

Structural Studies of Benzene Derivatives.

VII.* The Structure of *p*-Aminobenzoic Acid Hydrochloride

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Abstract

Crystals of *p*-aminobenzoic acid hydrochloride, $C_7H_8NO_2^+ \cdot Cl^-$, are monoclinic, space group $P2_1/c$, with $a = 5.579(4)$, $b = 8.254(4)$, $c = 17.096(6)$ Å, $\beta = 96.55(7)^\circ$, $Z = 4$. The final R is 0.0381 for 1672 counter intensities. The benzene ring has only approximate C_{2v} (mm) symmetry, owing to small deviations from planarity; the internal angles at the *ipso* positions are $\alpha_{NH_3^+} = 121.8(2)^\circ$ and $\alpha_{COOH} = 120.4(2)^\circ$. An unusual feature of the crystal structure is the absence of the carboxylic dimer. The cations are linked in endless chains by direct hydrogen bonds, $O \cdots H-N$, and bridging Cl^- ions, $O-H \cdots Cl^- \cdots H-N$. Other $Cl^- \cdots H-N$ hydrogen bonds connect adjacent chains into a three-dimensional network.

Introduction

Comparison of molecular geometries of several *para*-substituted benzoic acids, $p-X-C_6H_4-COOH$, has shown that the structural effects of the *para* substituent, although quite marked in the C(3)–C(4)–C(5) region of the ring (Fig. 1), are by no means confined to this part of the molecule (Colapietro, Domenicano & Marciante, 1978; Colapietro, Domenicano, Marciante & Portalone, 1979). Small systematic changes occur in several geometrical parameters, including the C(2)–C(1)–C(6) angle, the C(1)–C(7) length, and the length of the hydrogen bond that normally connects the molecules in centrosymmetric pairs. To provide the data needed for analysing these effects we have determined the molecular geometries of some members of this class of compounds. Results have been presented for $X = NO_2$,

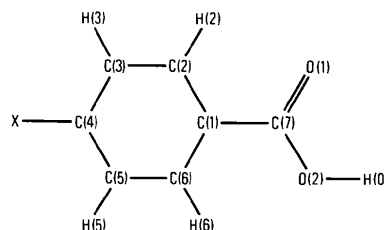


Fig. 1. Numbering scheme in *para*-substituted benzoic acids.

OCH_3 , F, OH (Colapietro & Domenicano, 1977, 1978; Colapietro, Domenicano & Pela Ceccarini, 1979; Colapietro, Domenicano & Marciante, 1979); here we report the structure of *p*-aminobenzoic acid hydrochloride, $X = NH_3^+$.

Experimental

p-Aminobenzoic acid hydrochloride was obtained as a white powder by adding concentrated HCl to an ethanolic solution of commercial *p*-aminobenzoic acid (Carlo Erba). Pale pink tablets were grown by slow evaporation of an aqueous solution. A crystal $0.73 \times 0.34 \times 0.17$ mm was mounted on a Syntex $P2_1$ diffractometer. The cell parameters were refined by least squares from the measured θ values for 20 centred reflexions, lying in the θ range 17 – 19° and well distributed in reciprocal space. Crystal data are given in Table 1.

Intensities were collected at room temperature in the θ – 2θ scan mode with graphite-monochromatized $MoK\alpha$ radiation. The scanning interval was from $2\theta(K\alpha_1) - 1.2^\circ$ to $2\theta(K\alpha_2) + 1.2^\circ$. The scanning speed was varied according to the intensity, from a minimum value of 0.020 to a maximum of $0.49^\circ s^{-1}$. The background was measured for $\frac{1}{4}$ of the scanning time at each end of the scan. Three standard reflexions were

* Part VI: Colapietro, Domenicano & Marciante (1979).

Table 1. *Crystal data*

p-Aminobenzoic acid hydrochloride, $C_7H_8NO_2^+ \cdot Cl^-$, FW = 173.61, monoclinic, space group $P2_1/c$ (systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$), $Z = 4$.

$a = 5.579$ (4) Å*	$V = 782.1$ (7) Å ³
$b = 8.254$ (4)	$D_c = 1.474$ Mg m ⁻³
$c = 17.096$ (6)	$D_m = 1.479$ †
$\beta = 96.55$ (7)°	

* Measured at 293 K with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). E.s.d.'s are given in parentheses as units in the last digit.

† Measured at 293 K by flotation in a mixture of carbon tetrachloride and *n*-hexane.

monitored every 100 reflexions; their intensities indicated no counter or crystal instability. A recentring routine was run every 1000 reflexions. 2713 reflexions in the θ range $1.5\text{--}30^\circ$ were measured; 1845 of these, having $I \geq 4\sigma(I)$, were considered as non-zero. The reflexions of the $h = 0$ layer were measured both as $0kl$ and $Ok\bar{l}$; averaging and merging [internal $R(F_o) = 0.033$] led to a set of 1678 independent observations. The intensities were corrected for Lorentz and polarization effects, but not for absorption [$\mu(\text{Mo } K\alpha) = 0.438 \text{ mm}^{-1}$]. A secondary-extinction correction was applied during the final stages of refinement.

Structure determination and refinement

Preliminary atomic parameters for the non-H atoms were obtained by Patterson and Fourier techniques ($R = 0.181$). Isotropic and then anisotropic least-squares refinement, followed by the introduction of the H atoms as given by a difference synthesis, lowered R to 0.071. Further refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms, converged to $R = 0.045$ (four intense reflexions having $|F_o|$ much lower than $|F_c|$

Table 2. *Final coordinates ($\times 10^5$) for non-hydrogen atoms*

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>
Cl ⁻	9870 (8)	11052 (6)	23505 (3)
O(1)	53301 (33)	19289 (23)	65115 (9)
O(2)	81968 (29)	4850 (21)	60236 (9)
N	40493 (31)	43767 (22)	29327 (9)
C(1)	57459 (29)	21739 (20)	51502 (10)
C(2)	36332 (31)	30752 (22)	50012 (10)
C(3)	30401 (31)	37756 (22)	42682 (10)
C(4)	45944 (30)	35779 (20)	36959 (10)
C(5)	66734 (32)	26601 (23)	38305 (11)
C(6)	72430 (32)	19434 (23)	45619 (11)
C(7)	63701 (34)	15127 (23)	59605 (10)

Table 3. *Final coordinates ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms*

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(2)	259 (5)	320 (3)	544 (2)	2.0 (5)
H(3)	166 (4)	443 (3)	416 (1)	0.9 (4)
H(5)	773 (5)	254 (3)	348 (2)	1.8 (5)
H(6)	865 (5)	127 (3)	465 (2)	1.7 (5)
H(1N)	393 (6)	363 (5)	259 (2)	4.0 (8)
H(2N)	271 (5)	497 (4)	292 (2)	2.2 (5)
H(3N)	529 (7)	498 (4)	281 (2)	4.3 (8)
H(O)	844 (6)	18 (4)	645 (2)	3.0 (7)

were excluded from this refinement). Inspection of the structure factor list revealed that secondary extinction was present and strongly anisotropic, being particularly marked for the $0kl$ reflexions. A plot of $\log(I_c/I_o)$ vs I_c for this class of reflexions was linear (the only serious outlier being the most intense reflexion, 023) and gave a value of 2.4×10^{-5} for the secondary-extinction coefficient g (Stout & Jensen, 1968). The corresponding plot for $1kl$ reflexions was, however, far from linear. The extinction correction was thus applied only to $0kl$ reflexions.

The final refinement was by full-matrix least squares, minimizing $\sum w(|F_o| - k|F_c|)^2$; the number of observations per refined parameter was $1672/132 = 12.7$.* Weights were $w = 1/(a + b|F_o| + c|F_o|^2)$, with $a = 9.67$, $b = 1.0$ and $c = 0.258$. The final R and R_w were 0.0381 and 0.0574, with all final shifts $< 0.05\sigma$. Atomic parameters are given in Tables 2 and 3.† Alternative refinements, based on other selections of a and c , and also on $w = 1.0$ and $w = \sin \theta/\lambda$, gave a higher dispersion for the mean values of the function minimized over ranges of either $|F_o|$ or $\sin \theta/\lambda$, and afforded a less symmetrical C hexagon.

Calculations were carried out on the Univac 1100/22 computer of the University of Rome and on the HP 21MX minicomputer of the CNR Research Area. The computer programs and atomic form factors were the same as those in part V (Colapietro, Domenicano & Pela Ceccarini, 1979).

Results and discussion

Bond lengths and angles are given in Fig. 2 and Table 4; they have not been corrected for the effects of

* The 023 reflexion and five strong $1kl$ and $2kl$ reflexions (100, 10 $\bar{2}$, 121, 106 and 20 $\bar{6}$) which were seriously affected by secondary extinction were not included in the refinement.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34817 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

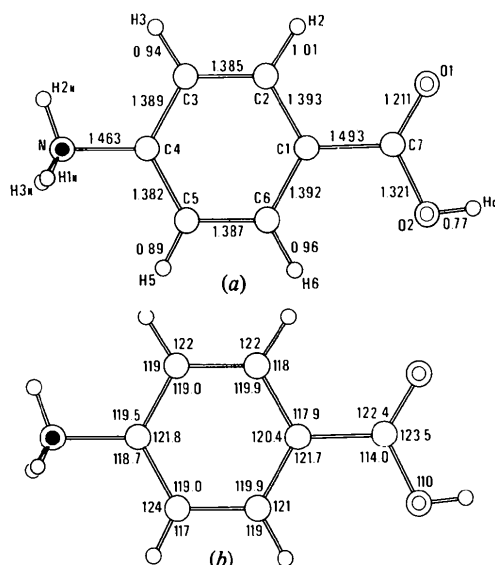


Fig. 2. Geometry of the cation in *p*-aminobenzoic acid hydrochloride: (a) bond lengths (Å), (b) bond angles (°). E.s.d.'s (calculated from the e.s.d.'s in the atomic parameters given in Tables 2 and 3) are 0.002–0.003 Å for C–C, C–O and C–N bonds, 0.02–0.03 Å for C–H and O–H bonds, 0.15–0.17° for angles not involving H atoms, and 1–2° for angles involving H atoms.

Table 4. Bond lengths (Å) and angles (°) involving the NH_3^+ substituent

E.s.d.'s are given in parentheses as units in the last digit.

C(4)–N	1.463 (2)	C(4)–N–H(1N)	106 (2)
N–H(1N)	0.85 (4)	C(4)–N–H(2N)	111 (2)
N–H(2N)	0.89 (3)	C(4)–N–H(3N)	112 (2)
N–H(3N)	0.90 (4)	H(1N)–N–H(2N)	113 (3)
		H(1N)–N–H(3N)	104 (3)
		H(2N)–N–H(3N)	111 (3)

Table 5. Deviations from planarity

Equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes): $2.6437x + 6.7818y + 4.4566z = 5.2765$. The e.s.d.'s in the atomic positions are 0.0016–0.0018 Å for the non-H atoms, 0.025 Å for the H atoms of the ring, and 0.03–0.04 Å for other H atoms.

Displacements (Å) of atoms from the plane

C(1)*	–0.012	O(2)	0.096
C(2)*	0.002	H(2)	0.00
C(3)*	0.010	H(3)	–0.02
C(4)*	–0.012	H(5)	–0.04
C(5)*	0.001	H(6)	0.06
C(6)*	0.011	H(1N)	0.62
C(7)	–0.090	H(2N)	–0.11
N	–0.069	H(3N)	–0.75
O(1)	–0.343	H(O)	0.05

* Atoms defining the plane.

Table 6. Torsion angles (°)

Signs are given according to the convention of Klyne & Prelog (1960). E.s.d.'s are 0.2° for angles not involving H atoms, 2° for angles involving H atoms.

(a) NH_3^+ substituent

H(1N)–N–C(4)–C(3)	–121
H(1N)–N–C(4)–C(5)	60
H(2N)–N–C(4)–C(3)	2
H(2N)–N–C(4)–C(5)	–177
H(3N)–N–C(4)–C(3)	126
H(3N)–N–C(4)–C(5)	–53

(b) COOH substituent

O(1)–C(7)–C(1)–C(2)	–11.4
O(1)–C(7)–C(1)–C(6)	166.9
O(2)–C(7)–C(1)–C(6)	–11.0
O(2)–C(7)–C(1)–C(2)	170.7

thermal motion. The equation of the least-squares plane through the six C atoms of the ring and the displacements of all atoms from this plane are presented in Table 5. Torsion angles are given in Table 6.

The benzene ring

As in *p*-hydroxybenzoic acid monohydrate (Colapietro, Domenicano & Marciante, 1979) the C hexagon has only approximate C_{2v} (*mm*) symmetry, owing to minor deviations from planarity (Table 5). The pattern of the deviations is the same for both molecules, but here they are slightly larger. C(1) and C(4) are displaced by –0.012 Å from the least-squares plane, C(3) and C(6) by 0.010–0.011 Å, whilst C(2) and C(5) lie in the plane. In both molecules the exocyclic atoms C(7) and X are displaced from the ring plane on the same side as C(1) and C(4), but to a much larger extent (here by –0.090 and –0.069 Å, respectively). The deviations from planarity may be caused by the complex system of intermolecular hydrogen bonds that occurs in both crystals. No such deviations occur in other *para*-substituted benzoic acids (*p*-X–C₆H₄–COOH; X = NO₂, OCH₃, F, Cl) where the only intermolecular hydrogen bond is that of the carboxylic dimer.

The bond lengths and angles of the ring conform to the axial symmetry observed in most *para*-disubstituted benzene derivatives. Possible exceptions are the C(3)–C(4) and C(4)–C(5) lengths, whose difference (0.007 Å, 3σ) may perhaps be real.

The internal angles of the ring show the expected pattern of deviations from 120°. The angle *ipso* to the carboxy group, $\alpha_{\text{COOH}} = 120.4$ (2)°, is at the upper limit of the range of values observed in *para*-substituted benzoic acids (Colapietro & Domenicano, 1978). The angle *ipso* to the NH_3^+ group, $\alpha_{\text{NH}_3^+} = 121.8$ (2)°, compares well with the mean value of 121.7 (2)° obtained from several anilinium cations

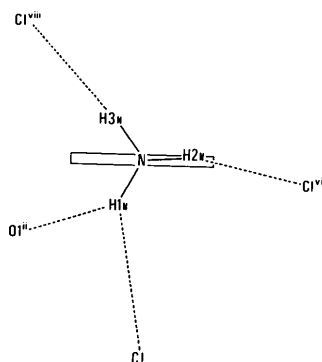


Fig. 3. Projection of the NH_3^+ group along $\text{N}-\text{C}(4)$. The system of intermolecular hydrogen bonds is also shown. The superscripts refer to the symmetry operations given in the caption of Fig. 4.

(Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977).

The NH_3^+ substituent

The length of $\text{C}(4)-\text{N}$, 1.463 (2) Å, agrees with the values observed in *p*-phenylenediamine dihydrochloride [1.463 (2) Å, Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977], and in *m*-aminobenzoic acid hydrochloride [1.461 (4) Å, Arora, Sundaralingam, Dancz, Stanford & Marsh, 1973]. Also the conformation of the substituent (Fig. 3 and Table 6) and the slight bending of $\text{C}(4)-\text{N}$ in the plane of the ring (Fig. 2*b*) are essentially the same.

The COOH substituent

As in *p*-hydroxybenzoic acid monohydrate (Colapietro, Domenicano & Marciante, 1979), the network of intermolecular hydrogen bonds prevents the orientational disorder of the carboxy group often occurring in crystals of aromatic carboxylic acids (Leiserowitz, 1976). Thus the two $\text{C}-\text{O}$ bonds and $\text{C}-\text{C}-\text{O}$ angles have quite different values and $\text{C}(1)-\text{C}(7)$ is bent in the plane of the ring (Fig. 2). The carboxy group is also twisted (Table 6) and bent (Table 5) out of the ring plane; the angle between the least-squares plane of the ring and the plane through $\text{C}(7)$, $\text{O}(1)$ and $\text{O}(2)$ is 12.2°.

The $\text{C}(1)-\text{C}(7)$ bond, 1.493 (2) Å, is the longest ever reported for a *para*-substituted benzoic acid.

The crystal structure

p-Aminobenzoic acid hydrochloride is unique among the *para*-substituted benzoic acids whose crystal structures have been determined in not forming the centrosymmetric dimer in the solid state. The cations are linked in endless chains running along *c* by direct hydrogen bonds, $\text{O}\cdots\text{H}-\text{N}$, and bridging Cl^-

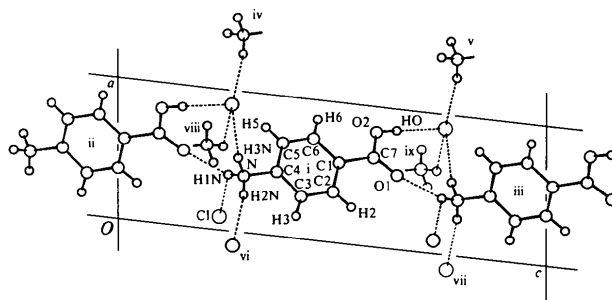


Fig. 4. Projection of the crystal structure of *p*-aminobenzoic acid hydrochloride down *b*. The broken lines represent intermolecular hydrogen bonds. The symmetry operations relating the various pairs of ions to pair (i) (which is at x, y, z) are: (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 + x, y, z$; (v) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $-x, -y, 1 - z$; (viii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ix) $1 - x, -y, 1 - z$.

Table 7. Geometry of the hydrogen bonds

E.s.d.'s are given in parentheses as units in the last digit. The superscripts refer to the symmetry operations given in the caption of Fig. 4.

(a) Distances (Å)

$\text{O}(1^{\text{ii}})\cdots\text{N}$	2.823 (2)	$\text{O}(1^{\text{ii}})\cdots\text{H}(1\text{N})$	2.13 (4)
$\text{Cl}^{\text{ix}}\cdots\text{O}(2)$	3.061 (2)	$\text{Cl}^{\text{ix}}\cdots\text{H}(\text{O})$	2.30 (3)
$\text{Cl}\cdots\text{N}$	3.288 (2)	$\text{Cl}\cdots\text{H}(1\text{N})$	2.66 (4)
$\text{Cl}^{\text{vi}}\cdots\text{N}$	3.139 (2)	$\text{Cl}^{\text{vi}}\cdots\text{H}(2\text{N})$	2.27 (3)
$\text{Cl}^{\text{viii}}\cdots\text{N}$	3.201 (2)	$\text{Cl}^{\text{viii}}\cdots\text{H}(3\text{N})$	2.32 (4)

(b) Angles (°)

$\text{O}(1^{\text{ii}})\cdots\text{H}(1\text{N})-\text{N}$	138 (3)
$\text{Cl}^{\text{ix}}\cdots\text{H}(\text{O})-\text{O}(2)$	171 (3)
$\text{Cl}\cdots\text{H}(1\text{N})-\text{N}$	132 (3)
$\text{Cl}^{\text{vi}}\cdots\text{H}(2\text{N})-\text{N}$	167 (3)
$\text{Cl}^{\text{viii}}\cdots\text{H}(3\text{N})-\text{N}$	167 (3)

ions, $\text{O}-\text{H}\cdots\text{Cl}^-\cdots\text{H}-\text{N}$. Other $\text{Cl}^-\cdots\text{H}-\text{N}$ hydrogen bonds connect adjacent chains into a three-dimensional network (Fig. 4). Geometrical details of the five independent hydrogen bonds are given in Table 7. $\text{H}(1\text{N})$ is involved in a bifurcated hydrogen bond (Figs. 3 and 4). The network of hydrogen bonds is different from that occurring in *m*-aminobenzoic acid hydrochloride (Arora *et al.*, 1973), where the cations are joined in centrosymmetric pairs through their carboxy groups, and each Cl^- ion is hydrogen bonded to three NH_3^+ groups only.

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The Structure of Tetrathiafulvalenium Perchlorate, $\text{TTF}^+ \cdot \text{ClO}_4^-$

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Abstract

Tetrathiafulvalenium perchlorate ($\text{TTF}^+ \cdot \text{ClO}_4^-$) is orthorhombic, space group *Pbca*, with $a = 16.762$ (1), $b = 20.906$ (2), $c = 12.538$ (1) Å, $Z = 16$. The structure was solved by the direct method and refined by the full-matrix least-squares method to an R of 0.064 for 2324 independent reflections. The TTF^+ ions form dimers, which are arranged in pairs in the crystals. A charge-transfer interaction between TTF^+ ions takes place mostly within a dimer, but a weak interaction is also possible between dimers. The polarized absorption spectrum of a single crystal of $\text{TTF}^+ \cdot \text{ClO}_4^-$ can be interpreted according to the crystal structure.

Introduction

Tetrathiafulvalene (TTF, $\text{C}_6\text{H}_4\text{S}_4$) is an organic molecule of low ionization potential, which forms solid molecular complexes or charge-transfer salts with a variety of electron acceptors. Some TTF complexes exhibit behavior characteristic of one-dimensional metals. The solid complex with tetracyano-*p*-quinodimethane (TCNQ) is a typical example of such an organic metal. $\text{TTF} \cdot \text{Br}_{0.7}$ and $\text{TTF} \cdot \text{I}_{0.76}$ are also known to exhibit metallic behavior at room temperature. All these highly conductive TTF complexes have one-dimensional TTF stacks in their crystal

structures, which have mixed valences, *i.e.* the TTF molecules are partially in the state of a monocationic ion (TTF^+) and partially in the state of a neutral molecule (TTF^0). In our previous study on the absorption spectra of the crystals of TTF halides and related salts, we found that the spectrum of $\text{TTF}^+ \cdot \text{ClO}_4^-$ shows several features distinctly different from those of the spectra of the mixed-valence TTF halides (Sugano, Yakushi & Kuroda, 1978). Thus it becomes necessary to determine the crystal structure to interpret the observed spectrum. It is also of interest to know the geometry of the TTF^+ ion. Although the TTF geometries in several mixed-valence TTF salts have been reported, the geometry of the TTF^+ ion in crystals where TTF molecules are entirely in the form of monocationic ions has not been reported so far. Since $\text{TTF}^+ \cdot \text{ClO}_4^-$ is completely ionic, the analysis of its crystal structure can provide data concerned with the molecular geometry of the TTF^+ ion.

Experimental

$\text{TTF}^+ \cdot \text{ClO}_4^-$ was prepared according to the method reported by Wudl (1975). The dark-purple crystals of $\text{TTF}^+ \cdot \text{ClO}_4^-$ were grown by slowly cooling a solution in acetonitrile; they were elongated along a , developing the (001) crystal face. From Weissenberg photographs the space group was determined to be *Pbca*, since the