

p-Phenylazoaniline hydrochloride from powder data: protonation site and UV–visible spectra

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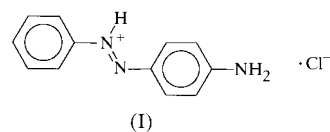
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The crystal structure of the title compound, (4-amino-phenyl)phenyldiazonium chloride, $C_{12}H_{12}N_3^+ \cdot Cl^-$, was determined from X-ray laboratory powder data, and the protonation on the azo group was confirmed by the neutron powder data. The cations form stacks along [100], while the

chloride anions form hydrogen bonds to all three H atoms attached to N atoms. The absorption maximum of the crystalline salt is shifted bathochromically by 850 cm^{-1} , compared with that in ethanol solution.

Comment

Aromatic azo compounds containing the amino group may be protonated either on the amino group or on the azo group to give a tautomeric mixture (Cox & Buncel, 1975). In polar solvents capable of effective hydrogen-bond formation, the equilibrium is shifted towards the ammonium form, whereas in solvents of lower polarity the azonium form prevails. This is due to the dipole moment of the ammonium cation being more than twice as large as that of the azonium cation (Liwo *et al.*, 1994). The UV–visible spectra of solutions contain two



peaks centered at 325 and 500 nm, attributable to the ammonium and azonium forms, respectively (Kuroda *et al.*, 1980). Surprisingly, in the solid state most of these salts exist in the azonium form, although ordinarily the tautomeric equilibria are shifted in the same way as in extremely polar solvents.

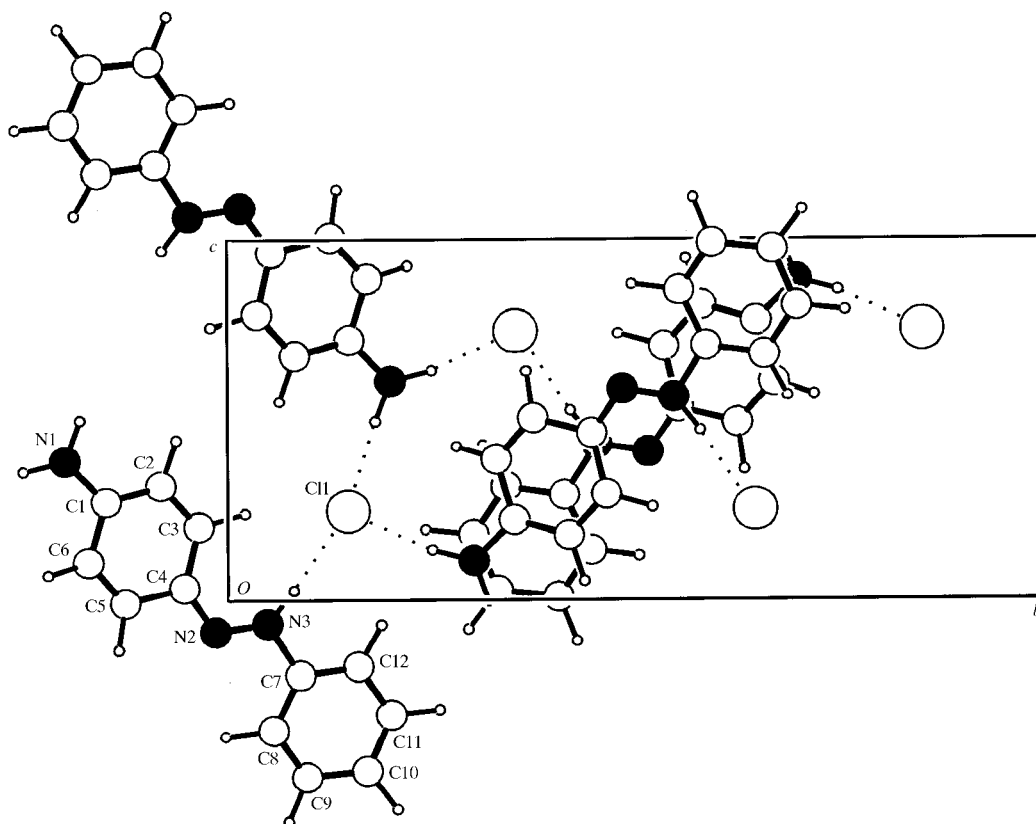


Figure 1

The packing diagram for (I) showing the atom-numbering scheme (ellipsoids and spheres represent the 50% probability level).

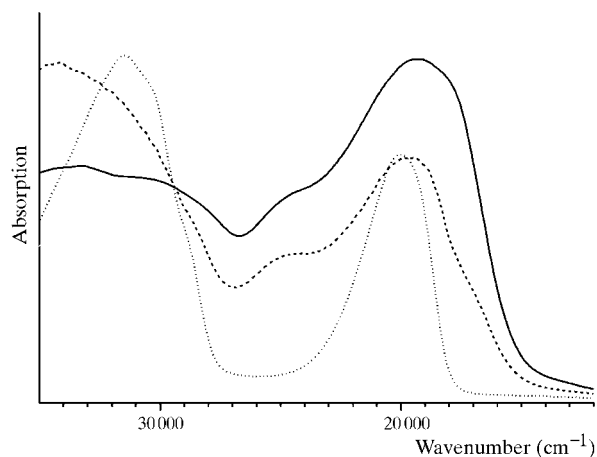


Figure 2
UV-visible spectra of (I): ethanol solution (dotted line), solid ground with BaSO₄ without (dashed line) and with (solid line) 1 M HCl.

The cation of the title compound, (I), is close to planar; the two phenyl rings form a 9.8 (5)^o dihedral angle. Large s.u.'s for bond lengths and angles preclude their comparison to 2,4-diaminoazobenzene hydrochloride (Moreiras *et al.*, 1981). The crystal packing is illustrated in Fig. 1; the dotted lines represent the hydrogen bonds (Table 1). The neighboring molecules within the stack are related by inversion centers, with interplanar distances of 3.34 (1) and 3.48 (1) Å. The bond-restrained Rietveld refinement of (I) on neutron diffraction data led to $R_B = 0.14$ and 0.18 for azonium and ammonium cations, respectively.

The UV-visible absorption spectrum of the ethanol solution of (I) and the reflection spectra of solid samples prepared by grinding (I) with BaSO₄ are presented in Fig. 2. When a dry sample is ground, the reflection spectrum exhibits the same intensity ratio of the long-wavelength (azonium) and short-wavelength (ammonium) absorption maxima as in the solution; thus, the azonium form prevails in this specimen. However, if a sample is ground in the presence of 1 M HCl, the intensity of the azonium band increases and the ammonium

maximum becomes diffuse and indistinct indicating that the tautomeric shift towards the azonium form occurs. This finding is in line with the well known fact that the salts of many *p*-aminoazo compounds can be prepared as the metastable yellow phases, which rapidly undergo transformation into the dark-red crystalline form (Bershtein & Ginzburg, 1972). In the presence of HCl solution, the recrystallization of dispersed (I) can occur, and a stable crystalline azonium form results from the amorphous ammonium form. There are two very probable reasons why the crystal packing stabilizes the azonium form. First, the azonium cations allow a more uniform distribution of chloride anions in the unit cell, and the closest Cl^{••}·Cl contacts in (I) are 5.865 (6) Å, whereas in the structures of chlorides of simple aniline derivatives all the anions are localized in the vicinity of NH₃⁺ groups, and multiple Cl^{••}·Cl contacts shorter than 5.2 Å are present (Colapietro *et al.*, 1981; Ploug-Soerensen & Andersen, 1985; Linden *et al.*, 1995). Second, the charge in the azonium cation is delocalized over the azo group and the amino-substituted ring, and such delocalization can be stabilized by the intermolecular π - π interactions within the stacks, whereas in the ammonium form the charge is localized on the NH₃⁺ group.

The main maximum at 19160 cm⁻¹ in the reflection spectrum has a shoulder at 24200 cm⁻¹, which can be attributed to Davydov splitting. When transferring from the solution to the solid state, the azonium and ammonium bands demonstrate opposite wavelength shifts, *i.e.* bathochromic and hypsochromic, respectively. In solutions, both bands demonstrate blue shifts when the polarity of the solvent increases; thus, the red shift of the azonium band can be attributed only to the splitting of the energy levels of cations in the zones due to the π - π interactions within the stacks.

Experimental

The title compound was prepared dissolving *p*-phenylazoaniline (Solvent Yellow 1) in hot 1 M HCl. The UV-visible spectra (absorption and reflection) were recorded on a Specord M-40 spectrophotometer (Carl Zeiss, Jena).

Crystal data

C₁₂H₁₂N₃⁺·Cl⁻
 $M_r = 233.70$
 Monoclinic, $P2_1/c$
 $a = 7.400$ (3) Å
 $b = 18.511$ (5) Å
 $c = 8.920$ (3) Å
 $\beta = 111.91$ (2)^o
 $V = 1133.7$ (9) Å³
 $Z = 4$

$D_x = 1.369$ Mg m⁻³
 Cu $K\alpha$ radiation
 $\mu = 2.768$ mm⁻¹
 $T = 295$ (2) K
 Specimen shape: flat sheet
 25.0 × 25.0 × 1.5 mm
 Particle morphology: plate
 Black

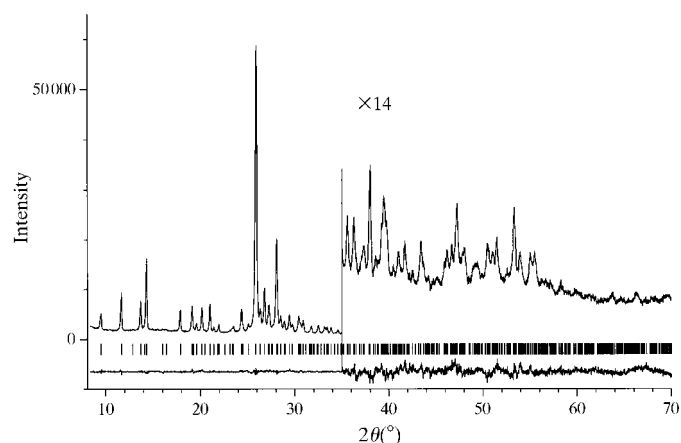


Figure 3
The Rietveld plot for (I) showing the observed and difference profiles. The reflection positions are shown above the difference profile.

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H14 ⁱ ···Cl1 ⁱ	1.03	2.17	3.18 (2)	166
N1—H15 ⁱⁱ ···Cl1 ⁱⁱ	1.03	2.29	3.27 (2)	158
N3—H13 ⁱⁱⁱ ···Cl1 ⁱⁱⁱ	1.03	2.27	3.27 (2)	163

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Data collection

DRON-3M (Burevestnik, Russia)	465 measured reflections
horizontal diffractometer	465 independent reflections
Specimen mounting: pressed in the specimen holder	$h = 0 \rightarrow 5$
Specimen mounted in reflection mode	$k = 0 \rightarrow 13$
	$l = -5 \rightarrow 5$
$T = 295$ (2) K	$2\theta_{\min} = 6.00$, $2\theta_{\max} = 70.00^\circ$
	Increment in $2\theta = 0.02^\circ$

Refinement

Refinement on I_{net}	109 parameters
$R_p = 0.030$	H-atom parameters not refined
$R_{\text{wp}} = 0.040$	Weighting scheme based on
$R_{\text{exp}} = 0.023$	measured s.u.'s
$S = 1.75$	$(\Delta/\sigma)_{\max} = 0.06$
$2\theta_{\min} = 8.40$, $2\theta_{\max} = 70.00^\circ$	$\Delta\rho_{\max} = 0.8 \text{ e } \text{\AA}^{-3}$
Increment in $2\theta = 0.02^\circ$	$\Delta\rho_{\min} = -1.2 \text{ e } \text{\AA}^{-3}$
Excluded region(s): 6.00–8.38	Preferred orientation correction:
Profile function: split-type pseudo-Voigt	March–Dollase (Dollase, 1986)
	along [100], $G_1 = 0.7759$ (6)

The monoclinic cell dimensions were determined with *TREOR90* (Werner *et al.*, 1985) and refined to $M_{20} = 31$ and $F_{30} = 69$ (0.009, 45) using the first 60 peaks from the X-ray pattern. Because of reflections overlapping, the space groups $P2_1/n$ and $P2_1/c$ were indistinguishable on the basis of systematic extinctions, and the final choice was made at the stage of structure determination. The neutron-diffraction experiment was carried out at the high-resolution multi-counter powder diffractometer G4.2 situated at the Orphee reactor of the Léon Brillouin Laboratory. The position and orientation of the cation was determined with the grid-search procedure (Chernyshev & Schenk, 1998) on neutron data and the initial molecular model was built with *MOPAC7* (Stewart, 1993). The position of the Cl atom was determined by grid search on the X-ray data, with fixed position and orientation of the cation. Because of high background, the signal-to-noise ratio in the neutron diffraction pattern was significantly worse than that obtained in the X-ray experiment, thus the details of refinement on the neutron data are not discussed here. The X-ray diffraction profile and the difference between the measured and calculated profiles after the Rietveld refinement are shown in Fig. 3, final $R_B = 0.068$. The Cl atom was refined anisotropically, the C and N atoms isotropically, and the planarity of the phenyl rings was constrained. H atoms were placed in geometrically calculated positions, with a common isotropic displacement parameter U_{iso} fixed at

0.076 \AA^2 . The anisotropy of diffraction-line broadening was approximated by a quartic form in hkl (Popa, 1998). The final $(\Delta/\sigma)_{\max}$ value is relatively high due to a correlation between the line-broadening parameters, whereas for the atomic positional parameters these values do not exceed 0.01.

Data collection: local program; cell refinement: *LSPAID* (Visser, 1986); program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *PLUTON* (Spek, 1992); software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1286). Services for accessing these data are described at the back of the journal.

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