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The Crystal Structure of *p*-Aminophenol

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The structure of crystalline *p*-aminophenol has been determined by the X-ray method. The dimensions of the orthorhombic unit cell, which contains four molecules of  $C_6H_4(OH).NH_2$ , are

$$a = 12.90 \pm 0.03, \quad b = 8.19 \pm 0.03, \quad c = 5.25 \pm 0.03 \text{ \AA.},$$

and the space group is  $P2_1nb$ , [ $a$ ] being the polar axis. The calculated specific gravity is 1.305, while that observed by flotation is 1.295. X-ray intensities were obtained from Weissenberg moving-film photographs for all layers of the three principal axes, and the approximate structure was derived by analogy from that of aniline hydrochloride. The atomic co-ordinates were refined by means of successive two- and three-dimensional Fourier syntheses using finally 605 experimental structure amplitudes as coefficients of the series. The bond lengths within the benzene ring are normal but the C-N bond is shorter (1.39 Å.) than that given by the sum of the covalent radii. Molecules of *p*-aminophenol are linked together by three hydrogen bonds of length 2.83, 3.13 and 3.18 Å.

## Introduction

During a survey of the unit-cell dimensions of organic crystals, it was observed that those of one form of *p*-aminophenol (Caspari, 1927*b*) bore some resemblance to those of aniline hydrochloride (Brown, 1949). As the atomic configuration of the greater part of the two molecules is the same, it was suggested that the crystal structures might be similar. The structure determination of aniline hydrochloride was carried only as far as two-dimensional projections because the unsuitable nature of the crystals gave reason to doubt the reliability of the X-ray intensities, and the bond lengths obtained might suffer in accuracy. It was considered therefore that a full three-dimensional determination of the structure of *p*-aminophenol would give necessary data on this class of compound, in particular, the lengths of C-O and C-N bonds attached to a benzene ring, and would provide further information concerning the lengths of N-H-O hydrogen bonds.

## Experimental

The crystals used in this investigation were grown from aqueous solution containing a small quantity of a surface-active agent. They were generally lath-shaped, elongated along [ $c$ ], and tabular on (010). The axial ratios given by Winchell (1943) reporting the work of Bolland (1910) are 0.785:1:0.721, and are only

partially correct, seeing that they are not consistent with our values (1.575:1:0.641). No cleavage or defects were observed and growth of suitable specimens was relatively simple. The crystals were the so-called stable  $\alpha$ -modification of Caspari (1927*b*); it has later been learned (Powell & Holmes, 1950) that the unstable  $\beta$ -modification reported by Caspari is actually a condensation compound of *p*-aminophenol with acetone.

The dimensions of the unit cell were obtained by measurement of the layer lines of single-crystal rotation photographs:

$$[a] = 12.90 \pm 0.03, \quad [b] = 8.19 \pm 0.03, \quad [c] = 5.25 \pm 0.03 \text{ \AA.}$$

For four molecules per unit cell, the specific gravity required is 1.305, while that observed by flotation is 1.295. Observed extinctions were  $\{h0l\}$  for ( $h+l$ ) odd and  $\{hk0\}$  for  $k$  odd, whence the space group may be either  $Pmnb$  or  $P2_1nb$ . The impossibility of fitting the *p*-aminophenol molecule in the mirror plane in  $Pmnb$  confirms the correct space group as  $P2_1nb-C_{2v}^2$ .

X-ray intensity data were obtained from Weissenberg moving-film photographs about [ $a$ ] (zero and five layers), [ $b$ ] (zero and three layers), and [ $c$ ] (zero and two layers). As the temperature coefficient of the structure amplitudes was obviously moderately high, i.e. the intensities of the reflexions fell off to zero before  $\theta = 90^\circ$ , it was considered that all the experimental intensities

Table 1. *Cell dimensions of analogous structures*

Diphenyl	8.11 Å.	5.67 Å.	9.57 Å.	94½°	Clark & Pickett (1931)
Terphenyl	8.08	5.60	13.59	92°	Pickett (1933)
Quaterphenyl	8.14	5.64	18.4	97°	Hertel & Römer (1933)
Aniline hydrochloride	8.58	5.33	15.84	101°	Brown (1949)
<i>p</i> -Aminophenol	8.19	5.25	12.90	—	—
$\gamma$ -Quinol	8.11	5.20	13.24	107°	Caspari (1926, 1927a)

were recorded on these photographs. In all, reflexions from 605 sets of planes were obtained. The intensities were estimated by comparison with a time-exposure calibrated strip on batches of films exposed with the multiple-film technique. The various batches were related and corrected for geometrical and polarization factors in the usual way.

### Structure determination by analogy

The trial structure was obtained by adopting the same molecular disposition as was found for aniline hydrochloride. The justification for this procedure was that two of the cell dimensions of the two crystals corresponded very closely, as indeed they do to quite a number of other compounds containing benzene rings (Table 1). It is apparent that all these six substances, and others as well, possess the same molecular packing in two directions, corresponding to the two shorter unit-cell dimensions. This packing is dependent solely on the closest approach of benzene rings, subject to slight variations due to the arrangement and bonding of the substituents at opposite ends of the ring. Moderately good structure-amplitude agreement was immediately obtained for  $\{hk0\}$  terms.

### Refinement of the atomic co-ordinates

From the trial structure two successive Fourier projections along  $[c]$  were sufficient to complete the refinement of the  $x$  and  $y$  co-ordinates. The resolution of the atoms was not particularly good, as only 75  $\{hk0\}$  terms were available for the synthesis, and many of these were numerically small. The  $z$  co-ordinates were suggested by space-group considerations and geometry, and were refined by successive three-dimensional line syntheses. Finally, a set of three sections parallel to (001) at appropriate values of  $z$  (0.81, 0 and 0.19) to include all the atoms was computed, using the method of Cox, Gross & Jeffrey (1947) on Hollerith tabulators.

The final atomic co-ordinates obtained from these syntheses are listed in Table 2. The two-dimensional Fourier projections are shown in Figs. 1–3, and the final (composite) three-dimensional Fourier sections in Fig. 4.

Table 2. *Final atomic co-ordinates*

	$x$	$y$	$z$
C <sub>1</sub>	0.350	0.353	0.012
C <sub>2</sub>	0.308	0.258	0.816
C <sub>3</sub>	0.204	0.227	0.814
C <sub>4</sub>	0.140	0.295	0.992
C <sub>5</sub>	0.177	0.389	0.184
C <sub>6</sub>	0.283	0.420	0.191
N	0.456	0.381	0.021
O	0.029	0.255	0.983

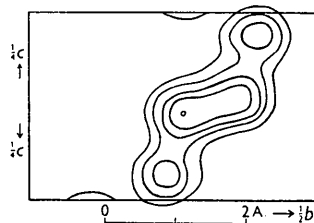
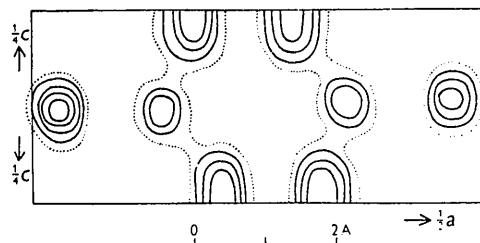
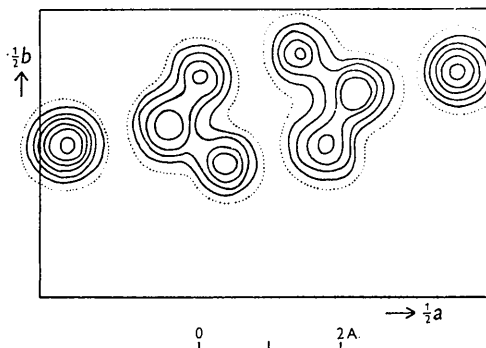
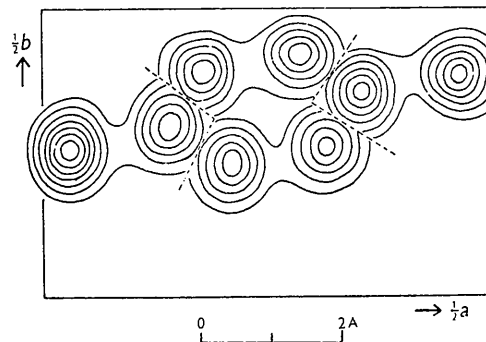
Fig. 1. Fourier projection along  $[a]$ .Fig. 2. Fourier projection along  $[b]$ .Fig. 3. Fourier projection along  $[c]$ . Contours of electron density plotted at intervals of  $1 \text{ e.A.}^{-2}$ , commencing at  $2 \text{ e.A.}^{-2}$  (dotted).Fig. 4. Composite electron-density map obtained by computing sections of a three-dimensional Fourier synthesis at  $z=0.81, 0$  and  $0.19$ . Contours plotted at intervals of  $1 \text{ e.A.}^{-3}$ , commencing at  $2 \text{ e.A.}^{-3}$ .

Fig. 5 is a schematic diagram showing the molecular arrangement in a complete unit cell.

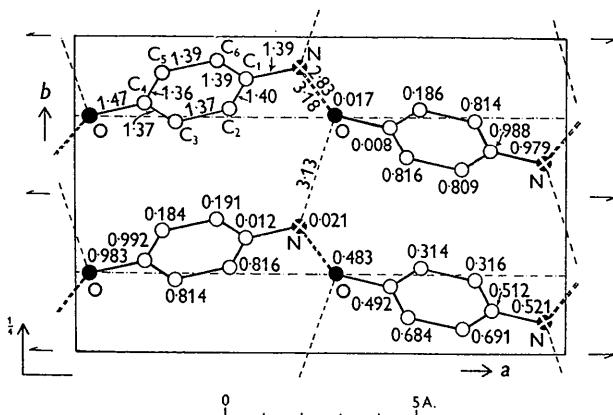


Fig. 5. Schematic diagram of contents of one unit cell. Hydrogen bonds are represented by broken lines.

### Structure-amplitude calculations

It was found that the best agreement between the experimental and calculated structure amplitudes was obtained when the value of  $B$  in the temperature factor was taken as  $5.0 \times 10^{-16} \text{ A.}^2$ . The values of the experimental and calculated structure amplitudes, together with the calculated phase angles, are available for perusal by anyone interested. It is a peculiarity of this structure that a rather large number (135) out of a total of 605 planes give very weak reflexions owing to their small structure amplitudes. Neglecting these weak structure amplitudes, the errors as represented by the function  $\frac{\sum |F(\text{exp.})| - |F(\text{calc.})|}{\sum |F(\text{exp.})|}$  amount to 0.17 for the  $\{hk0\}$ ,  $\{0kl\}$  and  $\{h0l\}$  terms, and to 0.19 for all the  $\{hkl\}$  terms.

In the structure-amplitude calculations the scattering factor for nitrogen was taken as  $\frac{7}{5}$ , and for oxygen as  $\frac{4}{3}$  that of carbon, while the hydrogen atoms were neglected.

### Description of the structure

*p*-Aminophenol is a simple hydrogen-bonded molecular structure. The benzene rings are packed together in layers, the planes of the rings being perpendicular to the plane (100) of the layer, and inclined at  $70^\circ$  to one another. The amino and hydroxyl groups protrude on opposite sides of the layers, all the amino groups pointing in the same direction throughout the structure, thereby conferring the polar character on the crystals. The molecules are linked together by systems of three hydrogen bonds, the amino group giving two hydrogens and accepting one, and the hydroxyl group giving one hydrogen and accepting two. These hydrogen-bond lengths are 2.83, 3.13 and 3.18 Å. The bond lengths within the molecule are:

$C_1-C_2$	1.40 Å.	$C_5-C_6$	1.39 Å.
$C_2-C_3$	1.37	$C_6-C_1$	1.39
$C_3-C_4$	1.37	$C_1-N$	1.39
$C_4-C_5$	1.36	$C_4-O$	1.47

The angles are all  $120 \pm 1^\circ$ . The nearest inter-molecular contacts are

$$C_2-C'_6 = 3.80; \quad C_3-C'_6 = 3.76; \quad C_3-C'_5 = 3.82 \text{ Å.}$$

The planarity of the molecule was investigated by evaluating the equations of the planes containing groups of atoms, thus:

$$C_1-C_3-C_5 \quad x - 6.39y + 4.54z = 10.13,$$

$$C_2-C_4-C_6 \quad x - 6.31y + 4.42z = 9.58.$$

If a mean of these planes is taken by averaging the coefficients such that

$$x - 6.35y + 4.48z = 9.86,$$

then the following are the perpendicular distances of each atom from this mean plane:

$$C_1 - 0.018 \quad C_3 - 0.014 \quad C_5 - 0.006 \quad N + 0.028 \text{ Å.}$$

$$C_2 + 0.014 \quad C_4 + 0.018 \quad C_6 + 0.005 \quad O + 0.049 \text{ Å.}$$

It is therefore concluded that the molecule is truly planar, the errors being experimental.

### Discussion

The method of structure determination by analogy with substances having similar cell dimensions calls for some comment. It has been used previously as, for example, by Robertson, Prasad & Woodward (1936), in the series dibenzyl, stilbene, tolane, azobenzene; these instances however had all three cell lengths approximately equal. It was also applied in the series oxalic acid dihydrate, acetylenedicarboxylic acid dihydrate, diacetylenedicarboxylic acid dihydrate (Dunitz & Robertson, 1947); in these instances, the substances investigated were of the same chemical type. The present work has involved an extension of these ideas to cover different classes of substances whose only common property is that of being mono- or *p*-disubstituted benzene derivatives.

Something similar was envisaged by Groth (1906) who, observing changes in axial ratios when a substituent was added to a crystalline substance, was able to suggest the orientation of the molecules in the crystal in a large number of cases. The idea is probably capable of wide extension.

The bond lengths in the molecule of *p*-aminophenol do not present any unusual features. The mean side of the benzene hexagon is 1.38 Å., in agreement with the values obtained in a wide variety of other aromatic substances. The C-O bond (1.47 Å.) is rather longer than that generally accepted for a pure C-O single bond (1.42 Å.), although it is similar to that observed in pentaerythritol (1.46 Å.) (Llewellyn, Cox & Goodwin, 1937) and is considerably longer than those found in phenols, e.g. 1.36 Å. in resorcinol (Robertson, 1936) and 1.36 Å. in quinol (Palin & Powell, 1947). The C-N bond (1.39 Å.) is shorter than that taken as the pure C-N single bond (1.47 Å.), but is in agreement with other C-N bonds adjacent to benzene rings (for examples see Brown, 1949).

Table 3. N-H-O hydrogen-bond lengths

(A.)		
Diketopiperazine	2.85	Corey (1938)
Acetamide	2.83, 2.89	Senti & Harker (1940)
Cyanuric acid	2.80, 2.81	Wiebenga & Moerman (1938)
Urea-H <sub>2</sub> O <sub>2</sub>	2.94, 3.04	Lu, Hughes & Giguère (1941)
Hydroxylamine HCl	3.15, 3.30	Jerslev (1948)
Pyrimidine	2.78, 2.89	Pitt (1948)
<i>p</i> -Nitroaniline	3.07, 3.11	Abrahams & Robertson (1948)
Glycine	2.76, 2.88, 2.93, 3.05	Albrecht & Corey (1939)
Alanine	2.78, 2.84, 2.88	Levy & Corey (1941)
Nickel glycine 2H <sub>2</sub> O	2.96, 3.13	Stosick (1945)
Adenine HCl	2.87	Broomhead (1948)
Acetanilide	2.94	Brown & Corbridge (1948)
Potassium sulphamate	3.15, 3.16	Brown & Cox (1940)
		Ketelaar & Heilmann (1940)
Urea	2.97, 3.03	Wyckoff & Corey (1934)

The lengths of the N-H-O hydrogen bonds (2.83, 3.13 and 3.18 Å.) may be compared with the values obtained in previous structure determinations (Table 3). It would appear that, broadly speaking, these values fall into two groups having average values of about 2.85 and 3.15 Å. One of the hydrogen bonds in *p*-aminophenol would correspond to the shorter of these two values and the other two hydrogen bonds to the longer. The significance of these differences is at present somewhat obscure; a convenient suggestion would be that the shorter bond is due to the phenolic hydrogen, while the two longer bonds are due to the amino hydrogens, but it is difficult to reconcile this idea with the roles of the hydrogen atoms in the other structures listed in Table 3. Further speculation must obviously await a more complete understanding of the nature of the hydrogen bond.

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