

Fig. 12. The same view as in Fig. 11, with perylene species III and IV and thf molecules shown instead of the PF_6^- anions. The centroids of some molecules are indicated.

I–II 3.38 (2) Å. The crystallographically independent overlap patterns within a stack are almost indistinguishable and differ only in the direction of the slips. The two extreme examples, overlaps I–II and I–I', are shown in Fig. 13 (deposited). As in the 6:1 and 3:1 salts there is no structural evidence concerning the localization of the positive charges. Intuition would suggest that the charges are distributed in the stacks, but there are some physical arguments against this idea.

Obviously the structure of the 6:1 salt is quite different from those of the 3:1 and 2:1 salts. The latter two have some features in common: stacks of perylene molecules flanked by other perylene species and by the anions. In the 3:1 salt the stacks are clearly tetrameric, with only a weak overlap between the tetramers. The stacks of the 2:1 salt bear some similarity to the tetrameric nature of the stacks of the 3:1 compound. However, as all the interplanar distances in the stacks are identical and the relative displacements of adjacent

molecules are very similar, the stacks are much more regular than in the 3:1 salt. These three compounds differ markedly from the previously reported (perylene)₂(PF₆)_{1.1}·0.8CH₂Cl₂ (Keller *et al.*, 1980). In this salt regular perylene stacks occur with the molecules inclined to the stacking axis, resulting in a herring-bone arrangement (Fig. 14, deposited), and there are no additional perylene species flanking the stacks.

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Structure Determination of *p*-Chloroaniline Hydrochloride, $\text{C}_6\text{H}_7\text{ClN}^+\cdot\text{Cl}^-$, and Redetermination of *p*-Chloroaniline, $\text{C}_6\text{H}_6\text{ClN}$

BY G. PLOUG-SØRENSEN AND E. KROGH ANDERSEN

Department of Chemistry, The University of Odense, Campusvej 55, DK-5230 Odense M, Denmark

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Abstract. *p*-Chloroaniline hydrochloride, $M_r = 164.1$, monoclinic, $P2_1/c$, $a = 8.728$ (1), $b = 9.649$ (1), $c = 9.823$ (1) Å, $\beta = 108.6$ (1)°, $V = 784.0$ (3) Å³, $Z = 4$,

$D_m = 1.390$ (1), $D_x = 1.389$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.74$ mm⁻¹, $F(000) = 336$, $T = 295$ K. $R = 0.04$ for 1959 unique observed reflexions. The

structure is held together by ionic bonds and by hydrogen bonds (average N...Cl⁻ distance is 3.136 Å). The benzene ring is planar; the nitrogen and chlorine atoms lie out of this plane on the same side. *p*-Chloroaniline (redetermination), $M_r = 127.6$, orthorhombic, *Pnma*, $a = 8.668$ (1), $b = 7.409$ (1), $c = 9.289$ (1) Å, $V = 596.4$ (2) Å³, $Z = 4$, $D_m = 1.421$ (1), $D_x = 1.420$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.52$ mm⁻¹, $F(000) = 264$, $T = 295$ K. $R = 0.03$ for 671 unique observed reflexions. The chloroaniline molecules are held together by van der Waals forces. The benzene ring is planar; the nitrogen and chlorine atoms lie out of this plane on the same side.

Introduction. The structure of *p*-chloroaniline was determined by Trotter, Whitlow & Zobel (1966) from visually measured film data. We have made a determination with diffractometer data. We wanted to have a determination of approximately the same accuracy as our determination of the structure of *p*-chloroaniline hydrochloride. The structure determinations were made in order to see the changes in the molecular structure of *p*-chloroaniline on protonation.

Experimental. *p*-Chloroaniline was recrystallized from toluene. Colourless needles cut to 0.25 × 0.21 × 0.20 mm, Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized, pulse-height discriminated Mo $K\alpha$, lattice parameters from Guinier-Hägg photographs with Cu $K\alpha_1$ ($\lambda = 1.54051$ Å) and quartz as internal standard, 918 unique reflexions ($0 \leq h \leq 12$, $0 \leq k \leq 10$, $0 \leq l \leq 13$) with $2.5 < \theta < 30^\circ$, 671 with $I > 2.5\sigma(I)$, mixed $\omega/2\theta$ scan, standard reflexion 422 (max. correction for decrease 8%), systematic absences $0kl$ with $k+l$ odd, $hk0$ with h odd, Lp correction, absorption ignored; direct methods [independent of previous determination (Trotter *et al.*, 1966), *N.B.* to compare the two determinations **b** and **c** should be interchanged], full-matrix least-squares refinement, non-H anisotropic, H (starting positions from difference maps) fixed thermal parameters, $\sum w|F|^2$ minimized, all parameters refined except temperature factors for H, total: 52, final $R = 0.03$, $wR = 0.04$; weights $w = 1/(3.20 + |F_o| + 0.0047|F_o|^2)$ gave average $w\Delta(|F|^2)$ independent of $\sin\theta$ and $|F_o|$; $(\Delta/\sigma)_{\max}$ for N, Cl and O 0.03, for H 0.3; max. height in final difference Fourier map in locations outside atom positions was low. Scattering factors from *International Tables for X-ray Crystallography* (1962), computer programs from *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

The experimental conditions for *p*-chloroaniline hydrochloride were as above except: Crystals were obtained by adding concentrated hydrochloric acid to a solution of *p*-chloroaniline in ether. This product was

Table 1. *p*-Chloroaniline: final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å²) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j b_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cl	5257 (1)	2500	7032 (1)	3.55 (4)
C(1)	1206 (3)	2500	3959 (2)	3.20 (15)
C(2)	1836 (2)	882 (2)	4445 (2)	3.30 (11)
C(3)	3075 (2)	875 (2)	5396 (2)	3.10 (10)
C(4)	3678 (2)	2500	5858 (2)	2.74 (13)
N	-9 (3)	2500	2989 (3)	5.18 (23)

Table 2. *p*-Chloroaniline hydrochloride: final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å²) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j b_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cl(1)	933 (1)	1118 (1)	3345 (1)	3.64 (3)
C(1)	7848 (2)	2614 (2)	4952 (2)	3.23 (11)
C(2)	6448 (3)	2042 (2)	5058 (3)	4.13 (14)
C(3)	4982 (3)	2670 (2)	4350 (3)	4.47 (16)
C(4)	4960 (3)	3860 (2)	3564 (2)	3.88 (14)
C(5)	6363 (3)	4435 (3)	3465 (3)	4.42 (16)
C(6)	7826 (3)	3801 (2)	4165 (3)	4.15 (15)
Cl	3115 (1)	4655 (1)	2696 (1)	5.58 (5)
N	9403 (2)	1964 (2)	5710 (2)	3.56 (11)

recrystallized from a mixture of ethanol and concentrated hydrochloric acid. The recrystallized product was dried over phosphorus pentoxide. The formula weight was determined to 167 (theoretical value 164) by titration with 0.1M sodium hydroxide. Colourless crystals cut to 0.46 × 0.43 × 0.26 mm, 2376 unique reflexions ($-12 \leq h \leq 12$, $0 \leq k \leq 13$, $0 \leq l \leq 13$) with $2.5 \leq \theta \leq 30^\circ$, 1959 with $I \geq 2.5\sigma(I)$, standard reflexion $\bar{4}15$ (max. correction for decrease 7%), systematic absences $h0l$ with l odd, $0k0$ with k odd; all parameters refined except temperature factors for H, total: 103, final $R = 0.042$, $wR = 0.058$, $w = 1/(2.40 + |F_o| + 0.0097|F_o|^2)$, $(\Delta/\sigma)_{\max} 0.013$.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Tables 1 and 2.*

The crystal structure of *p*-chloroaniline was adequately described by Trotter *et al.* (1966). They obtained a standard deviation of 0.02 Å on bond lengths and 1.4° on angles. Within these limits their structure determination does not deviate significantly from ours.

* Lists of structure factors, anisotropic temperature parameters, H-atom parameters and deviations of atoms from least-squares planes through the carbon rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39925 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

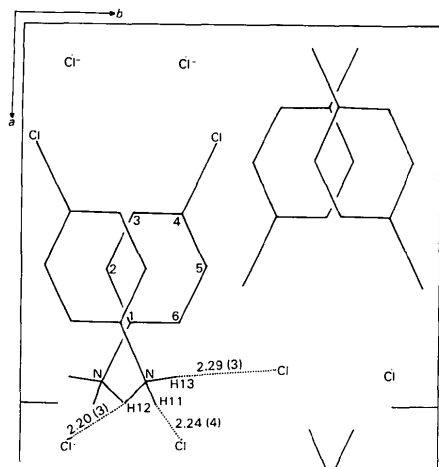


Fig. 1. The structure of *p*-chloroaniline hydrochloride viewed down the *c* axis; contact distances are in Å (e.s.d.'s in parentheses).

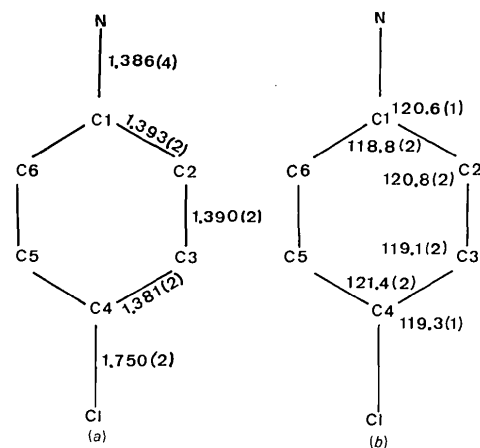


Fig. 2. The molecular structure of *p*-chloroaniline. (a) Bond lengths in Å. (b) Angles in degrees. (Values in parentheses are standard deviations.)

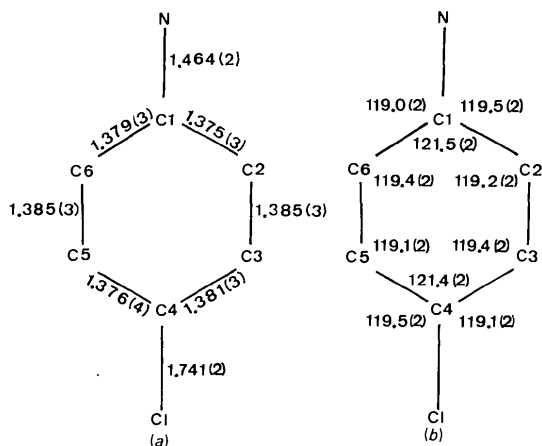


Fig. 3. The molecular structure of the *p*-chloroanilinium ion. (a) Bond lengths in Å. (b) Angles in degrees. (Values in parentheses are standard deviations.)

Table 3. Carbon–nitrogen bond lengths, and lengths of carbon–carbon bonds adjacent to amine and aminium groups (in Å) and the angle between them (in degrees) (e.s.d.'s in parentheses)

	<i>p</i> -Nitro- aniline (Trueblood, Donohue, 1961)	<i>p</i> -Chloro- aniline (this deter- mination)	<i>p</i> -Nitro- anilinium ion (Ploug- Sørensen & Andersen, 1982)	<i>p</i> -Chloro- anilinium ion (this determina- tion)
C–N	1.371 (7)	1.386 (4)	1.472 (5)	1.464 (2)
C(1)–C(2)	1.408 (6)	1.393 (2)	1.379 (6)	1.375 (3)
C(6)–C(1)	1.415 (7)	1.393 (2)	1.379 (5)	1.379 (3)
C(6)–C(1)–C(2)	118.9 (4)	118.8 (2)	121.9 (4)	121.5 (2)

The crystal structure of *p*-chloroaniline hydrochloride is shown in Fig. 1. The structure is composed of puckered layers of *p*-chloroanilinium ions held together by ionic forces and by hydrogen bonds to the chloride ions. The NH_3^+ group acts as donor in hydrogen bonds to three chloride ions (average $\text{N}\cdots\text{Cl}^-$ distance 3.136 Å).

Details of the molecular structures of *p*-chloroaniline and of the *p*-chloroanilinium ion are given in Fig. 2(a and b) and in Fig. 3(a and b). The carbon rings are planar*. The nitrogen and chlorine atoms in both molecules lie out of the ring planes on the same side by *ca* 0.02 Å (more in the case of the *p*-chloroaniline molecule and slightly less in the other molecule). The change in structure on protonation of amines obviously involves the bond between the nitrogen atom of the amino group and the carbon atom to which it is attached. This is clearly borne out by Figs. 2(a) and 3(a). There is a lengthening of this bond of about 0.1 Å when anilines are protonated. Further changes are shown in Table 3. It may be seen in this table that the carbon bonds adjacent to the amine groups shrink about 0.02 Å and that the C(6)–C(1)–C(2) angle opens about 2° on protonation. This holds for *p*-nitroaniline also.

* See deposition footnote.

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