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Structural Studies of Benzene Derivatives. IX.* The Structures of *p*-Fluoroaniline and *p*-Cyanoaniline Hydrochlorides

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Abstract

The crystals of the title compounds, $C_6H_7FN^+.Cl^-$ and $C_7H_7N_2^+.Cl^-$, are triclinic, space group $P\bar{1}$, $Z = 2$, with unit cells of closely related dimensions: a = 4·266 (1), b = 5·865 (1), c = 13·635 (2) Å, α = 91·90 (1), β = 90·05 (2), γ = 99·15 (2)° (*p*-fluoroaniline hydrochloride), and a = 4·267 (2), b = 5·967 (1), c = 14·555 (3) Å, α = 91·64 (2), β = 92·18 (2), γ = 99·59 (2)° (*p*-cyanoaniline hydrochloride). The structures were determined from 1768 and 1856 counter intensities and refined to final R values of 0·0421 and 0·0374, respectively. Apart from minor deviations from planarity, the benzene rings have *mm* symmetry. The deviations from 6/*mmm* symmetry are highly significant, and involve bond distances as well as angles. The internal angles at the *ipso* positions of the rings are all >120° [$\alpha_{NH_3^+}$ = 121·8 (2), 122·5 (2); α_F = 123·2 (2); α_{CN} = 121·0 (2)°], due to the strongly σ-electron-withdrawing properties of the NH_3^+, F and CN substituents. The crystal structures of the two compounds are essentially the same. The NH_3^+ groups and Cl^- ions are connected in infinite ribbons through $Cl^-\cdots H{-}N$ hydrogen bonds, 3·15–3·32 Å long. Adjacent ribbons are joined in layers through additional, longer $Cl^-\cdots H$ contacts.

Introduction

As part of a research project aimed at measuring the effect of different *para* substituents on the geometry of the anilinium cation we have determined the crystal structures of *p*-fluoroaniline and *p*-cyanoaniline hydrochlorides (hereafter referred to as *p*-fluoro and *p*-cyano derivatives). Previous work has included X-ray diffraction studies of *p*-phenylenediamine dihydrochloride (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977) and *p*-aminobenzoic acid hydrochloride (Colapietro, Domenicano & Portalone, 1980). A preliminary communication of the present work has been given (Colapietro, Domenicano, Marciante & Portalone, 1980).

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* Part VIII: Di Rienzo, Domenicano & Riva di Sanseverino (1980).

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Experimental

The compounds were obtained as white powders by allowing gaseous HCl to pass through solutions of the free bases in Et_2O. Pale-brown tablets were grown by evaporation of aqueous solutions containing a few drops of concentrated HCl. The two crystals selected for the analysis were 0·5 × 0·5 × 0·1 mm.

Preliminary oscillation and Weissenberg photographs showed the crystals to be triclinic, with unit cells of closely related dimensions and a similar pattern of intensities. The cell parameters were refined by least squares from the θ values of 15 reflexions centred on a Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation. The reflexions used were well distributed in reciprocal space and had θ ranges of 17–22° (*p*-fluoro) and 14–19° (*p*-cyano). Crystal data are given in the *Abstract* and Table 1.

Intensities were collected at room temperature in the θ–2θ scan mode with graphite-monochromatized Mo $K\alpha$ radiation. The scanning interval was from $2\theta(K\alpha_1) - 1{\cdot}2$ to $2\theta(K\alpha_2) + 1{\cdot}1°$ for the *p*-fluoro derivative, from $2\theta(K\alpha_1) - 1{\cdot}3$ to $2\theta(K\alpha_2) + 1{\cdot}0°$ for the *p*-cyano. The scanning speed was varied according to the intensity, from a minimum of 0·017 to a maximum of 0·49° s^{-1}. The background was measured for a quarter of the scanning time at each end of the scan. A recentring routine was run periodically during the data collection. The reciprocal space was explored from θ = 1·5 to 34°.

Three standard reflexions, monitored every 100 reflexions, consistently showed a steady decrease of intensity, totalling 22% for the *p*-fluoro derivative, 35% for the *p*-cyano. This was due to decomposition of the crystals, which gradually turned opaque. The intensities were corrected for the decrease and for Lorentz and polarization effects, but not for absorption [μ(Mo $K\alpha$) = 0·494 and 0·442 mm^{-1}, respectively].

For *p*-fluoroaniline hydrochloride 2798 reflexions were scanned. 1833 of these, having $I > 4\sigma(I)$, were considered as non-zero. The 64 reflexions of the $l = 0$ layer were measured as $hk0$ and as $\bar{h}\bar{k}0$; averaging and merging [internal $R(F_o) = 0{\cdot}020$] led to a set of 1769 independent observations.

For *p*-cyanoaniline hydrochloride 3825 reflexions were scanned, of which 2422, having $I > 4\sigma(I)$, were considered as non-zero. 538 reflexions were scanned two or more times; these included the reflexions of the $l = 0$ layer, which were measured as $hk0$ and as $\bar{h}\bar{k}0$. After averaging and merging [internal $R(F_o) = 0{\cdot}027$] a set of 1858 independent observations was obtained.

Table 1. *Crystal data*

Crystal data were measured at 293 K with Mo $K\alpha$ radiation (λ = 0·71069 Å). E.s.d.'s are given in parentheses as units in the last digit. Crystals are triclinic, space group $P\bar{1}$.

$C_6H_7FN^+.Cl^-$, M_r = 147·59
$C_7H_7N_2^+.Cl^-$, M_r = 154·61

	p-Fluoroaniline hydrochloride	*p*-Cyanoaniline hydrochloride
a (Å)	4·266 (1)	4·267 (2)
b (Å)	5·865 (1)	5·967 (1)
c (Å)	13·635 (2)	14·555 (3)
α (°)	91·90 (1)	91·64 (2)
β (°)	90·05 (2)	92·18 (2)
γ (°)	99·15 (2)	99·59 (2)
V (Å^3)	336·6 (1)	364·9 (2)
D_c (Mg m^{-3})	1·456	1·407
D_m (Mg m^{-3})	1·462*	1·410*

* Measured at 298 K by flotation in a mixture of carbon tetrachloride and *n*-hexane.

Structure determination and refinement

p-Fluoroaniline hydrochloride

Preliminary atomic parameters for the non-H atoms were obtained by Patterson and Fourier techniques, assuming the centrosymmetric space group $P\bar{1}$ (R =

Table 2. *Final coordinates* (×10^5) *and equivalent values of the anisotropic temperature factors 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.

(*a*) *p*-Fluoroaniline hydrochloride

	x	y	z	B_{eq} (Å^2)*
Cl^-	10384 (12)	23945 (7)	42386 (3)	2·74
F	16450 (51)	26890 (31)	98783 (11)	5·20
N(1)	57807 (44)	23213 (29)	60339 (12)	2·84
C(1)	46328 (41)	23916 (28)	70444 (12)	2·45
C(2)	51138 (56)	6642 (32)	76647 (14)	3·07
C(3)	40868 (65)	7664 (38)	86296 (15)	3·60
C(4)	26223 (61)	25876 (40)	89288 (15)	3·55
C(5)	20969 (60)	43079 (38)	83195 (17)	3·59
C(6)	31221 (49)	42010 (32)	73541 (15)	2·97

(*b*) *p*-Cyanoaniline hydrochloride

	x	y	z	B_{eq} (Å^2)*
Cl^-	9862 (11)	23951 (7)	42985 (3)	2·57
N(1)	59650 (40)	23445 (29)	59509 (10)	2·56
N(2)	14357 (59)	27460 (34)	103707 (13)	3·86
C(1)	48789 (38)	23926 (26)	68947 (10)	2·18
C(2)	53979 (47)	6886 (29)	74738 (12)	2·64
C(3)	44451 (51)	7877 (31)	83752 (12)	2·81
C(4)	30182 (43)	25900 (29)	86733 (11)	2·45
C(5)	24703 (47)	42895 (30)	80775 (12)	2·68
C(6)	34229 (45)	41890 (29)	71738 (12)	2·51
C(7)	21064 (53)	26923 (32)	96178 (13)	3·09

* Defined as $(B_1.B_2.B_3)^{1/3}$.

Table 3. *Final coordinates* ($\times 10^3$) *and isotropic temperature factors 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.

(*a*) *p*-Fluoroaniline hydrochloride

	x	y	z	B (Å^2)
H(2)	619 (7)	−57 (5)	743 (2)	2·5 (6)
H(3)	431 (8)	−41 (6)	910 (3)	3·6 (7)
H(5)	104 (8)	553 (6)	855 (2)	3·5 (7)
H(6)	285 (6)	536 (5)	691 (2)	1·9 (5)
H(1N)	689 (8)	361 (6)	590 (2)	3·0 (7)
H(2N)	698 (7)	115 (5)	594 (2)	2·5 (6)
H(3N)	422 (7)	213 (5)	559 (2)	2·0 (5)

(*b*) *p*-Cyanoaniline hydrochloride

	x	y	z	B (Å^2)
H(2)	641 (7)	−56 (5)	725 (2)	2·4 (6)
H(3)	477 (7)	−40 (5)	876 (2)	2·5 (6)
H(5)	140 (6)	557 (4)	829 (2)	1·5 (5)
H(6)	300 (6)	537 (4)	678 (2)	1·2 (4)
H(1N)	721 (7)	361 (5)	585 (2)	2·5 (6)
H(2N)	700 (8)	127 (6)	586 (2)	3·1 (7)
H(3N)	430 (7)	223 (5)	549 (2)	2·0 (5)

0·252). Isotropic and then anisotropic least-squares refinement, followed by the introduction of the H atoms as given by a difference synthesis, lowered R to 0·060. The final refinement was by full-matrix least squares, minimizing $\sum w(|F_o| - k|F_c|)^2$, with the H atoms treated isotropically. Weights were given according to $w = 1/(a + b|F_o| + c|F_o|^2)$, with $a = 3{\cdot}0$, $b = 1{\cdot}0$, and $c = 0{\cdot}040$. This type of weighting function has been shown (Di Rienzo, Domenicano & Riva di Sanseverino, 1980, and references therein) to be superior to others since (i) it gives a lower dispersion for the mean values of the minimized function over ranges of $|F_o|$ and $\sin\theta/\lambda$, and (ii) it yields a better approximation to the axially symmetrical molecular geometry expected on chemical grounds for *para*-disubstituted benzene derivatives. The number of observations per refined parameter was 1768/110 = 16·1.* The final R and R_w were 0·0421 and 0·0542, respectively, with all shifts $<0{\cdot}01\sigma$. The final atomic parameters are given in Tables 2 and 3.†

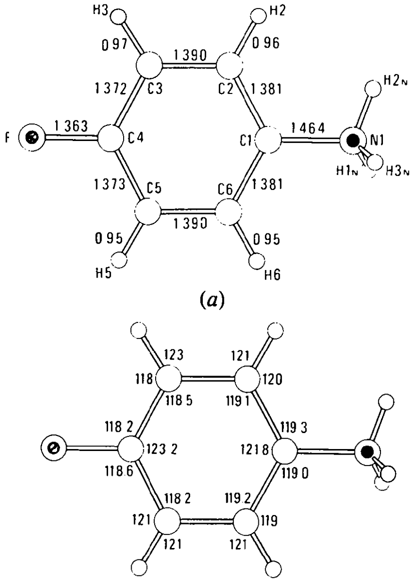
p-Cyanoaniline hydrochloride

A suitable starting model was based on the final positional parameters for the Cl, N, and C atoms of *p*-fluoroaniline hydrochloride. A structure factor calculation gave $R = 0{\cdot}410$; this was lowered to 0·239 by isotropic least-squares refinement. The atoms of the CN group were then located on a Fourier map. Further isotropic and then anisotropic least-squares refinement, followed by the introduction of the H atoms as given by a difference synthesis, lowered R to 0·042. The final refinement was carried out as with the *p*-fluoro derivative; the coefficients of the weighting function were $a = 2{\cdot}9$, $b = 1{\cdot}0$, and $c = 0{\cdot}028$. The number of observations per refined parameter was 1856/119 = 15·6.* The final R and R_w were 0·0374 and 0·0504, respectively, with all shifts $<0{\cdot}05\sigma$. The final atomic parameters are given in Tables 2 and 3.†

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 for the anilinium cations are given in Figs. 1 and 2 and in Table 4; no corrections



(*a*)

(*b*)

Fig. 1. Geometry of the cation in *p*-fluoroaniline 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 0·003 Å for C—C, C—N and C—F bonds, 0·03–0·04 Å for C—H bonds, 0·16–0·22° for angles not involving H atoms, 2° for C—C—H angles.

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* The reflexion 102 had $|F_o|$ much lower than $|F_c|$ and was excluded from the refinement.

† Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35695 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* The reflexions $01\bar{1}$ and $02\bar{2}$ had $|F_o|$ much lower than $|F_c|$ and were excluded from the refinement.

† See deposition footnote.

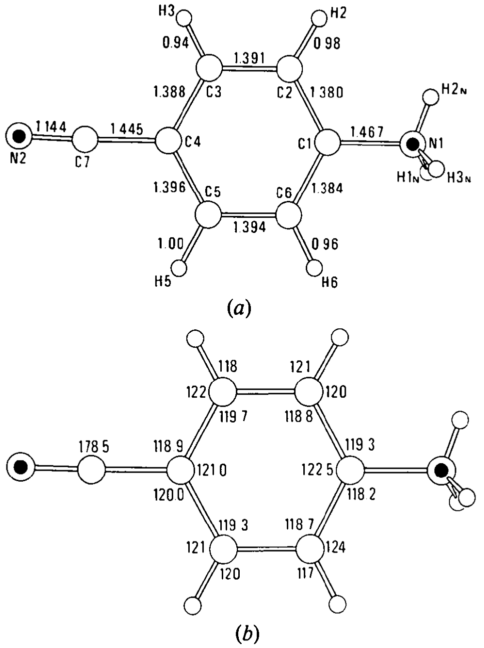

Fig. 2. Geometry of the cation in *p*-cyanoaniline hydrochloride: (*a*) bond lengths (Å), (*b*) bond angles (°). E.s.d.'s (calculated from the e.s.d.'s in the atomic parameters given in Tables 2 and 3) are 0·002–0·003 Å for C—C and C—N bonds, 0·03 Å for C—H bonds, 0·25° for the C(4)—C(7)—N(2) angle, 0·15–0·18° for other angles not involving H atoms, 2° for C—C—H angles.

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

E.s.d.'s are given in parentheses as units in the last digit. Signs for the torsion angles have been assigned according to the convention of Klyne & Prelog (1960).

	p-Fluoroaniline hydrochloride	*p*-Cyanoaniline hydrochloride
C(1)–N(1)	1·464 (2)	1·467 (2)
N(1)–H(1N)	0·85 (3)	0·87 (3)
N(1)–H(2N)	0·93 (3)	0·85 (4)
N(1)–H(3N)	0·89 (3)	0·95 (3)
C(1)–N(1)–H(1N)	110 (2)	110 (2)
C(1)–N(1)–H(2N)	111 (2)	112 (2)
C(1)–N(1)–H(3N)	113 (2)	114 (2)
H(1N)–N(1)–H(2N)	110 (3)	108 (3)
H(1N)–N(1)–H(3N)	104 (3)	105 (3)
H(2N)–N(1)–H(3N)	109 (3)	109 (3)
H(1N)–N(1)–C(1)–C(2)	−129 (2)	−124 (2)
H(1N)–N(1)–C(1)–C(6)	51 (2)	55 (2)
H(2N)–N(1)–C(1)–C(2)	−7 (2)	−5 (2)
H(2N)–N(1)–C(1)–C(6)	172 (2)	174 (2)
H(3N)–N(1)–C(1)–C(2)	115 (3)	119 (2)
H(3N)–N(1)–C(1)–C(6)	−66 (3)	−63 (2)

have been applied for the effects of thermal motion. Torsion angles involving the NH_3^+ substituents are given in Table 4. The equations of the least-squares planes through the C atoms of the benzene rings and the displacements of all atoms from these planes are reported in Table 5.

Table 5. *Deviations* (Å) *from planarity*

The equations of the least-squares planes through the six C atoms of the benzene rings, referred to the crystallographic axes, are $3·4585x + 2·2479y + 3·4486z = 4·5638$ for *p*-fluoroaniline hydrochloride, and $3·4512x + 2·2347y + 3·3735z = 4·5396$ for *p*-cyanoaniline hydrochloride.

	p-Fluoro[a]	*p*-Cyano[b]		*p*-Fluoro[a]	*p*-Cyano[b]
C(1)[c]	−0·005	−0·005	N(2)	—	−0·068
C(2)[c]	0·003	0·002	H(2)	−0·01	0·01
C(3)[c]	0·002	0·004	H(3)	0·03	0·03
C(4)[c]	−0·004	−0·007	H(5)	0·01	0·02
C(5)[c]	0·001	0·004	H(6)	−0·01	0·02
C(6)[c]	0·004	0·002	H(1N)	−0·67	−0·73
N(1)	−0·038	−0·050	H(2N)	−0·16	−0·14
F, C(7)	−0·016	−0·034	H(3N)	0·70	0·71

(*a*) The e.s.d.'s in the atomic positions are 0·0017–0·0024 Å for the C, N and F atoms, 0·027–0·034 Å for the H atoms. (*b*) The e.s.d.'s in the atomic positions are 0·0016–0·0021 Å for the C and N atoms, 0·024–0·033 Å for the H atoms. (*c*) Atoms defining the least-squares plane.

The benzene rings

In both cations the symmetry of the benzene ring is essentially C_{2v} (*mm*) (Figs. 1, 2 and Table 5). Within each ring the difference between chemically equivalent bond lengths and angles is never $>3\sigma$, and only in two cases $>2\sigma$; the internal agreement is especially good for the *p*-fluoroanilinium cation. The deviations from planarity, although hardly significant, suggest a minor deformation of the rings towards the boat model (Table 5). The effect is consistent with the slight bending of the substituents, which are all on the same side of the ring plane.

The distortions of the benzene rings from D_{6h} (6/*mmm*) symmetry are highly significant; they involve bond distances as well as angles.

In both cations the C—C bonds stemming from the C atom *ipso* to the NH_3^+ substituent, C(1)—C(2) and C(1)—C(6), are consistently shorter than the central C—C bonds of the ring, C(2)—C(3) and C(5)—C(6). The difference is 0·009–0·011 Å, in agreement with the corresponding difference in *p*-phenylenediamine dihydrochloride, 0·008–0·009 Å (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977). This effect was not observed in *p*-aminobenzoic acid hydrochloride (Colapietro, Domenicano & Portalone, 1980).

In the cation of the *p*-fluoro derivative the C—C bonds stemming from the C atom *ipso* to the F substituent, C(3)—C(4) and C(4)—C(5), are 0·017–0·018 Å shorter than the central C—C bonds of the ring; the corresponding shortening in *p*-fluorobenzoic acid is 0·016–0·018 Å (Colapietro, Domenicano & Pela Ceccarini, 1979).

Table 6. *Internal angles (°) of the benzene ring: observed vs predicted values*

The e.s.d.'s of the observed values are all 0·2°.

	p-Fluoroaniline hydrochloride		*p*-Cyanoaniline hydrochloride	
	Observed	Predicted*	Observed	Predicted*
C(2)–C(1)–C(6)	121·8	121·4	122·5	121·7
C(1)–C(2)–C(3)	119·1	119·3	118·8	119·1
C(1)–C(6)–C(5)	119·2		118·7	
C(2)–C(3)–C(4)	118·5	118·4	119·7	119·6
C(4)–C(5)–C(6)	118·2		119·3	
C(3)–C(4)–C(5)	123·2	123·3	121·0	121·0

* From the empirical angular parameters of Domenicano & Murray-Rust (1979).

In the cation of the *p*-cyano derivative the possible effect of the CN substituent on the C(3)—C(4) and C(4)—C(5) lengths is masked by the slight, disturbing asymmetry of this part of the ring [Fig. 2(*a*)].

The internal angles of the benzene ring *ipso* to the substituents, $\alpha_{NH_3^+}$, α_F and α_{CN}, are all significantly > 120°, as expected with σ-electron-withdrawing functional groups (Domenicano, Vaciago & Coulson, 1975). Recently, a full set of empirical angular parameters have been derived by linear regression for a number of substituents, including NH_3^+, F and CN (Domenicano & Murray-Rust, 1979). These parameters may be used to predict molecular geometries, insofar as the effects of the substituents on the internal angles of the ring may be assumed as independent and superimposable. In Table 6 the experimental values of the ring bond angles in the title compounds are compared with the predicted values. The agreement is excellent in the part of the ring facing the F or CN substituents, while a small systematic deviation occurs in the opposite part of the ring.

The NH_3^+ *substituents*

In both compounds N(1) is significantly out of the least-squares plane of the benzene ring. The deviation is 0·038 in the *p*-fluoro compound and 0·050 Å in the *p*-cyano; these values correspond to an out-of-plane bending of the NH_3^+ substituent by 1·3 and 1·8°, respectively. In the second compound the NH_3^+ substituent is also slightly bent in the plane of the ring [by 0·5°, Fig. 2(*b*)]. The conformation of the NH_3^+ groups is such that one of the H atoms is almost eclipsed with the ring (Fig. 3 and Table 4). This conformation has been observed in several anilinium salts (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977, and references therein; Colapietro, Domenicano & Portalone, 1980) and is probably that preferred in the solid state.

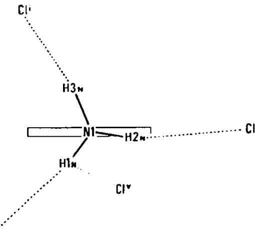

Fig. 3. Projection of the NH_3^+ group along the N(1)—C(1) bond in *p*-fluoroaniline and *p*-cyanoaniline hydrochlorides. The system of intermolecular hydrogen bonds is also shown. The superscripts refer to the symmetry operations given in the caption of Fig. 5.

The C(1)—N(1) lengths are 1·464 (2) and 1·467 (2) Å, in agreement with the lengths of the corresponding bonds in *p*-phenylenediamine dihydrochloride (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977) and *p*-aminobenzoic acid hydrochloride (Colapietro, Domenicano & Portalone, 1980), both equal to 1·463 (2) Å.

The F *substituent*

In *p*-fluoroaniline hydrochloride the F atom is out of the least-squares plane of the benzene ring by 0·016 Å, on the same side as N(1). The length of C(4)—F, 1·363 (3) Å, is essentially the same as in *p*-fluorobenzoic acid, 1·364 (3) Å (Colapietro, Domenicano & Pela Ceccarini, 1979). These bond lengths, however, are likely to be shortened to some extent by the effects of thermal motion. In both compounds the vibration of the F atom is in fact strongly anisotropic,* with the minor axis of the thermal ellipsoid almost exactly collinear with the C(4)—F bond.

The CN *substituent*

In *p*-cyanoaniline hydrochloride the CN group is bent out of the ring plane, again on the same side as the NH_3^+ group. C(7) and N(2) are out of the least-squares plane of the benzene ring by 0·034 and 0·068 Å, respectively, which corresponds to an out-of-plane bending by *ca* 1·3°. The group is also slightly bent in the plane of the ring [by 0·5°, Fig. 2(*b*)].

The geometry of the CN group obtained here is compared in Table 7 with those reported for other *para*-substituted derivatives of benzonitrile. The agreement is reasonably good, if the limited precision of some of the analyses is taken into account. It should be taken into account that CN groups bonded to aromatic

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* In *p*-fluoroaniline hydrochloride the principal axes of the thermal ellipsoid of the F atom are $B_1 = 2{\cdot}31$, $B_2 = 5{\cdot}95$, $B_3 = 10{\cdot}24$ Å^2. The corresponding figures for *p*-fluorobenzoic acid are 4·07, 8·51, and 11·21 Å^2.

Table 7. *Geometry of the* CN *group in para-substituted benzonitriles*

Bond lengths are given in Å, angles in degrees. E.s.d.'s are given in parentheses as units in the last digit. Only compounds with σ(C—C—N) < 1·0° have been included in this table.

Compound	Reference	C—C	C≡N	C—C—N
p-Hydroxybenzonitrile*	*a*	1·425 (4)	1·144 (5)	178·9 (4)
		1·430 (5)	1·142 (5)	178·0 (4)
p-Benzenedicarbonitrile*	*b*	1·438 (5)	1·147 (4)	179·3 (2)
	c	1·451 (7)	1·138 (7)	179·4 (7)
	d	1·445 (2)	1·146 (2)	179·5 (2)
p-Nitrobenzonitrile†	*e*	1·436 (12)	1·135 (15)	178·5 (9)
p-Fluorobenzonitrile	*f*	1·439 (2)	1·141 (2)	179·7 (2)
p-Chlorobenzonitrile*	*g*	1·447 (6)	1·110 (6)	179·3 (5)
5,11-(*p*-Cyanophenylimino)-5*H*,11*H*-dipyrido[2,3-*b*:2′,3′-*f*]-[1,5]dithiocin†	*h*	1·437 (10)	1·145 (11)	178·1 (7)
p-Aminobenzonitrile hydrochloride	*i*	1·445 (3)	1·144 (3)	178·5 (3)
Weighted mean values‡		1·441 (2) [1]	1·143 (2) [1]	—

References: (*a*) Higashi & Osaki (1977*a*). The asymmetric unit contains two crystallographically independent molecules. (*b*) van Rij & Britton (1977). (*c*) Drück & Littke (1978). (*d*) Colapietro, Domenicano & Portalone (to be published). (*e*) Higashi & Osaki (1977*b*). (*f*) Britton & Gleason (1977). (*g*) Britton, Konnert & Lam (1979). (*h*) Becher, Dreier & Simonsen (1979). (*i*) This work.

* The e.s.d.'s have been calculated from the e.s.d.'s of the atomic parameters quoted in the paper.

† The geometry has been calculated from the atomic parameters quoted in the paper.

‡ Mean values and their external ( ) and internal [ ] standard errors have been calculated as in part I of this series (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977).

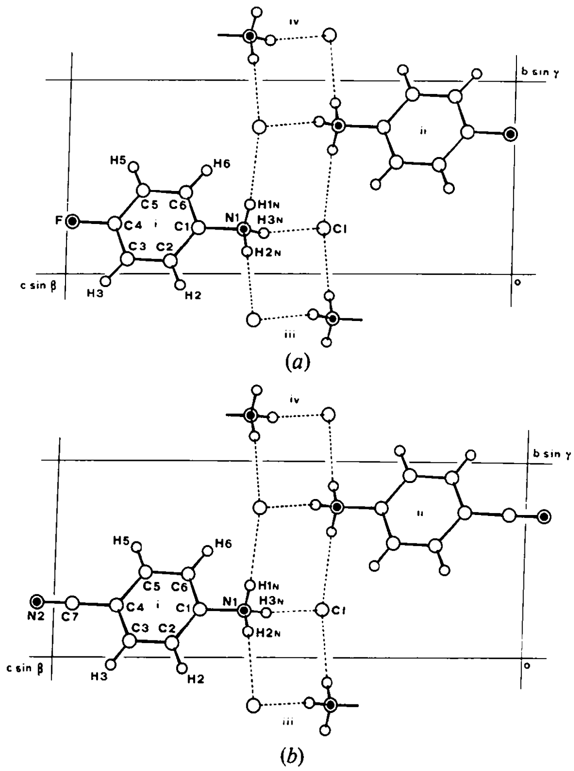

Fig. 4. Projection of the crystal structure down *a* in (*a*) *p*-fluoroaniline hydrochloride and (*b*) *p*-cyanoaniline hydrochloride. The symmetry codes are given in the caption of Fig. 5.

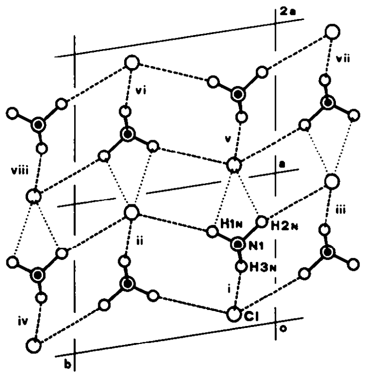

Fig. 5. The network of hydrogen bonds in *p*-fluoroaniline hydrochloride as projected on to the *ab* plane. The benzene rings have been omitted for clarity. The symmetry operations relating the various pairs of ions to pair (i) (which is at x, y, z) are: (ii) $1 - x$, $1 - y$, $1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $x, 1 + y, z$; (v) $1 + x, y, z$; (vi) $2 - x, 1 - y, 1 - z$; (vii) $2 - x, -y, 1 - z$; (viii) $1 + x, 1 + y, z$; (ix) $-1 + x, y, z$; (x) $-x, 1 - y, 1 - z$. The network of hydrogen bonds in *p*-cyanoaniline hydrochloride is essentially the same.

molecules are often affected by large thermal motions,* which may cause an apparent shortening of the C–C and C≡N bonds. Indeed, the mean values of the C–C and C≡N lengths of Table 7, 1·441 (2) and 1·143 (2) Å respectively, are significantly smaller than the values obtained by microwave spectroscopy for the corresponding bonds in benzonitrile, r_s = 1·4509 ± 0·0006 and 1·1581 ± 0·0002 Å respectively (Casado, Nygaard & Sørensen, 1971). The different physical meaning of the bond length obtained by the two techniques should also be considered, however.

The crystal structure

The crystals of *p*-fluoroaniline and *p*-cyanoaniline hydrochlorides are isostructural. The NH_3^+ groups and Cl^- ions are connected in ribbons through $Cl^- \cdots H$—N hydrogen bonds, 3·15–3·32 Å long, with $Cl^- \cdots H$ distances of 2·21–2·49 Å (Fig. 4). Adjacent ribbons are joined in layers through additional $Cl^- \cdots H$—N contacts, with $Cl^- \cdots H$ distances of 2·92–3·01 Å; the layers run parallel to *ab* (Fig. 5). The orientation of the $Cl^- \cdots H$—N contacts involving the NH_3^+ groups (Fig. 3) is the same as in *p*-phenylenediamine dihydrochloride (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977). The crystal structure of *p*-phenylenediamine dihydrochloride, although different from that of the present compounds, is based on the same two-dimensional network of hydrogen bonds (Figs. 6, 7). The repeat unit of the network is *ca* 4·3 × 5·9 Å in all cases.

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* In the present case the vibration of C(7) and N(2) is markedly anisotropic, with B_1 = 2·46 and 2·35, B_2 = 2·80 and 3·58, B_3 = 4·29 and 6·83 Å^2, respectively. The orientation of the thermal ellipsoids is the same as with the F atom of *p*-fluoroaniline hydrochloride.

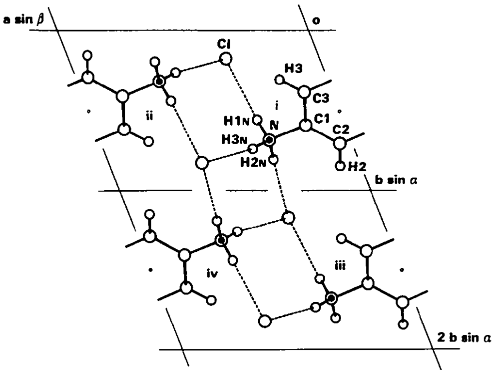

Fig. 6. *p*-Phenylenediamine dihydrochloride (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977): projection of the crystal structure down *c*. The symmetry codes are given in the caption of Fig. 7.

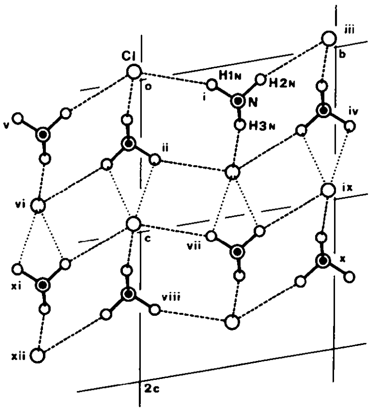

Fig. 7. *p*-Phenylenediamine dihydrochloride (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977): projection of the hydrogen-bond network on to the *bc* plane. The benzene rings have been omitted for clarity. The symmetry operations relating the various pairs of ions to pair (i) (which is at *x*, *y*, *z*) are: (ii) 1 − *x*, 1 − *y*, 1 − *z*; (iii) *x*, 1 + *y*, *z*; (iv) 1 − *x*, 2 − *y*, 1 − *z*; (v) *x*, −1 + *y*, *z*; (vi) 1 − *x*, −*y*, 1 − *z*; (vii) *x*, *y*, 1 + *z*; (viii) 1 − *x*, 1 − *y*, 2 − *z*; (ix) *x*, 1 + *y*, 1 + *z*; (x) 1 − *x*, 2 − *y*, 2 − *z*; (xi) *x*, −1 + *y*, 1 + *z*; (xii) 1 − *x*, −*y*, 2 − *z*.

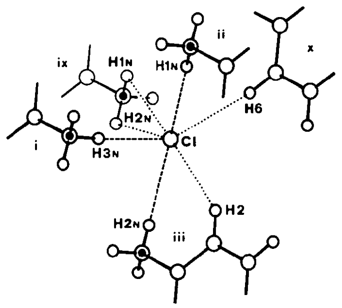

Fig. 8. Environment of the Cl$^-$ ion in *p*-fluoroaniline and *p*-cyanoaniline hydrochlorides. The broken lines represent intermolecular hydrogen bonds; the dotted lines other Cl$^-$···H contacts. The symmetry codes are given in the caption of Fig. 5.

Table 8. *Geometry of the* Cl$^-$···H–N *hydrogen bonds and other* Cl···H–*X contacts* (*X* = N, C)

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. 5.

	p-Fluoroaniline hydrochloride	*p*-Cyanoaniline hydrochloride
(*a*) Cl$^-$···*X* distances (Å)		
Cl···N(1^{ii})	3·213 (2)	3·228 (2)
Cl···N(1^{iii})	3·280 (2)	3·320 (2)
Cl···N(1^{i})	3·180 (2)	3·152 (2)
Cl···N(1^{ix})	3·318 (2)	3·279 (2)
Cl···C(2^{iii})	3·645 (2)	3·660 (2)
Cl···C(6^{x})	3·642 (2)	3·675 (2)
(*b*) Cl$^-$···H distances (Å)		
Cl···H(1N^{ii})	2·38 (3)	2·40 (3)
Cl···H(2N^{iii})	2·37 (3)	2·49 (4)
Cl···H(3N^{i})	2·31 (3)	2·21 (3)
Cl···H(1N^{ix})	3·01 (3)	2·97 (3)
Cl···H(2N^{ix})	2·94 (3)	2·92 (3)
Cl···H(2^{iii})	2·82 (3)	2·82 (3)
Cl···H(6^{x})	2·79 (3)	2·79 (3)
(*c*) Cl$^-$···H–*X* angles (°)		
Cl···H(1N^{ii})–N(1^{ii})	165 (3)	160 (3)
Cl···H(2N^{iii})–N(1^{iii})	167 (2)	168 (3)
Cl···H(3N^{i})–N(1^{i})	165 (2)	170 (2)
Cl···H(1N^{ix})–N(1^{ix})	104 (2)	104 (2)
Cl···H(2N^{ix})–N(1^{ix})	106 (2)	108 (2)
Cl···H(2^{iii})–C(2^{iii})	144 (2)	144 (2)
Cl···H(6^{x})–C(6^{x})	151 (2)	153 (2)

The environment of the Cl$^-$ ion in the *p*-fluoro and *p*-cyano compounds is shown in Fig. 8. The anion is involved in three hydrogen bonds with three NH_3^+ groups from adjacent cations, and is also approached by two H atoms of a fourth NH_3^+ group. The coordination sphere of Cl$^-$ is completed by two rather short contacts, 2·79–2·82 Å, with H atoms from the benzene rings of adjacent cations. Geometrical details of the hydrogen bonds and other Cl$^-$···H–*X* contacts (*X* = N, C) are given in Table 8.

The Cl$^-$ ion of *p*-phenylenediamine dihydrochloride has essentially the same environment. In this salt the two Cl$^-$···H–C contacts have Cl$^-$···H distances of 2·87 (3) and 2·74 (3) Å, and Cl$^-$···H–C angles of 140 (2) and 148 (2)°, respectively. Geometrical details of the Cl$^-$···H–N hydrogen bonds and contacts have been published (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977).

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Structure du Dihydro-10,11 5*H*-Dibenzo[*a*,*d*]cycloheptène. Support Tricyclique d'Analogues Structuraux des Antidépresseurs Imipraminiques

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Abstract

As part of an investigation of tricyclic compounds and related psychotropic molecules, the structure of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene ($C_{15}H_{14}$, $M_r = 194{\cdot}58$) is reported. This study was undertaken to analyse the modifications induced when the N atom of iminodibenzyl is replaced by a C atom. Crystals are monoclinic, $P2_1/c$, with $a = 11{\cdot}645$ (3), $b = 6{\cdot}436$ (2), $c = 17{\cdot}246$ (5) Å, $\beta = 122{\cdot}76$ (3)°, $V = 1087{\cdot}0$ Å^3, $Z = 4$, $D_c = 1{\cdot}18$, $D_m = 1{\cdot}19$ (2) Mg m^{-3}, $F(000) = 416$, $\mu(\text{Cu } K\alpha) = 0{\cdot}43$ mm^{-1}. The structure was determined by multisolution direct methods and refined by full-matrix least squares to an R of 0·044 for 820 independently measured reflexions. The dihedral angle between the two planes of the benzene rings is 123·1 (2)°.

Introduction

Depuis 1977 nous conduisons des recherches d'ordre cristallographique sur certaines structures tricycliques et sur les médicaments psychotropes qui en dérivent; à côté d'analyses paramétriques à visée pharmacochimique (Reboul & Cristau, 1977, 1978) nous avons récemment résolu la structure de l'iminodibenzyle (Reboul, Cristau, Estienne & Astier, 1980) et celle de l'iminostilbène (Reboul, Cristau, Soyfer & Estienne, 1980).

Dans le présent mémoire nous présentons la structure d'un composé apparenté, le dihydro-10,11 5*H*-dibenzo[*a*,*d*]cycloheptène (DDCH) dont un dérivé, l'amineptine (Tableau 1) est utilisé comme médicament antidépresseur.

Données expérimentales

Le DDCH, fourni par Aldrich–Europe, a été dissous dans l'éthanol absolu (10 g/50 ml). L'évaporation lente à 273 K a fourni des cristaux incolores sous forme de plaquettes.

La maille cristalline et le groupe d'espace ont été déterminés sur chambre de précession avec la radiation Cu $K\alpha$. Les paramètres cristallins ont été affinés sur

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