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Zigzag hydrogen-bonded sheets in the structure of *p*-phenylazoaniline hydrochloride

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The structure of *p*-phenylazoanilinium chloride, $C_{12}H_{12}N_3^+\cdot Cl^-$, consists of sheets each comprising organic cations and chloride anions linked by N—H···Cl and C—H···Cl hydrogen bonds. The *p*-phenylazoaniline molecule is protonated at the azo site to form the azonium cation, while the amine group remains unchanged. The structure of the title compound has also been determined recently from powder diffraction data [Yatsenko *et al.* (2000). *Acta Cryst.* C**56**, 892–894].

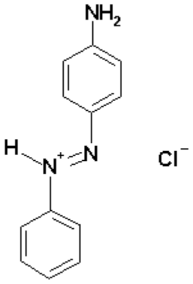
Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.003 Å
R factor = 0.052
wR factor = 0.150
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Azo compounds have not only been used in many chemical syntheses but they also constitute an important class of organic dyes with a wide range of industrial applications. Yatsenko *et al.* (2000) have recently reported the crystal structure of the title compound, (I), from powder diffraction data, where a constrained model of the organic cation and an isotropic refinement of non-H atoms, except for the chloride ion, were applied during structure refinement. Here we present a redetermination of this structure using single-crystal data from a Siemens SMART CCD diffractometer.



(I)

The crystal structure of (I) is shown in Fig. 1 and selected geometrical parameters are given in Table 1. The N═N bond distance of 1.291 (3) Å is significantly larger than the corresponding distances of 1.2493 (13) Å for *p*-phenylazoanilinium oxalate, and 1.246 (5) and 1.243 (5) Å for *p*-phenylazoanilinium phenylphosphonate (Mahmoudkhani & Langer, 2001*a*,*b*). In these compounds, the amine groups are protonated rather than the azo group. Furthermore, there is a shortening of the N2—C14 and N1—C11 bonds to 1.344 (3) and 1.324 (3) Å, respectively, compared to the C—N(H_3) distances of 1.4637 (12) and 1.458 (5) Å, and the (N═)N—C distances of 1.4303 (14) and 1.427 (6) Å in the above-mentioned compounds. These differences can be attributed to a resonance hybrid of the organic cation, as shown in Scheme

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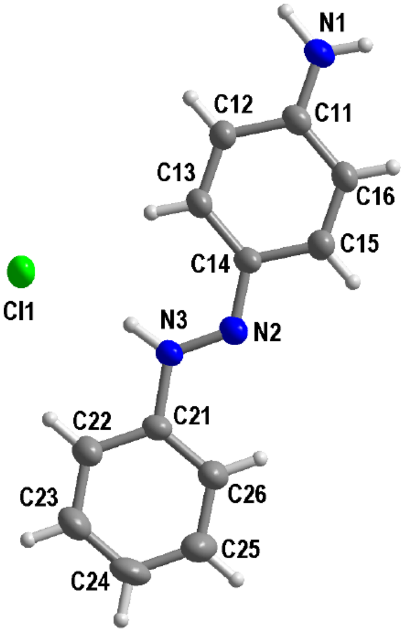
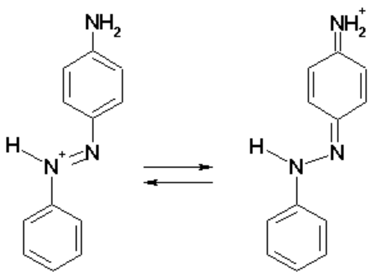


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

2. The same feature has been reported by Moreiras *et al.* (1981). The structure exhibits both N—H···Cl and C—H···Cl hydrogen bonds. As shown in Fig. 2 (top), each organic cation is bonded to the chloride anions through hydrogen bonds *via* C13, C22 and N3. Each ion pair is then linked to another pair through the N1—H2···Cl hydrogen bond, thus forming a dimer. The dimers are connected to each other, in a zigzag fashion, *via* N1—H1···Cl hydrogen bonds to form sheets [see Fig. 2 (bottom)]. The sheets are stacked along the *a* axis (see Fig. 3), with chloride ions sandwiched between organic cations. The existence of C—H···Cl hydrogen bonds has recently been reviewed by Aakeröy *et al.* (1999), though they have not been invoked by Yatsenko *et al.* (2000).



Scheme 2

Experimental

The title compound was prepared by the reaction of a solution of *p*-phenylazoaniline in ethanol and HCl solution (37% in water) in a molar ratio of 1:1.5, at ambient temperature. Crystals suitable for X-ray diffraction analysis were obtained by very slow evaporation of the solution after several days.

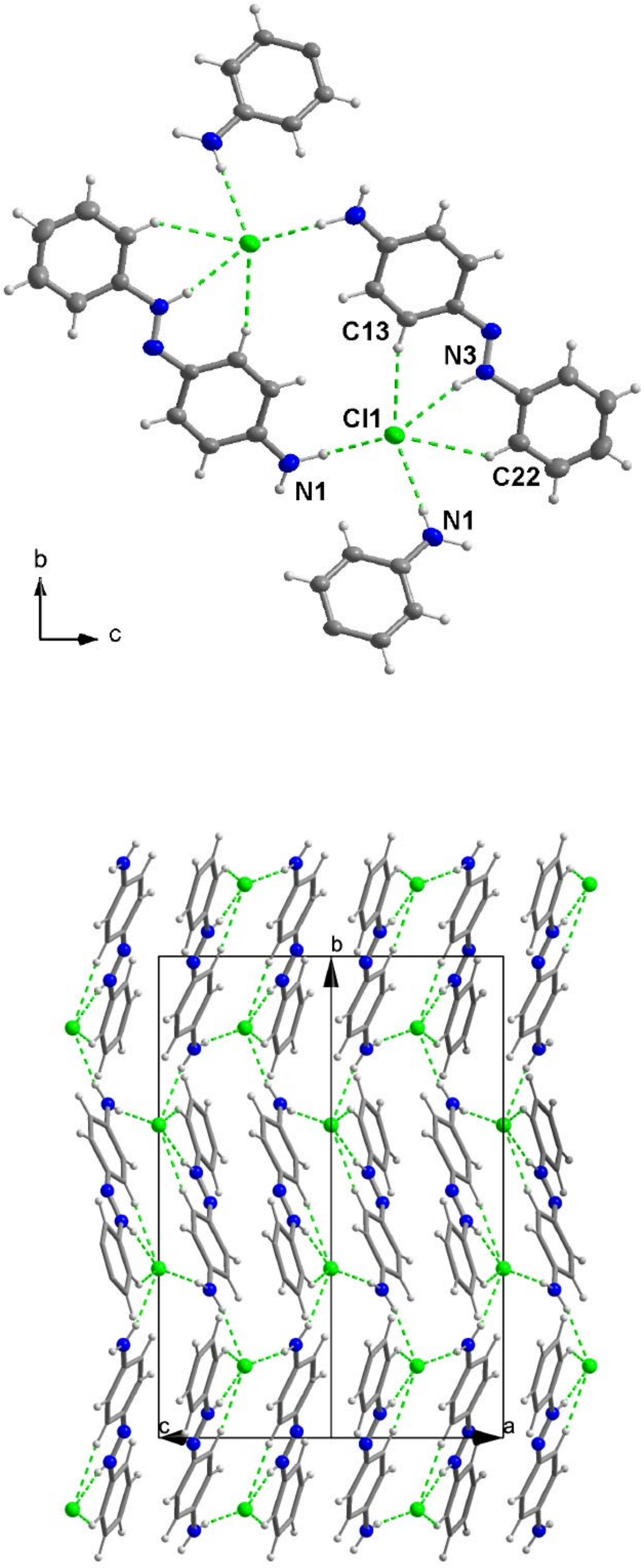


Figure 2
Top: formation of a dimer by hydrogen bonds in the structure of (I). Bottom: representation of a hydrogen-bonded sheet.

Crystal data

$C_{12}H_{12}N_3^{+}\cdot Cl^{-}$
$M_r = 233.70$
Monoclinic, $P2_1/c$
$a = 7.3718\ (3)$ Å
$b = 18.5164\ (7)$ Å
$c = 8.9123\ (1)$ Å
$\beta = 111.913\ (1)^\circ$
$V = 1128.63\ (6)$ Å^3
$Z = 4$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2394 reflections
$\theta = 1–25^\circ$
$\mu = 0.31$ mm^{-1}
$T = 297\ (2)$ K
Needle, dark-red
$0.60 \times 0.20 \times 0.20$ mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.835$, $T_{max} = 0.940$
3608 measured reflections
1982 independent reflections
1476 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 25.4^\circ$
$h = -8 \rightarrow 8$
$k = -22 \rightarrow 10$
$l = -10 \rightarrow 8$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.150$
$S = 1.05$
1982 reflections
166 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2 + 0.0439P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C11	1.324 (3)	N2—C14	1.344 (3)
N2—N3	1.291 (3)	N3—C21	1.418 (3)
N3—N2—C14	121.29 (19)	N2—N3—C21	118.97 (19)
N3—N2—C14—C13	−0.2 (4)	C21—N3—N2—C14	−178.7 (2)
N2—N3—C21—C26	−8.2 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl^{i}	0.876 (17)	2.405 (18)	3.273 (2)	171 (2)
N1—H2···Cl^{ii}	0.878 (17)	2.379 (19)	3.227 (2)	162 (2)
N3—H3···Cl	0.879 (16)	2.330 (17)	3.200 (2)	170 (2)
C13—H13···Cl	0.93	2.70	3.609 (2)	166
C22—H22···Cl	0.93	2.84	3.617 (3)	142

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, 1-y, -z$.

The H atoms of the amine and azonium groups were located from difference Fourier maps and refined with a bond distance constrained to 0.85 Å. The other H atoms were restrained to idealized geometries using the appropriate riding model.

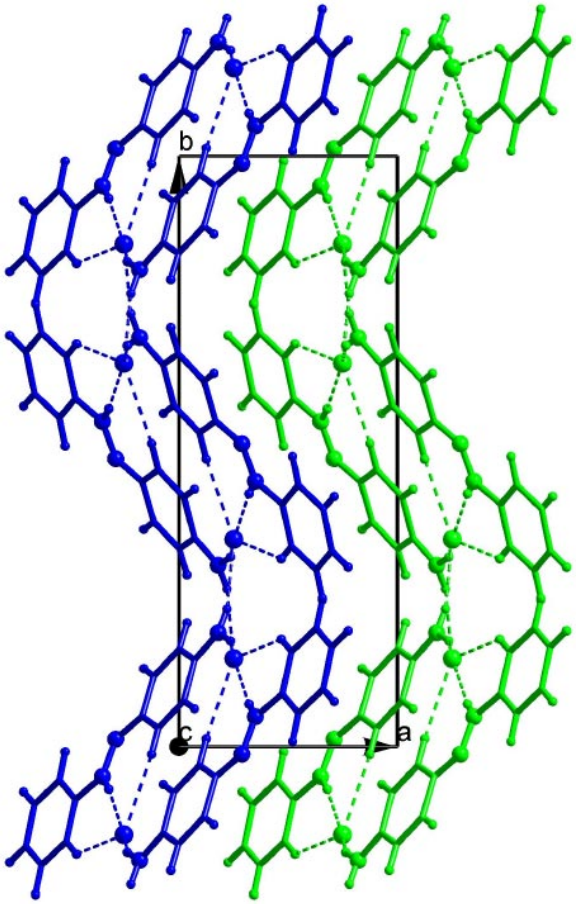


Figure 3
Zigzag stacking of hydrogen-bonded sheets, shown by different colors.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000).

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