $k$ odd. The density was measured by flotation. Crystallographic data are given in Table 1.

Table 1. *Crystal data*

| | |
|---|---|
| *p*-Aminobenzoic acid | F.W. 137·14 |
| $C_7H_7NO_2$ | $F(000)=576$ |

Monoclinic; space group $P2_1/n$

$a=18{\cdot}551\pm0{\cdot}002$ Å
$b=3{\cdot}860\pm0{\cdot}010$
$c=18{\cdot}642\pm0{\cdot}003$
$\beta=93{\cdot}56\pm0{\cdot}02°$

| | |
|---|---|
| $V=1332$ Å$^3$ | $D_m=1{\cdot}360$ g.cm$^{-3}$ |
| $Z=8$ | $D_x=1{\cdot}367$ g.cm$^{-3}$ |

Our photographs seem to correspond with those described by KTWY. As reported by them, the $h0l$ photograph has almost exact *mm* symmetry and the apparent cell dimensions are approximately 12·7 and 13·6 Å; however, rather than doubling both axes, we have been able to index the upper-level photographs by choosing a new set of $a$ and $c$ axes rotated by approximately 45° from the **a** and **b** directions of KTWY. With this transformation of axes, our values of the cell dimensions are in excellent agreement with those reported by KTWY, their values of $a$ and $b$ corresponding, on the basis of our cell, to $a=c=18{\cdot}63$ Å, $\beta=93{\cdot}6°$.

Intensities were estimated visually from multiple-film equi-inclination Weissenberg photographs (Cu $K\alpha$) of layers 0 to 3 about **b**. A standard deviation was assigned to each observation according to the expression given by Sharma & McConnell (1965), and was used in obtaining film and pack factors for each set of photographs and an average intensity (and its standard deviation) for each reflection. These and all subsequent calculations were carried out on an IBM 7094 computer under the CRYRM system (Duchamp, 1964).

The intensities were corrected for Lp factors but not for absorption ($\mu R\simeq0{\cdot}1$). Data from the different levels were scaled together by preparing, for each level, an equi-inclination Weissenberg photograph and a zero-level anti-equi-inclination photograph, both photographs covering the same oscillation range, being carefully timed, and recorded on different portions of the same film (Brown & Marsh, 1963). The resulting list of data comprised 2509 independent reflections, of which 573 were too weak to be observed above background and 15 were cut off by the beam-stop.

## Determination and refinement of the structure

Approximate scale and temperature factors were obtained by Wilson's method, and unsharpened Patterson projections onto (010) were calculated. The sharpened map gave clear evidence as to the orientations of the benzene rings and also indicated the probable positions of the atoms adjacent to the rings; packing and hydrogen-bonding considerations led to a trial set of $x$ and $z$ coordinates for the twenty heavy atoms (two molecules) in the asymmetric unit. After five cycles of least-squares refinement, including individual isotropic temperature parameters, the $R$ index for the $h0l$ reflections was 0·113. Approximate $y$ coordinates were deduced assuming planar molecules, and three least-squares cycles based on the entire set of three-dimensional data led to an $R$ index of 0·125.

During these preliminary refinement cycles, the weighting function was that suggested by Hughes (1941); since the quantity minimized was $\Sigma w(F_o^2-F_c^2)^2$, this function represents a compromise between unit weights and those appropriate if the only errors were due to observational uncertainties (in which case $\sqrt{w}=1/\sigma(F_o^2)\simeq1/F_o^2$). We have found such a compromise scheme useful in early refinement stages.

For the final refinement stages, weights $\sqrt{w}$ were taken equal to the reciprocals of the standard deviations of the individual values of $F_o^2$ as derived during the data reduction process (see *Experimental*); five strong reflections apparently suffering from extinction were given zero weight. Atomic form factors were taken from *International Tables for X-ray Crystallography* (1962). The full matrix of normal equations was collected until it became too large (over 207 parameters) to fit into core memory.

After two least-squares cycles including anisotropic temperature factors, a three-dimensional difference synthesis was calculated; this map gave clear indication of the approximate positions of all the hydrogen atoms. Their coordinates were further adjusted through two least-squares cycles in which the remaining parameters were held fixed. For the final four cycles, the complete list of 237 parameters was adjusted: coordinates of all 34 atoms, anisotropic temperature parameters for the 20 heavy atoms, isotropic temperature factors for the

Table 2. *The heavy-atom parameters and their standard deviations (in parentheses)*

All values have been multiplied by $10^4$. The anisotropic temperature factor is expressed in the form $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$.

| | $x$ | $y$ | $z$ | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| | Molecule *A* | | | | | | | | |
| N | 3461 (1) | 5079 (8) | −1666 (2) | 28 (1) | 1388 (34) | 42 (1) | −37 (9) | 10 (2) | 49 (10) |
| C(1) | 1542 (1) | 2733 (7) | −0711 (1) | 26 (1) | 649 (24) | 25 (1) | −6 (7) | −2 (1) | −12 (7) |
| C(2) | 2214 (2) | 1898 (8) | −0372 (2) | 28 (1) | 846 (27) | 28 (1) | −4 (8) | −3 (1) | −11 (8) |
| C(3) | 2842 (2) | 2738 (8) | −0675 (2) | 27 (1) | 832 (28) | 31 (1) | 4 (8) | −5 (2) | −23 (8) |
| C(4) | 2829 (2) | 4379 (8) | −1343 (2) | 27 (1) | 821 (27) | 31 (1) | −28 (8) | 9 (2) | −56 (8) |
| C(5) | 2160 (2) | 5258 (8) | −1686 (2) | 32 (1) | 756 (27) | 31 (1) | 0 (8) | 5 (2) | 21 (8) |
| C(6) | 1531 (2) | 4422 (8) | −1374 (2) | 28 (1) | 722 (26) | 29 (1) | 16 (8) | 1 (1) | −4 (7) |
| C(7) | 0879 (2) | 1681 (8) | −0394 (2) | 28 (1) | 708 (24) | 24 (1) | 8 (7) | 0 (1) | −7 (7) |
| O(1) | 0866 (1) | 0089 (6) | 0180 (1) | 29 (1) | 1083 (23) | 28 (1) | −22 (6) | −1 (1) | 57 (6) |
| O(2) | 0276 (1) | 2586 (6) | −0754 (1) | 23 (1) | 1192 (22) | 35 (1) | −2 (6) | −1 (1) | 115 (6) |
| | Molecule *B* | | | | | | | | |
| N | 3304 (1) | −5445 (7) | 3401 (1) | 38 (1) | 1154 (28) | 27 (1) | −57 (8) | 3 (1) | 36 (8) |
| C(1) | 4286 (1) | −2821 (7) | 1519 (2) | 26 (1) | 594 (23) | 28 (1) | 27 (7) | −1 (1) | −8 (7) |
| C(2) | 4624 (2) | −2073 (8) | 2194 (2) | 29 (1) | 708 (25) | 30 (1) | −8 (8) | −4 (2) | −1 (8) |
| C(3) | 4309 (2) | −2967 (8) | 2817 (2) | 29 (1) | 716 (25) | 29 (1) | −2 (8) | −5 (2) | −5 (8) |
| C(4) | 3642 (2) | −4648 (8) | 2783 (2) | 28 (1) | 748 (25) | 27 (1) | 37 (8) | 2 (1) | 7 (7) |
| C(5) | 3300 (2) | −5452 (8) | 2111 (2) | 28 (1) | 762 (25) | 29 (1) | −33 (8) | 0 (2) | −7 (8) |
| C(6) | 3622 (2) | −4530 (8) | 1489 (2) | 28 (1) | 708 (25) | 27 (1) | 16 (8) | −3 (1) | −19 (7) |
| C(7) | 4615 (2) | −1727 (8) | 0862 (2) | 25 (1) | 706 (24) | 29 (1) | 21 (7) | 1 (1) | −13 (8) |
| O(1) | 5213 (1) | −0236 (6) | 0883 (1) | 29 (1) | 1198 (24) | 30 (1) | −61 (7) | 4 (1) | 12 (6) |
| O(2) | 4248 (1) | −2343 (6) | 0262 (1) | 36 (1) | 1218 (23) | 25 (1) | −81 (7) | −5 (1) | 21 (6) |

14 hydrogen atoms, and a scale factor. The parameters of the hydrogen atoms were kept in one matrix and the heavy-atom parameters and the scale factor in a second matrix.

During the last cycle, no heavy-atom parameter shifted by as much as one-third of its standard deviation, nor any hydrogen-atom parameter by 0·5 e.s.d. The final $R$ index for 1916 observed reflections of non-zero weight is 0·073 and the goodness of fit, $(\Sigma w(F_o^2-F_c^2)/m-s)^{\frac{1}{2}}$, is 1·29.

The heavy-atom parameters and their standard deviations are given in Table 2; those of the hydrogen atoms, in Table 3. The standard deviations were calculated from the diagonal elements of the least-squares inverse matrices; since two separate matrices were collected, the e.s.d.'s may be slightly low.

Table 3. *The parameters, and their standard deviations, of the hydrogen atoms*

Values for the coordinates have been multiplied by $10^3$. The temperature factors are in the form $\exp(-B\sin^2\theta/\lambda^2)$.

| | $x(\sigma_x)$ | $y(\sigma_y)$ | $z(\sigma_z)$ | $B(\sigma_B)$ |
|---|---|---|---|---|
| Molecule *A* | | | | |
| H(1) | −009 (2) | 135 (10) | −053 (2) | 5·1 (0·9) |
| H(2) | 224 (2) | 065 (8) | 011 (2) | 2·7 (0·7) |
| H(3) | 330 (2) | 238 (8) | −044 (2) | 3·2 (0·7) |
| H(4) | 390 (2) | 484 (9) | −139 (2) | 4·6 (0·8) |
| H(5) | 346 (2) | 678 (10) | −199 (2) | 6·9 (1·0) |
| H(6) | 215 (2) | 666 (9) | −217 (2) | 5·2 (0·9) |
| H(7) | 106 (1) | 490 (7) | −163 (1) | 2·2 (0·7) |
| Molecule *B* | | | | |
| H(1) | 450 (2) | −111 (11) | −013 (2) | 7·7 (1·1) |
| H(2) | 508 (2) | −067 (8) | 220 (2) | 3·1 (0·7) |
| H(3) | 457 (2) | −250 (8) | 330 (2) | 3·8 (0·8) |
| H(4) | 359 (2) | −517 (9) | 383 (2) | 4·2 (0·8) |
| H(5) | 301 (2) | −711 (11) | 341 (2) | 6·3 (1·0) |
| H(6) | 282 (1) | −671 (7) | 206 (1) | 2·2 (0·6) |
| H(7) | 337 (1) | −506 (7) | 100 (2) | 2·9 (0·7) |

The observed and calculated structure factors are listed in Table 4. The electron density projected onto (010), calculated at the conclusion of the refinement, is shown in Fig. 1; the corresponding difference map, for which the contributions of the hydrogen atoms were omitted from the $F_c$'s, is shown in Fig. 2.

## Discussion

### *The molecular structure*

In each of the two structurally distinct molecules in the asymmetric unit (*A* and *B*), the atoms of the six-membered benzene ring are coplanar within 0·01 Å; however, the substituent amino and carboxyl groups are displaced significantly from the plane. The equations of the best planes of the two rings, and the deviations of the various atoms from these planes, are given in Table 5.

In both molecules atoms C(7) and N are displaced from the planes of the ring atoms by about the same amounts, 0·06–0·07 Å, and in the same directions. Atoms C(1), C(7), O(1), and O(2) of the carboxyl groups are themselves coplanar, but these planes are bent out of the planes of the benzene rings and also rotated slightly – by about 1·5° for molecule *A* and 2·5° for *B* – about the C(1)–C(7) bonds.

The intramolecular bond distances and angles are shown in Fig. 3. The estimated standard deviations in distances involving the heavier atoms are about 0·006 Å, and about 0·4° in the angles; for bonds involving hydrogen atoms, the uncertainties are approximately ten times larger. In light of the scatter among chemically equivalent distances, these standard deviations seem quite reasonable.

Table 4. *Observed and calculated structure factors*

Within each group are given the values of $h$, $10F_o$, and $10F_c$. Reflections indicated with an asterisk were omitted from the least-squares refinement. A minus sign preceding $F_o$ signifies 'less than'; these reflections have been omitted from the refinement unless the value of $F_c$ exceeds the threshold value of $F_o$.

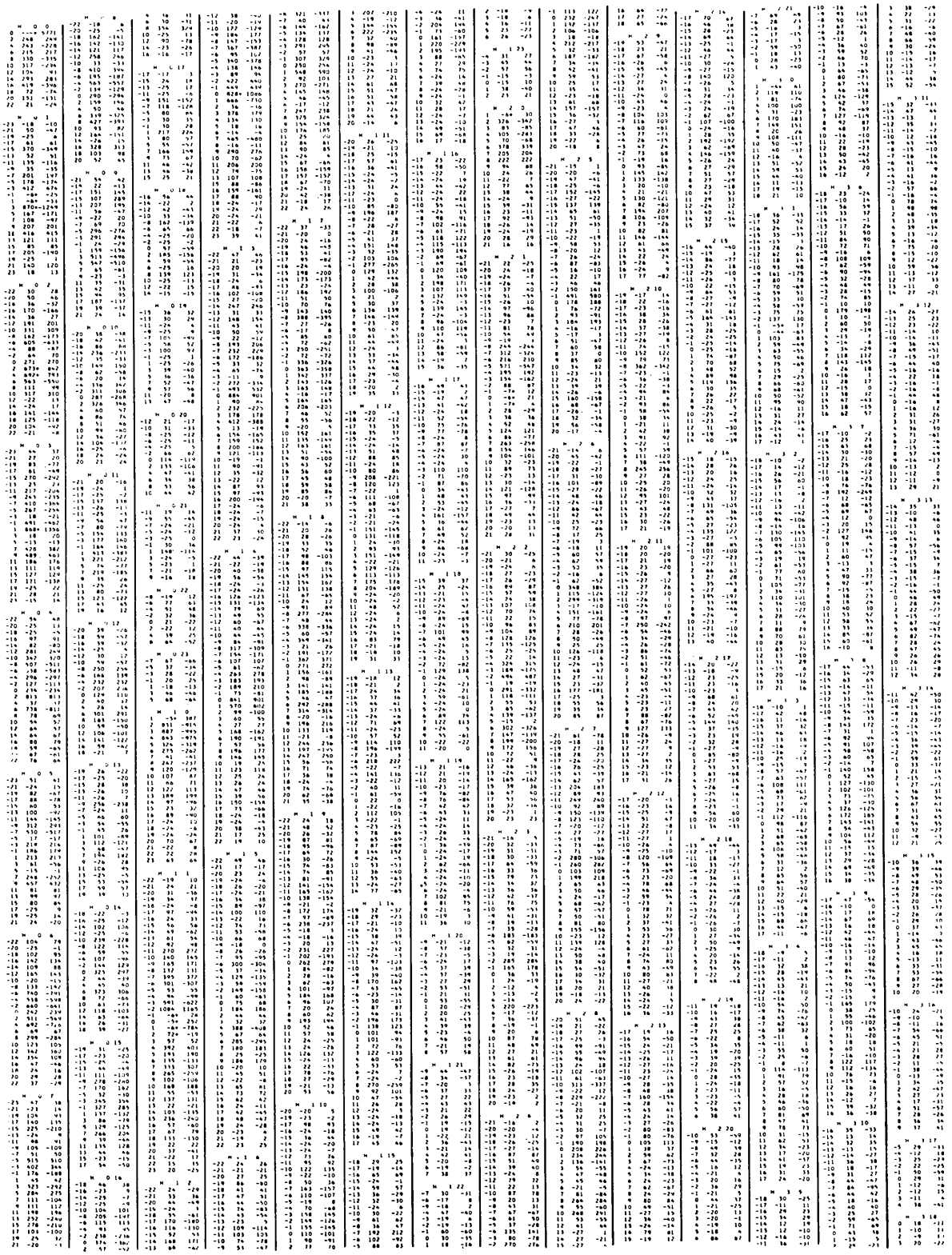


Table 5. *The best planes of the benzene rings, atoms* C(1)–C(6), *and the deviations of the individual atoms from these planes*

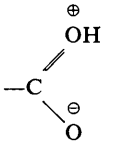
The direction cosines $q$ are relative to $a$, $b$, and $c^*$, respectively; $D$ is the origin-to-plane distance.

| Molecule *A* | | Molecule *B* | |
|---|---|---|---|
| $q_1 =$ | −0·0094 | $q_1 =$ | 0·4645 |
| $q_2 =$ | 0·8878 | $q_2 =$ | −0·8855 |
| $q_3 =$ | 0·4599 | $q_3 =$ | 0·0031 |
| $D =$ | 0·287 Å | $D =$ | 4·570 Å |

| | Deviation | |
|---|---|---|
| C(1) | −0·001 | −0·004 |
| C(2) | −0·004 | 0·003 |
| C(3) | 0·009 | 0·002 |
| C(4) | −0·009 | −0·005 |
| C(5) | 0·005 | 0·003 |
| C(6) | 0·001 | 0·001 |
| N | −0·061 | −0·057 |
| C(7) | −0·073 | −0·058 |
| O(1) | −0·118 | −0·046 |
| O(2) | −0·065 | −0·137 |
| H(1) | −0·29 | −0·22 |
| H(2) | −0·01 | −0·08 |
| H(3) | 0·08 | 0·05 |
| H(4) | 0·09 | 0·07 |
| H(5) | 0·23 | 0·25 |
| H(6) | 0·05 | 0·02 |
| H(7) | −0·05 | −0·01 |

The distances indicate a small but significant contribution of the quinoid structure. The average value of the central bond distances C(2)–C(3) and C(5)–C(6) is 1·375 Å, compared with an average value of 1·399 Å for the remaining ring C–C distances; the C(1)–C(7) and C(4)–N bonds are about 0·06 Å shorter than normal single bonds. Despite the shortening of the C–N bonds, the nitrogen atoms are significantly non-planar; the positions of the hydrogen atoms H(4) and H(5) correspond to a configuration about midway between tetrahedral and planar.

The only significant differences between corresponding distances in the two molecules involve the C–O bonds, the C(7)–O(1) distance being shorter and the C(7)–O(2) distance longer in molecule *A*. Apparently there is less contribution of the structure




in molecule *A*. As a concomitance, the O(2)–H···O(1) hydrogen bonds between pairs of *A* molecules are weaker, and longer, than those between pairs of *B* molecules (see later discussion).

The C–H, N–H, and O–H distances are typical for X-ray diffraction investigations, being somewhat shorter than the standard values for internuclear separations.

Some interesting comparisons can be made with the molecular dimensions of 2-amino-3-methylbenzoic acid (Brown & Marsh, 1963). In general, the C–C distances in that molecule suggest very nearly the same amount of *o*-quinone contribution as of *p*-quinone contribution in the present compound; however, the C(1)–C(2) and C(3)–C(2) distances (C(2) is the atom bonded to the *o*-amino group) are slightly longer, perhaps as a result of overcrowding, and the C(2)–N distance is a bit shorter – 1·367 Å, compared with an average value of

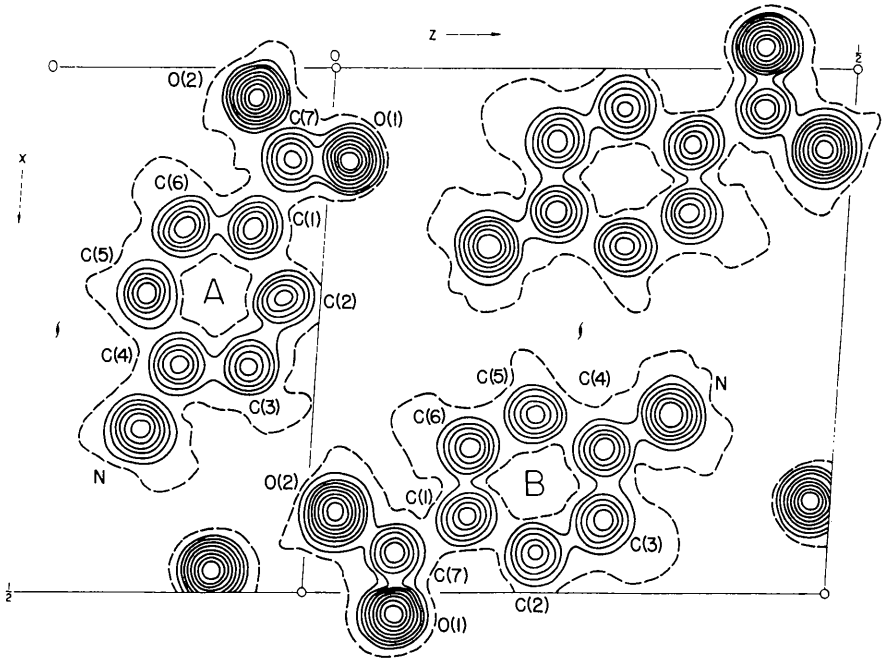



Fig. 1. The electron density projected on to (010). Contours are at intervals of 1 e.Å$^{-2}$, beginning with the 1 e.Å$^{-2}$ contour which is dashed.

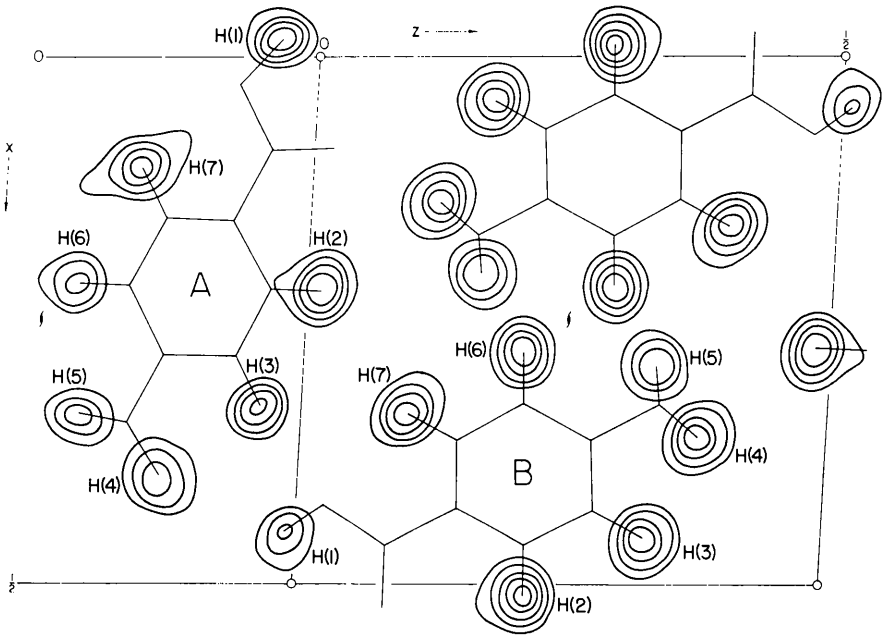



Fig. 2. A composite representation of the final three-dimensional difference map in which the hydrogen contributions were omitted from the $F_c$'s. Contours are at intervals of 0·1 e.Å$^{-3}$ beginning with 0·1 e.Å$^{-3}$.

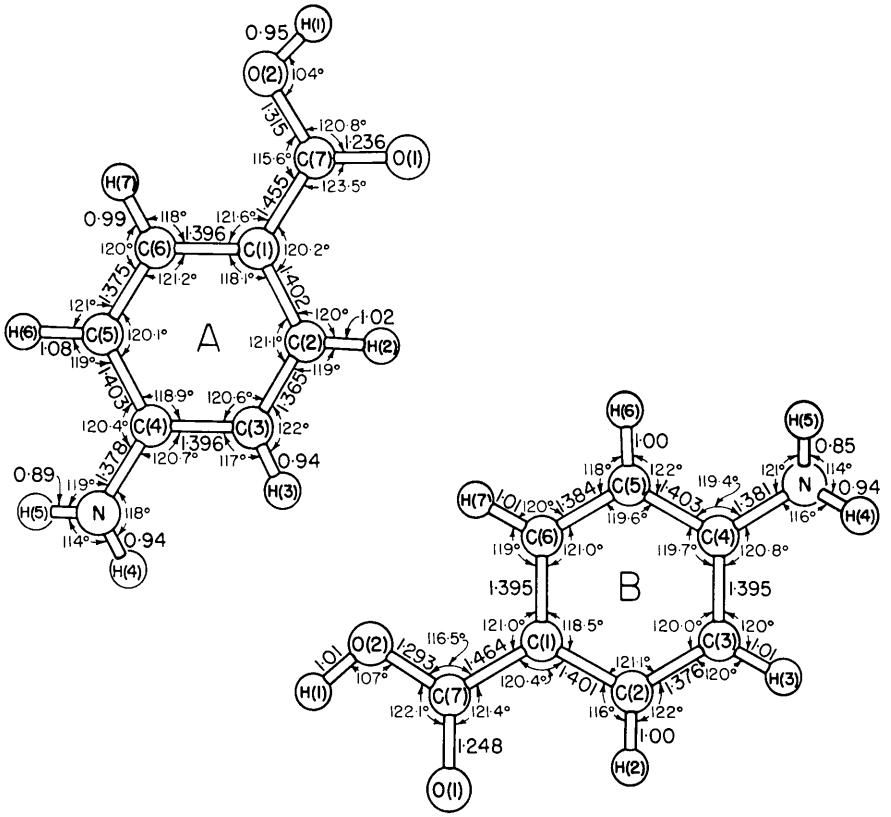



Fig. 3. Bond distances and angles.

1·380 Å in the present case. The additional double-bond character in the C–N bond is reflected in a more nearly planar nitrogen atom in 2-amino-3-methylbenzoic acid.

The dimensions of the carboxyl group and the O···O hydrogen-bond distance in 2-amino-3-methylbenzoic acid agree within experimental error with the values we find for molecule *A*.

*The hydrogen bonding*

The structure viewed down the *b* axis is shown in Fig. 4. As is typical of carboxylic acids, pairs of molecules of each type (*A* and *B*) form dimers linked together by two hydrogen bonds across a center of symmetry (rather than along a $2_1$ axis, as was indicated by KTWY). The two O–H···O distances are significantly different: 2·64 Å for pairs of *A* molecules and 2·61 Å for *B*. The O–H···O angles are 167 and 166°, respectively.

The more interesting hydrogen bonds – more interesting in that they appear to be the focal points of the twinning and the disorder – are the N–H···O bonds linking molecules of type *A* to those of type *B*. The nitrogen atom of molecule *B* forms a single, relatively strong (2·985 Å) N–H(4)···O(1) bond to molecule *A*; this bond is approximately linear, the N–H···O angle being about 174°. On the other hand, H(4) of molecule *A* points approximately midway between two O(1) atoms of *B* molecules lying one on top of the other along **b**. If these N···O interactions can be called hydrogen bonds at all ('bifurcated', presumably), they are extremely weak, for the N···O distances are 3·35 and 3·42 Å, the N–H···O angles 142 and 137°, and the H···O distances over 2·5 Å; it is probably more resonable to categorize them as van der Waals interactions.

The question immediately arises as to why the two types of molecules have different environments; at first thought, it would seem a simple matter to arrange them so as to be structurally equivalent, each forming a single, strong N–H···O hydrogen bond to a neighbor. Indeed, there is a nearly exact twofold screw operation, along the direction [101], relating molecules *A* and *B* (Fig. 4), and another screw operation relating pairs of molecules along the direction [10$\bar{1}$]. However, incorporation of these operations in a lattice so as to form a four-molecule orthorhombic cell, as is necessary to make the molecules equivalent, leads to one of the two space groups $P2_12_12_1$ or $P2_122_1$, thus requiring that the two molecules within a dimer be related by either a $2_1$ or a 2 axis rather than by a center. Quite obviously there is no satisfactory arrangement of equivalent mol-

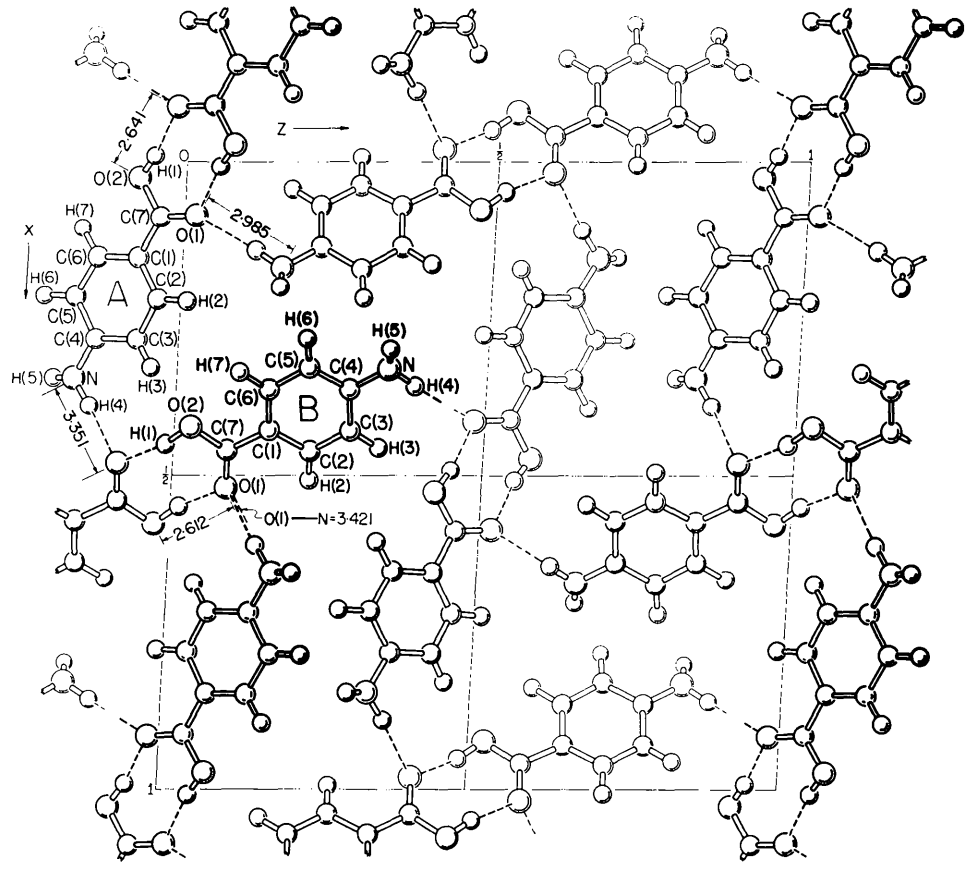



Fig. 4. The structure viewed along the *b* axis.

ecules which maintains the sanctity of the hydrogen-bonded dimers.

The disordered orthorhombic structure (see *Introduction*) apparently is achieved by introducing a randomness as to whether molecule *A* or molecule *B* forms the strong N–H···O hydrogen bond. This has the effect of introducing a mirror plane perpendicular to the *b* axis – that is, in the plane of Fig. 4. Thus, if molecule *B* (Fig. 4) and its centrosymmetrically related mate are reflected through a mirror plane at $y=\frac{1}{4}$, they are in position to accept strong (2·98 Å) hydrogen bonds from molecule *A* and from another molecule – also type *A* – toward the lower left-hand corner of Fig. 4; however, they would no longer be able to form hydrogen bonds with the molecules in the center of the cell. A random distribution of the two arrangements, together with a very small adjustment of the atomic coordinates, leads to an orthorhombic unit cell, space group *Pnma*, half as large as the monoclinic cell and with its *a* and *c* axes directed along the [10$\bar{1}$] and [101] directions of the monoclinic cell. The four molecules in the orthorhombic cell would occupy eightfold general positions, each site being occupied half the time. This arrangement seems to explain satisfactorily the appearance of the upper-level photographs.

Twinning is a common phenomeon when there is a simple metric relationship between cell dimensions. In the present case it is doubtless due to the near equality of the *a* and *c* axes, which, in turn, reflects the pseudo-orthorhombic symmetry and the structural similarities between the two types of molecules.

### *The temperature factors*

The magnitudes and orientations of the vibration ellipsoids derived from the anisotropic temperature factors (Table 2) are given in Table 6. While the principal vibrations of all the atoms tends to be directed along the *b* axis, only the nitrogen and oxygen atoms show pronounced anisotropy. For each of them, the maximum vibration is approximately perpendicular to the molecular plane.

Table 6. *Description of thermal ellipsoids*

$q_i^1$, $q_i^2$, $q_i^3$ are the direction cosines of the principal axes relative to the unit cell axes.

| | Axis *i* | $B_i$ (Å$^2$) | $q_i^1$ | $q_i^2$ | $q_i^3$ |
|---|---|---|---|---|---|
| Molecule *A* | | | | | |
| N | 1 | 8·51 | −0·099 | 0·965 | 0·248 |
| | 2 | 5·78 | 0·234 | −0·213 | 0·932 |
| | 3 | 3·64 | −0·967 | −0·151 | 0·265 |
| C(1) | 1 | 3·96 | −0·493 | −0·630 | 0·629 |
| | 2 | 3·89 | −0·640 | 0·730 | 0·279 |
| | 3 | 3·21 | 0·589 | 0·265 | 0·726 |
| C(2) | 1 | 5·06 | −0·004 | −0·991 | 0·135 |
| | 2 | 4·32 | −0·716 | 0·097 | 0·734 |
| | 3 | 3·47 | 0·698 | 0·093 | 0·665 |
| C(3) | 1 | 5·16 | −0·260 | −0·848 | 0·477 |
| | 2 | 4·46 | −0·547 | 0·524 | 0·686 |
| | 3 | 3·40 | 0·796 | 0·082 | 0·550 |
| C(4) | 1 | 5·59 | 0·246 | −0·785 | 0·552 |
| | 2 | 3·78 | 0·328 | 0·620 | 0·691 |
| | 3 | 3·55 | −0·912 | 0·011 | 0·466 |
| C(5) | 1 | 4·71 | 0·093 | 0·824 | 0·552 |
| | 2 | 4·40 | 0·970 | −0·201 | 0·076 |
| | 3 | 4·03 | −0·225 | −0·530 | 0·830 |
| C(6) | 1 | 4·44 | −0·445 | −0·854 | 0·297 |
| | 2 | 4·02 | −0·275 | 0·417 | 0·882 |
| | 3 | 3·73 | 0·853 | −0·311 | 0·366 |
| C(7) | 1 | 4·29 | −0·379 | −0·909 | 0·199 |
| | 2 | 3·89 | −0·876 | 0·413 | 0·303 |
| | 3 | 3·21 | 0·299 | 0·060 | 0·932 |
| O(1) | 1 | 6·76 | −0·157 | 0·946 | 0·292 |
| | 2 | 4·04 | −0·890 | −0·260 | 0·430 |
| | 3 | 3·52 | 0·429 | −0·193 | 0·854 |
| O(2) | 1 | 8·00 | −0·061 | 0·881 | 0·473 |
| | 2 | 4·06 | −0·305 | −0·465 | 0·849 |
| | 3 | 3·14 | 0·950 | −0·092 | 0·237 |
| Molecule *B* | | | | | |
| N | 1 | 7·29 | −0·369 | 0·920 | 0·159 |
| | 2 | 4·86 | 0·925 | 0·348 | 0·094 |
| | 3 | 3·68 | −0·092 | −0·182 | 0·983 |
| C(1) | 1 | 4·26 | −0·602 | −0·433 | 0·707 |
| | 2 | 3·65 | 0·363 | 0·601 | 0·689 |
| | 3 | 3·15 | 0·712 | −0·672 | 0·160 |
| C(2) | 1 | 4·68 | −0·678 | 0·146 | 0·761 |
| | 2 | 4·22 | 0·007 | −0·979 | 0·204 |
| | 3 | 3·54 | 0·735 | 0·144 | 0·615 |
| C(3) | 1 | 4·67 | −0·691 | −0·083 | 0·759 |
| | 2 | 4·27 | −0·111 | 0·994 | 0·016 |
| | 3 | 3·43 | 0·714 | 0·074 | 0·651 |
| C(4) | 1 | 4·75 | −0·491 | −0·871 | 0·004 |
| | 2 | 3·82 | −0·452 | 0·229 | 0·889 |
| | 3 | 3·45 | 0·745 | −0·436 | 0·459 |
| C(5) | 1 | 4·78 | −0·465 | 0·885 | 0·050 |
| | 2 | 4·11 | −0·383 | −0·223 | 0·918 |
| | 3 | 3·52 | 0·798 | 0·409 | 0·393 |
| C(6) | 1 | 4·60 | −0·547 | −0·690 | 0·507 |
| | 2 | 3·88 | −0·611 | 0·716 | 0·375 |
| | 3 | 3·40 | 0·572 | 0·105 | 0·776 |
| C(7) | 1 | 4·47 | −0·355 | −0·779 | 0·537 |
| | 2 | 3·95 | 0·044 | 0·537 | 0·838 |
| | 3 | 3·37 | 0·934 | −0·322 | 0·098 |
| O(1) | 1 | 7·39 | −0·255 | 0·966 | 0·063 |
| | 2 | 4·10 | 0·233 | 0·013 | 0·956 |
| | 3 | 3·78 | −0·938 | −0·259 | 0·287 |
| O(2) | 1 | 7·82 | −0·399 | 0·910 | 0·138 |
| | 2 | 4·60 | −0·856 | −0·414 | 0·363 |
| | 3 | 3·28 | 0·330 | 0·027 | 0·921 |

Corresponding atoms in the two molecules have closely similar thermal motions. The slightly larger

amplitude of the nitrogen atom in molecule *A* over that in molecule *B* undoubtedly reflects the weaker N···O interaction discussed earlier.

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# The Conformation of Non-Aromatic Ring Compounds. XXVIII*. The Crystal Structure of α-Chloro-δ-valerolactam


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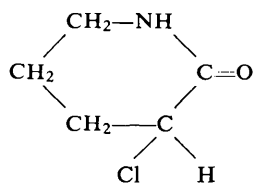
Crystals of α-chloro-δ-valerolactam are monoclinic with space group $P2_1/c$ and $Z=4$. The lattice constants at room temperature are $a=11{\cdot}73$, $b=6{\cdot}20$, $c=9{\cdot}51$ Å, $\beta=112{\cdot}0°$. The structure was solved from a minimum function $M_4$ which was directly computed and contoured at the machine output. Both *b*- and *c*-axis data were refined separately with a least-squares program and the results are compared. The molecule has a half-chair conformation with the chlorine atom in equatorial position. The peptide linkage NH–CO has the *cis* configuration. Unusual bond lengths are not observed.


## Introduction

During the synthesis of α,ω-diaminohexanecarboxylic acid, *via* the amination of α-chloro-oenantholactam (Brenner & Rickenbacker, 1958) the corresponding compound α-chloro-δ-valerolactam




was used as a model substance for the study of the reactivity of the chloro-amino substitution (Henniger, 1966). The title compound contains the peptide linkage –NH–CO– in the *cis* configuration. In addition, it belongs to a class of non-aromatic cyclic compounds which are being extensively investigated in this laboratory [*trans*-2,5-, *cis*-2,3- and *trans*-2,3-dichloro-1,4-dioxane, Altona, Knobler & Romers (1963), Altona & Romers (1963*a*,*b*); *trans*-2,3-dichloro-, 2-phenyl- and *trans*-2,5-dibromo-1,4-dithiane, Kalff & Romers (1965, 1966*a*, 1966*b*); cyclohexane-1,4-dione, Mossel & Romers (1964)].

* Part XXVII, Geise (1967).

## Experimental

α-Chloro-δ-valerolactam, $C_5H_8NOCl$, melting point 121–122 °C, was crystallized from toluene. The monoclinic crystals are colourless, lath-shaped, frequently twinned and elongated along [010] with main face (100). The needle direction [010] appears to be bent about [001] in such a way as to give the main face (100) a slightly curved shape. The reflexions *h*00, and to a less degree reflexions *hk*0, but not 0*k*0, recorded on a zero layer non-integrated Weissenberg photograph, are extended on one side of the film and contracted on the other, in accordance with the focusing geometry of the reflecting plane (100).

Very small crystals cut perpendicular to the needle axis do not show this effect and, moreover, their reflexions at high $\theta$ values appear to be stronger than the corresponding ones of *b*-axis exposures. The diffraction photographs were taken with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). The lattice constants at room temperature were determined from zero layer non-integrated Weissenberg photographs about [010] and [001]. These exposures were superposed with aluminum powder lines ($a=4{\cdot}0489$ Å at 20 °C) for calibration purposes. The diffraction data

$a=11{\cdot}73\pm0{\cdot}02$ Å $\beta=112{\cdot}0°\pm0{\cdot}2°$ $Z=4$

$b=6{\cdot}20\pm0{\cdot}01$ Å $d_{exp}=1{\cdot}38$ g.cm$^{-3}$ $F(000)=280$

$c=9{\cdot}51\pm0{\cdot}01$ Å $d_x=1{\cdot}42$ g.cm$^{-3}$ $\mu$(Cu $K\alpha$)$=43$ cm$^{-1}$