

4-(Phenyldiazenyl)naphthalen-1-amine and its hydrochloride

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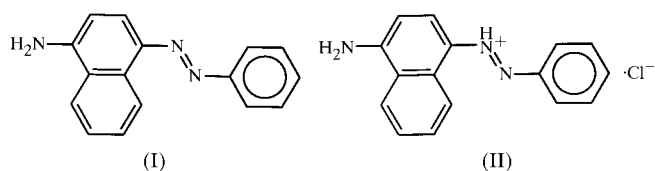
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The crystal structures of 4-(phenyldiazenyl)naphthalen-1-amine, C₁₆H₁₃N₃, (I), and its hydrochloride, (4-aminonaphthalen-1-yl)phenyldiazonium chloride, C₁₆H₁₄N₃⁺·Cl⁻, (II), have been determined from X-ray single-crystal and powder data, respectively. The effect of the crystal environment on the molecular electronic structure was analysed on the AM1 level. One of the two symmetry-independent molecules in (I) is involved in intermolecular hydrogen bonding, so that its dipole moment is twice as large as that of the other molecule. The cations in (II) form stacks along [100], with the Cl⁻ anions forming hydrogen bonds to all three H atoms attached to N atoms.

Comment

Azo derivatives of α -naphthylamine form a family of widely used dyes. However, the structure of only one representative of this family has been determined up to now (Foitzik *et al.*, 1991). Solvent Yellow 4, (I), is the simplest molecule of this class. We present here the single-crystal X-ray structure determination of (I) and the powder structure determination of the hydrochloride, (II).



In the crystal, the two independent molecules of (I) form pairs, as shown in Fig. 1. Both molecules are close to being planar, the dihedral angles formed by the least-squares planes through the naphthalene and phenyl moieties being 5.19 (6) and 2.12 (5)° in molecules (Ia) and (Ib), respectively. The C1–N1 and C21–N4 bond lengths fall in between the values for planar and pyramidal amino groups (Yatsenko & Paseshnichenko, 1999). The shortest intermolecular distance within a pair (C12···C31) is 3.392 (3) Å, and the dihedral angle between the least-squares planes of (Ia) and (Ib) is 3.31 (3)°.

The molecular pairs in (I) are packed in a herring-bone manner into layers perpendicular to [100]. In addition, molecules of (Ia) are linked by weak N1–H10···N3ⁱ hydrogen bonds: N1···N3ⁱ 3.188 (3) Å and N1–H10···N3ⁱ 166 (2)° [symmetry code: (i) $\frac{1}{2} - x, -y, z - \frac{1}{2}$]. The polarization of molecule (Ia) under the effect of this bond does not cause any noticeable difference in bond lengths in the amino–azo chains of (Ia) and (Ib) (Table 1). However, the AM1 calculations, in which the polarization effect of the surrounding molecules in the crystal was modelled *via* the incorporation of an electrostatic field into the Hamiltonian of a molecule, indicate the pronounced non-equivalence of (Ia) and (Ib); their calculated dipole moments were 6.09 and 2.95 D, respectively, whereas for an isolated molecule of (I) the calculations yield 2.69 D. It is noteworthy that the polarization effect of the crystal environment on the electronic structure of (Ia) is stronger than the possible effect of polar solvent modelled with COSMO (Klamt & Schüürmann, 1993); the calculated dipole moment of a molecule of (I) placed into a medium with a dielectric constant of 81 is 5.10 D.

The crystal-packing motif adopted by (II) is presented in Fig. 2, with the dotted lines representing the hydrogen bonds (Table 2). The cation is close to being planar; the phenyl ring is twisted by 4.4 (2)° with respect to the naphthalene residue. Neighbouring cations within the stack are related by inversion centres, with interplanar distances of 3.42 (1) and 3.48 (1) Å. The very close packing motif – columns of inversion-related cations with the Cl⁻ anions in the intercolumnar channels – has been observed in the structure of *p*-phenylazoaniline hydrochloride (Yatsenko *et al.*, 2000), and in the structure of 2,4-diaminoazobenzene hydrochloride dihydrate (Moreiras *et al.*, 1981), the cations also form stacks, although they are not parallel. The cation–anion and cation–cation interactions facilitate charge transfer from the amino group to the azonium linkage; according to the AM1 calculations, the total effective charges on the amino group in an isolated cation and in the

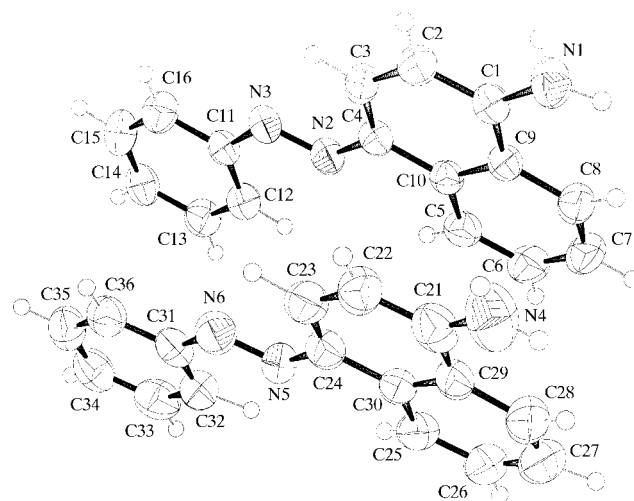


Figure 1

The two independent molecules of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii. Atoms N1–C16 belong to molecule (Ia) and the remainder to molecule (Ib).

cation in the crystal environment are +0.24 and +0.39 e, respectively, and the effective charges on the azonium linkage are +0.27 and +0.19 e, respectively.

The first π - π^* -excitation of (I) and (II) is almost pure HOMO \rightarrow LUMO (highest occupied molecular orbital \rightarrow lowest unoccupied molecular orbital) one-electron excitation. Thus, in order to study the properties of the frontier orbitals, we modelled the effect of the crystal environment on the HOMO-LUMO energy gap. For (II), the gap extends from 5.95 eV for an isolated cation to 6.33 eV for a cation in the crystal lattice, whereas in (I), the two non-equivalent molecules behave in different ways: in (Ia), this gap decreases from 7.10 to 6.79 eV, and in (Ib), it remains essentially unchanged (7.16 and 7.14 eV, respectively). In line with these calculations, (I) and (II) demonstrate red and blue shifts, respectively, on transfer from alcohol solution to the solid state, *i.e.* from 22 800 cm^{-1} to 21 350 cm^{-1} for (I), and from 18 850 cm^{-1} to 19 400 cm^{-1} for (II).

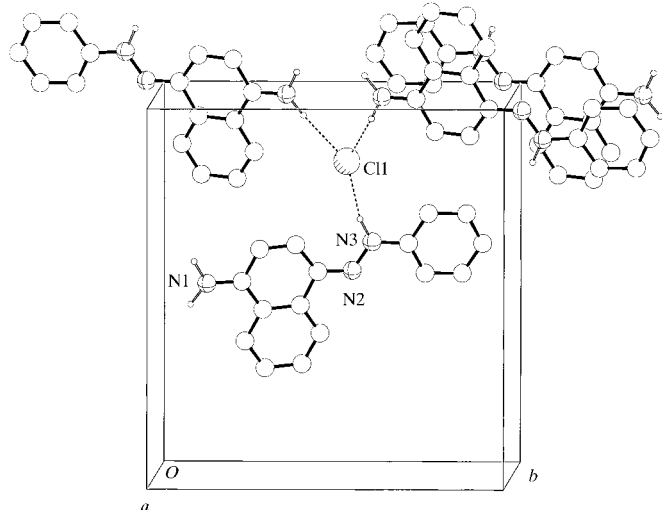


Figure 2
The packing diagram of (II) viewed along *c*. The atom-numbering scheme is the same as for (Ia). Dashed lines indicate hydrogen bonds.

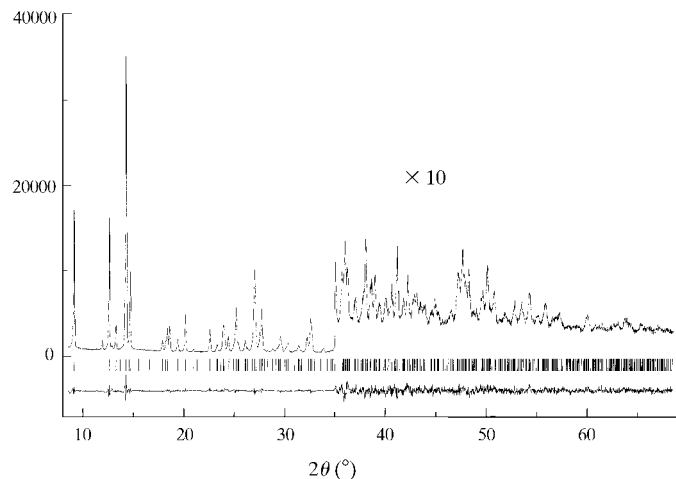


Figure 3
The Rietveld plot for (II) showing the observed and difference profiles. The reflection positions are shown above the difference profile.

Table 1
Selected geometric parameters (Å) for (I).

N1—C1	1.368 (2)	N4—C21	1.362 (3)
C1—C2	1.381 (3)	C21—C22	1.369 (3)
C2—C3	1.383 (3)	C22—C23	1.384 (3)
C3—C4	1.376 (2)	C23—C24	1.386 (3)
C4—N2	1.400 (2)	C24—N5	1.412 (3)
N2—N3	1.270 (2)	N5—N6	1.262 (2)

Experimental

Single crystals of commercially obtained (I) were grown by slow evaporation of an acetone solution. Compound (II) was prepared by addition of a few drops of concentrated hydrochloric acid to a hot ethanol solution of (I). The UV-visible spectra were recorded on a Specord M-40 spectrophotometer (Carl Zeiss, Jena).

Compound (I)

Crystal data

$\text{C}_{16}\text{H}_{13}\text{N}_3$
 $M_r = 247.29$
Orthorhombic, *Pbca*
 $a = 26.120$ (5) Å
 $b = 18.473$ (4) Å
 $c = 10.379$ (3) Å
 $V = 5008$ (2) Å³
 $Z = 16$
 $D_x = 1.312$ Mg m⁻³
Data collection

Enraf-Nonius CAD-4 diffractometer
 ω scans
4915 measured reflections
4915 independent reflections
 $\theta_{\text{max}} = 25.97^\circ$

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
 $\theta = 14.7$ – 16.5°
 $\mu = 0.080$ mm⁻¹
 $T = 293$ (2) K
Plate, red
0.45 \times 0.38 \times 0.14 mm

$h = 0 \rightarrow 32$
 $k = 0 \rightarrow 22$
 $l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.118$
 $S = 1.282$
4915 reflections
443 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.021$
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0045 (3)

Compound (II)

Crystal data

$\text{C}_{16}\text{H}_{14}\text{N}_3^+\cdot\text{Cl}^-$
 $M_r = 283.76$
Monoclinic, *P2₁/c*
 $a = 7.426$ (3) Å
 $b = 13.305$ (4) Å
 $c = 14.027$ (4) Å
 $\beta = 95.32$ (2)^o
 $V = 1380$ (1) Å³
 $Z = 4$

$D_x = 1.366$ Mg m⁻³
Cu $K\alpha$ radiation
 $\mu = 2.378$ mm⁻¹
 $T = 295$ (2) K
Specimen shape: flat sheet
25 \times 25 \times 2 mm
Particle morphology: plate, dark blue

Data collection

DRON-3M diffractometer (Burevestnik, Russia)
Specimen mounting: pressed as a thin layer in the specimen holder; specimen was rotated in its plane
Specimen mounted in reflection mode

$T = 295$ (2) K
 $h = 0 \rightarrow 5$
 $k = 0 \rightarrow 9$
 $l = -10 \rightarrow 10$
 $2\theta_{\text{min}} = 5.5$, $2\theta_{\text{max}} = 70.0^\circ$
Increment in $2\theta = 0.02^\circ$

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

<i>D</i> —H... <i>A</i>	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H10...C11 ⁱⁱ	2.34	3.35 (1)	168
N1—H11...C11 ⁱⁱⁱ	2.21	3.26 (1)	175
N3—H33...C11	2.24	3.24 (1)	162

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

Refinement

Refinement on I_{net}	107 parameters
$R_p = 0.042$	H-atom parameters not refined
$R_{\text{wp}} = 0.052$	Weighting scheme based on
$R_{\text{exp}} = 0.032$	measured s.u.'s
$S = 1.60$	$(\Delta/\sigma)_{\text{max}} = 0.04$
$2\theta_{\text{min}} = 8.5, 2\theta_{\text{max}} = 68.5^\circ$	$\Delta\rho_{\text{max}} = 0.9 \text{ e } \text{Å}^{-3}$
Increment in $2\theta = 0.02^\circ$	$\Delta\rho_{\text{min}} = -1.3 \text{ e } \text{Å}^{-3}$
Wavelength of incident radiation:	Preferred orientation correction:
1.5418 Å	March–Dollase (Dollase, 1986)
Excluded region(s): 5.50–8.48	along [100], $G_1 = 1.4883$ (9)
Profile function: split-type pseudo-Voigt	

For (I), all H atoms except those belonging to the amino group of (Ib) (H4A and H4B) were refined isotropically. Amino-H atoms were refined assuming ideal 120° angles at the N4 atoms (AFIX94 in SHELXL97; Sheldrick, 1997). The monoclinic cell dimensions of (II) were determined with TREOR90 (Werner *et al.*, 1985) and refined to $M_{20} = 41$ and $F_{30} = 76$ (0.007,56) using the first 75 peaks. The positions of the cation and anion were determined by combining the grid-search (Chernyshev & Schenk, 1998) and simulated-annealing (Zhukov *et al.*, 2001) procedures. The initial molecular model was built with MOPAC7.0 (Stewart, 1993) on the AM1 level. The X-ray diffraction profile and the difference between the measured and calculated profiles after the Rietveld refinement are shown in Fig. 3, with the final $R_B = 0.076$. All atoms were refined isotropically, with an overall U_{iso} parameter for the C and N atoms. H atoms were placed in geometrically calculated positions, with a common isotropic displacement parameter $U_{\text{iso}} = 0.05 \text{ Å}^2$. The planarity of the phenyl and naphthalene groups was restrained. The anisotropy of diffraction-line broadening was approximated by a quartic form in hkl (Popa, 1998). The self-consistent electrostatic field produced by the crystal environment of a molecule was calculated, taking into account atomic point charges and hybridization dipoles, and the resulting electrostatic potentials and gradients in the positions of the atomic nuclei were used to modify the diagonal elements of the H_{core} matrix and the off-diagonals $H_{\mu\nu}$, where the indices $\mu\nu$ denote atomic orbitals centred at the same atom (Yatsenko & Paseshnichenko, 2000).

For compound (I), data collection: CAD-4 Software (Enraf–Nonius, 1989); cell refinement: CAD-4 Software; data reduction: PROFIT (Streltsov & Zavodnik, 1989); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97; molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

For compound (II), 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: PLUTON92 (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: BR1305). Services for accessing these data are described at the back of the journal.

References

- Chernyshev, V. V. & Schenk, H. (1998). *Z. Kristallogr.* **213**, 1–3.
 Dollase, W. A. (1986). *J. Appl. Cryst.* **19**, 267–272.
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Foitzik, J. K., Paulus, H., Haase, W. & Loub, J. (1991). *Acta Cryst.* **C47**, 1640–1643.
 Klamt, A. & Schüürmann, G. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 799–805.
 Moreiras, D., Solans, J., Solans, X., Miravittles, C., Germain, G. & Declercq, J. P. (1981). *Acta Cryst.* **B37**, 737–739.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Popa, N. C. (1998). *J. Appl. Cryst.* **31**, 176–180.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Spek, A. L. (1992). *PLUTON92*. University of Utrecht, The Netherlands.
 Stewart, J. J. P. (1993). *MOPAC7.0*. QCPE Program No. 455. Quantum Chemistry Program Exchange. Department of Chemistry, Indiana University, Bloomington, Indiana, USA.
 Streltsov, V. A. & Zavodnik, V. E. (1989). *Sov. Phys. Crystallogr.* **34**, 824–828.
 Visser, J. W. (1986). *Powder Diffr.* **1**, 66–76.
 Werner, P.-E., Eriksson, L. & Westdahl, M. (1985). *J. Appl. Cryst.* **18**, 367–370.
 Yatsenko, A. V., Chernyshev, V. V., Kurbakov, A. I. & Schenk, H. (2000). *Acta Cryst.* **C56**, 892–894.
 Yatsenko, A. V. & Paseshnichenko, K. A. (1999). *J. Mol. Struct. (Theochem)*, **492**, 277–283.
 Yatsenko, A. V. & Paseshnichenko, K. A. (2000). *Chem. Phys.* **262**, 293–301.
 Zhukov, S. G., Chernyshev, V. V., Babaev, E. V., Sonneveld, E. J. & Schenk, H. (2001). *Z. Kristallogr.* **216**, 5–8.
 Zlokazov, V. B. & Chernyshev, V. V. (1992). *J. Appl. Cryst.* **25**, 447–451.