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Hydrogen bonding in 4-nitrobenzene-1,2-diamine and two hydrohalide salts

David K. Geiger* and Dylan E. Parsons

Department of Chemistry, State University of New York–College at Geneseo,
1 College Circle, Geneseo, NY 14454, USA
Correspondence e-mail: geiger@geneseo.edu

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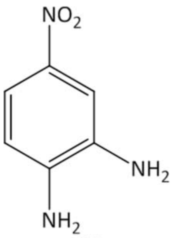
The structures of 4-nitrobenzene-1,2-diamine [$C_6H_7N_3O_2$, (I)], 2-amino-5-nitroanilinium chloride [$C_6H_8N_3O_2^+\cdot Cl^-$, (II)] and 2-amino-5-nitroanilinium bromide monohydrate [$C_6H_8N_3O_2^+\cdot Br^-\cdot H_2O$, (III)] are reported and their hydrogen-bonded structures described. The amine group *para* to the nitro group in (I) adopts an approximately planar geometry, whereas the *meta* amine group is decidedly pyramidal. In the hydrogen halide salts (II) and (III), the amine group *meta* to the nitro group is protonated. Compound (I) displays a pleated-sheet hydrogen-bonded two-dimensional structure with $R_2^2(14)$ and $R_4^4(20)$ rings. The sheets are joined by additional hydrogen bonds, resulting in a three-dimensional extended structure. Hydrohalide salt (II) has two formula units in the asymmetric unit that are related by a pseudo-inversion center. The dominant hydrogen-bonding interactions involve the chloride ion and result in $R_4^2(8)$ rings linked to form a ladder-chain structure. The chains are joined by N—H···Cl and N—H···O hydrogen bonds to form sheets parallel to (010). In hydrated hydrohalide salt (III), bromide ions are hydrogen bonded to amine and ammonium groups to form $R_4^2(8)$ rings. The water behaves as a double donor/single acceptor and, along with the bromide anions, forms hydrogen bonds involving the nitro, amine, and ammonium groups. The result is sheets parallel to (001) composed of alternating $R_5^5(15)$ and $R_6^4(24)$ rings. Ammonium N—H···Br interactions join the sheets to form a three-dimensional extended structure. Energy-minimized structures obtained using DFT and MP2 calculations are consistent with the solid-state structures. Consistent with (II) and (III), calculations show that protonation of the amine group *meta* to the nitro group results in a structure that is about 1.5 kJ mol^{-1} more stable than that obtained by protonation of the *para*-amine group. DFT calculations on single molecules and hydrogen-bonded pairs of molecules based on structural results obtained for (I) and for 3-nitrobenzene-1,2-diamine, (IV) [Betz & Gerber (2011). *Acta Cryst.* E**67**, o1359] were used to estimate the strength of the N—H···O(nitro) interactions for three observed motifs. The hydrogen-bonding interaction between the pairs of molecules examined was found to correspond to 20–30 kJ mol^{-1}.

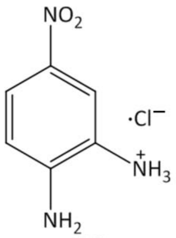
Keywords: crystal structure; hydrogen bonding; polymeric hydrogen-bonded systems; 4-nitrobenzene-1,2-diamine; hydrogen halide salt; density functional theory; MP2 method; computational chemistry.

1. Introduction

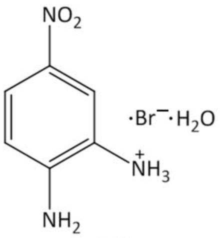
Hydrogen bonding plays an important role in areas ranging from drug design (Hao, 2006) to industrial uses such as explosives, pesticides and dyes (Helttunen *et al.*, 2013). The presence of the two additional acceptor sites from the nitro group makes nitro-substituted aromatic amines of interest with respect to their formation of extended hydrogen-bonding networks. One-, two-, and three-dimensional formations have been observed. For example, the structure of 3,5-dinitroaniline exhibits hydrogen-bonded chains that combine to form sheets containing puckered $R_{10}^{10}(58)$ rings (Glidewell *et al.*, 2001). In addition to neutral amines, nitroanilinium salts have been shown to possess extensive hydrogen-bonding interactions. In the structure of 4-nitroanilinium triiodide monohydrate, the extended structure exhibits a $C_3^3(14)$ hydrogen-bonding network involving water O—H···I and O—H···O(nitro) interactions, as well as $R_2^2(6)$ rings composed of the nitro group, water and the ammonium group (Billing *et al.*, 2010). In the isomorphous 2-methyl-4-nitroanilinium bromide and iodide salts, stacks of parallel cations are joined by one-dimensional chains of N—H···I or N—H···Br hydrogen bonds, resulting in an $R_2^2(8)$ scheme (Lemmerer & Billing, 2006).



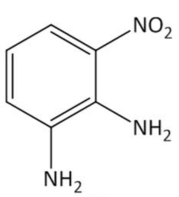
(I)



(II)



(III)



(IV)

Ammonium salts of nitro-substituted benzoic acid also exibit hydrogen-bonded polymeric structures (Smith, 2014). Ammonium 4-nitrobenzoate dihydrate forms a three-dimensional hydrogen-bonded structure and ammonium 3,5-dinitrobenzoate forms a two-dimensional extended structure, each with N—H···O interactions resulting in $R_4^3(10)$ rings. In

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Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_6H_7N_3O_2$	$C_6H_8N_3O_2^+ \cdot Cl^-$	$C_6H_8N_3O_2^+ \cdot Br^- \cdot H_2O$
M_r	153.15	189.60	252.08
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$	Orthorhombic, $Iba2$
Temperature (K)	199	200	200
a, b, c (Å)	3.7492 (6), 10.2864 (19), 17.238 (3)	4.4743 (11), 29.757 (7), 6.1706 (15)	14.352 (2), 20.086 (3), 6.4851 (9)
α, β, γ (°)	90, 90, 90	90, 97.774 (8), 90	90, 90, 90
V (Å^3)	664.8 (2)	814.0 (3)	1869.5 (5)
Z	4	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.12	0.43	4.38
Crystal size (mm)	0.65 × 0.50 × 0.05	0.50 × 0.20 × 0.05	0.40 × 0.40 × 0.05
Data collection			
Diffractometer	Bruker SMART X2S benchtop diffractometer	Bruker SMART X2S benchtop diffractometer	Bruker SMART X2S benchtop diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)	Multi-scan (*SADABS*; Bruker, 2013)	Multi-scan (*SADABS*; Bruker, 2013)
$T_{\min}$, $T_{\max}$	0.46, 0.99	0.58, 0.98	0.48, 0.81
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7773, 1170, 1010	5088, 2353, 1707	8617, 1695, 1387
R_{int}	0.066	0.073	0.069
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.595	0.596	0.602
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.072, 1.04	0.049, 0.102, 0.94	0.030, 0.071, 0.96
No. of reflections	1170	2353	1695
No. of parameters	116	251	146
No. of restraints	0	1	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.12, −0.15	0.44, −0.29	0.40, −0.34
Absolute structure	Flack x determined using 354 quotients (Parsons *et al.*, 2013)	Flack x determined using 460 quotients (Parsons *et al.*, 2013)	Flack x determined using 554 quotients (Parsons *et al.*, 2013)
Absolute structure parameter	−0.8 (10)	0.50 (12)	0.006 (13)

Computer programs: *APEX2* (Bruker, 2013), *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

contrast to these nitro-substituted aromatic systems, anilinium bromide and several halo-substituted anilinium halides exhibit a corrogated-ribbon (ladder) structure with successive $R_4^2(8)$ rings (López-Duplá *et al.*, 2003).

The addition of a second amine group increases the possibilities for hydrogen-bonding interactions and nitro-substituted diamines exhibit a wide range of hydrogen-bonded extended structures. For example, 3-nitrobenzene-1,2-diamine, (IV), displays a sheet structure resulting from N—H···O and N—H···N hydrogen bonds (Betz & Gerber, 2011) and 4-nitrobenzene-1,3-diamine exhibits nets built from $R_4^4(24)$ rings (Glidewell *et al.*, 2001).

4-Nitrobenzene-1,2-diamine, (I), is known to exhibit interesting nonlinear optical properties. A room-temperature crystallographic analysis was performed to investigate these properties (Kolev *et al.*, 2007). In the solid state, the molecule was shown to exhibit a quinoidal structure, with the C—N bond of the amino group *para* to the nitro group considerably shorter [1.367 (4) Å] than that of the *meta*-amino group [1.442 (4) Å]. In this work, we report the structure of (I) obtained at 200 K and the structures of its hydochloride salt [2-amino-5-nitroanilinium chloride, (II)] and its hydrobromide monohydrate salt [2-amino-5-nitroanilinium bromide monohydrate, (III)]. The hydrohalide salts were obtained from ethanol solutions by reaction with hydrochloric or hydrobromic acid. Although the crystal structure of *o*-phenylenediamine dihydrochloride has been reported (Stålhandske, 1974), *o*-phenylenediamine dihydrogen phosphate (Trojette *et al.*, 1998) and hydrohalide salts (II) and (III) are examples of the few structurally characterized monoprotonated *o*-phenylenediamines. To our knowledge, (II) and (III) are the only examples of structurally characterized protonated nitrobenzenediamine derivatives. The hydrogen-bonding networks exhibited are discussed and the crystallographic results are used to calculate the N—H···O—N hydrogen-bond energies in (I) and in 3-nitrobenzene-1,2-diamine, (IV) (Betz & Gerber, 2011), using density functional theory (DFT).

2. Experimental

2.1. Synthesis and crystallization

Commercially obtained 4-nitrobenzene-1,2-diamine was recrystallized from hot ethanol prior to use. Single crystals of (I) were obtained by slow evaporation of an ethanol solution. Single cystals of (II) and (III) were obtained by slow evaporation of an ethanolic solution containing a few drops of concentrated hydrochloric acid [to give salt (II)] or hydrobromic acid [to give hydrated salt (III)].

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For compound (I), a negative (meaningless) Flack x parameter value of −0.8 (10) was obtained. For compound (II), an ambiguous Flack x parameter of 0.50 (13) was obtained. For both (I) and (II), inversion of the structure and refinement as a racemic twin gave no improvement and so the absolute structures were assigned arbitrarily. Only for compound (III) was the absolute structure determined with confidence. All H atoms were located in difference Fourier maps. H atoms bonded to C atoms were refined using a riding model, with C—H = 0.95 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). For (I) and (III), H atoms bonded to N and O atoms were refined freely, including isotropic displacement parameters. For compound (II), the H atoms of the unprotonated amine group were refined freely, including isotropic displacement parameters. For the H atoms of the protonated amine group of (II), the coordinates were refined without restraints but attempts to refine the isotropic displacement parameters resulted in one of the H atoms going nonpositive definite. Thus, the H atoms of the protonated amine groups were refined with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(N).

2.3. Computations

Density functional theory (DFT) and MP2 calculations were performed (*Spartan'10*; Wavefunction Inc., 2010). The majority of the calculations employed DFT with the B3LYP procedure and a 6-311++G** basis set. Some calculations were performed with both DFT and MP2 procedures to evaluate the effects of the computational methods on the calculated hydrogen-bond energy. For the MP2 calculations, a smaller basis set (6-31G**) was used because of the higher processing demands. Single-point energy calculations on single molecules and pairs of hydrogen-bonded molecules were performed using the metrics obtained from the crystal structures. Energy-minimization calculations using DFT and MP2 methods were performed on single molecules only.

3. Results and discussion

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N2$^{\rm i}$	0.88 (3)	2.37 (3)	3.249 (3)	177 (2)
N1—H1B···O1$^{\rm ii}$	0.88 (3)	2.31 (3)	3.178 (3)	169 (2)
N1—H1B···O2$^{\rm ii}$	0.88 (3)	2.54 (3)	3.073 (3)	120 (2)
N2—H2A···O1$^{\rm ii}$	0.90 (3)	2.44 (3)	3.257 (3)	151 (2)
N2—H2B···O2$^{\rm iii}$	0.80 (3)	2.55 (3)	3.335 (3)	165 (3)
C3—H3···O2$^{\rm iii}$	0.95	2.59	3.411 (3)	145

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

The molecular structure of (I) is shown in Fig. 1. As was observed in the room-temperature structure (Kolev *et al.*, 2007), significant asymmetry is observed in the two amine groups, with C—N distances of 1.356 (3) and 1.415 (3) Å found for the amine groups *para* (N1) and *meta* (N2) to the nitro group, respectively. The *para*-amine group is essentially planar and lies in the plane of the benzene ring. Atoms H1A and H1B are −0.08 (3) and 0.06 (3) Å, respectively, out of the plane, whereas atoms H2A and H2B of the *meta*-amine group are 0.43 (3) and 0.12 (3) Å, respectively, out of the plane (*i.e.* a pyramidal amine group). These observations are consistent with greater delocalization of the *para*- than the *meta*-N atom lone pair of electrons. The corresponding C—N bond distances in the room-temperature structure are 1.367 (4) and 1.442 (4) Å (Kolev *et al.*, 2007) and in a 2:1 adduct of 4-nitrobenzene-1,2-diamine and 18-crown-6 (Weber, 1982), the *para* and *meta* C—N distances are 1.367 (3) and 1.378 (4) Å, respectively. The plane of the nitro group in (I) is slightly twisted from the benzene ring mean plane, with a dihedral angle of 2.66 (14)°. Stacking of canted molecules translated along the a axis results in π–π interactions with a ring centroid separation of 3.7492 (6) Å (*i.e.* the a-axis length). N—H···O interactions between adjacent molecules with cumulative $R^2_1(4)$, $R^2_3(6)$ and $R^1_2(7)$ rings (Etter *et al.*, 1990) result in chains of molecules parallel to [001]. Additional N—H···O and N—H···N hydrogen bonds between the chains form pleated sheets parallel to (100) that have an alternating $R^4_4(20)$ and $R^2_2(14)$ motif, as shown in Fig. 2. The three-

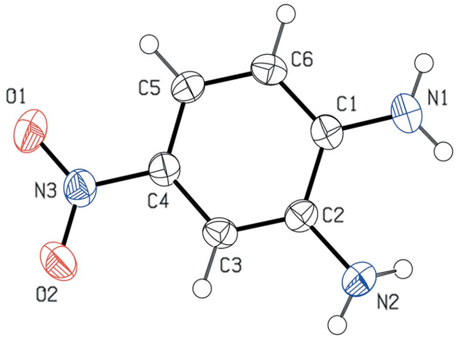


Figure 1
Perspective view of (I), showing the atom-labeling scheme. Displacement parameters for non-H atoms are displayed at the 50% probability level.

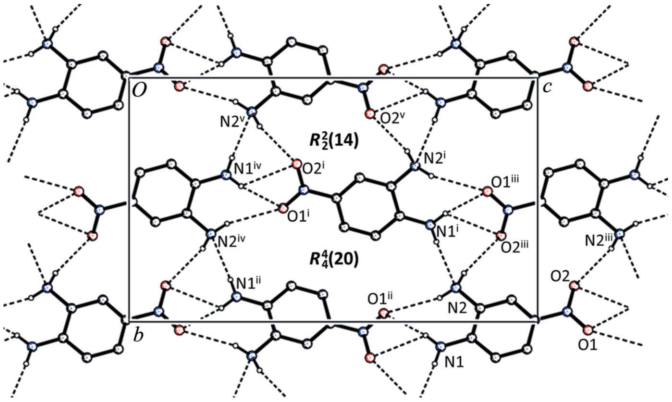


Figure 2
View of the pleated sheets in (I) formed by hydrogen bonds (shown as dashed lines). H atoms not involved in the interactions have been omitted. [Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, -y+2, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+2$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (v) $-x+\frac{3}{2}, -y+1, z-\frac{1}{2}$.]

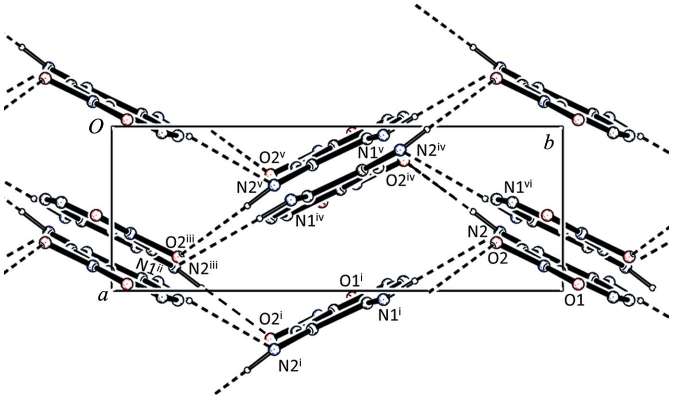


Figure 3
Packing diagram of (I), showing the three-dimensional extended structure. Hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions have been omitted. [Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x, y - 1, z$; (iii) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + \frac{3}{2}, -y + 2, z - \frac{1}{2}$.]

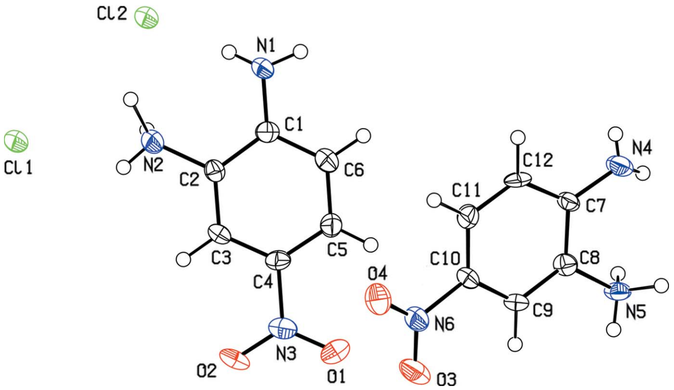


Figure 4
Perspective view of (II), showing the atom-labeling scheme. Displacement parameters for non-H atoms are displayed at the 50% probability level.

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl2	0.84 (7)	2.64 (7)	3.410 (7)	152 (6)
N1—H1*B*···O2$^{\rm i}$	0.89 (8)	2.30 (8)	3.176 (9)	170 (7)
N2—H2*A*···Cl2	0.68 (8)	2.70 (9)	3.249 (7)	139 (10)
N2—H2*B*···Cl1$^{\rm ii}$	1.19 (7)	1.95 (7)	3.103 (7)	161 (5)
N2—H2*C*···Cl1	0.83 (9)	2.69 (7)	3.217 (6)	123 (7)
N2—H2*C*···Cl2$^{\rm iii}$	0.83 (9)	2.55 (9)	3.254 (7)	143 (7)
N4—H4*A*···Cl1$^{\rm iv}$	0.91 (7)	2.54 (7)	3.426 (8)	164 (6)
N4—H4*B*···O3$^{\rm i}$	0.72 (8)	2.48 (8)	3.182 (10)	166 (9)
N5—H5*A*···Cl1$^{\rm v}$	0.83 (8)	2.49 (8)	3.269 (6)	157 (7)
N5—H5*A*···Cl2$^{\rm iv}$	0.83 (8)	2.80 (7)	3.225 (6)	114 (6)
N5—H5*B*···Cl2$^{\rm vi}$	1.12 (7)	2.06 (7)	3.128 (7)	157 (5)
N5—H5*C*···Cl1$^{\rm iv}$	1.00 (8)	2.42 (8)	3.240 (7)	139 (6)
N5—H5*C*···N4$^{\rm vii}$	1.00 (8)	2.54 (7)	3.253 (10)	128 (6)

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

dimensional extended structure formed by the sheets and interconnecting N1—H1*A*···N2$^{\rm i}$ and N2—H2*B*···O2$^{\rm iii}$ hydrogen bonds is shown in Fig. 3 (see Table 2 for geometric details and symmetry codes).

Based on the analysis of the amine groups in (I), the *meta*-amine group is expected to be protonated in the hydrohalide salts. This prediction is born out in (II) and (III). Salt (II) crystallizes with two formula units in the asymmetric unit, hereafter referred to as (II*a*) and (II*b*). The atom-labeling scheme is shown in Fig. 4. Both species exhibit a high degree of planarity in the benzene rings. The largest deviation in (II*a*) is 0.009 (5) Å for atom C6 and the largest deviation in (II*b*) is 0.011 (5) Å for atom C9. In each of the independent formula units, the plane of the nitro group is only slightly tilted out of the plane formed by the benzene ring [dihedral angle of 2 (1)° in (II*a*) and 8 (1)° in (II*b*)]. The protonated amine group in each formula unit exhibits an abnormally long N—H bond, as seen in Table 3. In each case, the associated H atom is involved in a tight interaction with a chloride anion. The strength of the N—H-···Cl interaction is evidenced by the short N···Cl distances of 3.103 (7) and 3.128 (7) Å for (II*a*) and (II*b*), respectively. Long N—H bond distances have been reported for protonated amines involved in strong hydrogen-bonding

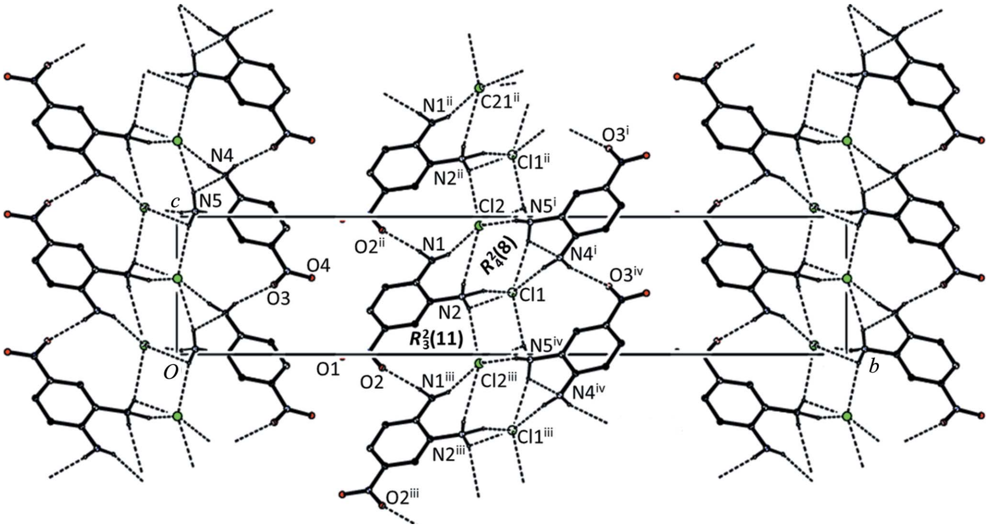


Figure 5
Packing diagram of (II), showing the ladder chains. Hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions have been omitted. [Symmetry codes: (i) $-x + 2, y + \frac{1}{2}, -z + 2$; (ii) $x, y, z + 1$; (iii) $x, y, z - 1$; (iv) $-x + 2, y + \frac{1}{2}, -z + 1$.]

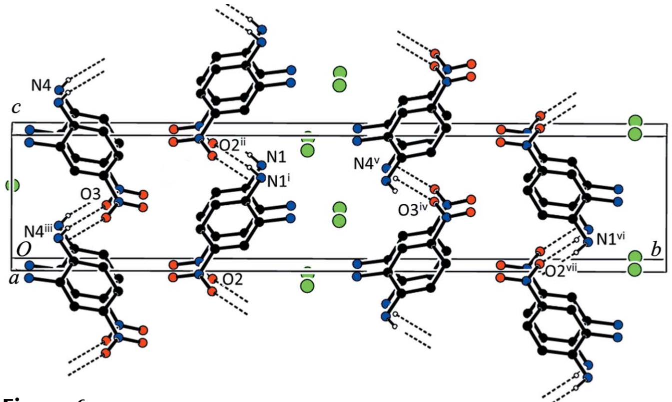


Figure 6
Packing diagram of (II), showing the sheets parallel to the *ac* plane. Hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions have been omitted. [Symmetry codes: (i) $x + 1, y, z$; (ii) $x, y, z + 1$; (iii) $x + 1, y, z - 1$; (iv) $-x + 2, y + \frac{1}{2}, -z + 1$; (v) $-x + 1, y + \frac{1}{2}, -z + 2$; (vi) $-x + 1, y + \frac{1}{2}, -z + 1$; (vii) $-x + 2, y + \frac{1}{2}, -z$.]

Table 4
Hydrogen-bond geometry (Å, °) for (III).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1S—H1SA⋯Br1	0.85 (8)	2.48 (8)	3.284 (6)	158 (7)
O1S—H1SB⋯O2^{i}	0.74 (7)	2.17 (7)	2.914 (8)	178 (7)
N1—H1A⋯Br1^{i}	0.89 (6)	2.73 (6)	3.565 (6)	156 (6)
N1—H1B⋯Br1^{ii}	0.79 (7)	2.74 (7)	3.524 (6)	173 (10)
N2—H2A⋯O1S	0.89 (7)	1.83 (8)	2.708 (7)	166 (12)
N2—H2B⋯Br1^{iii}	1.03 (12)	2.38 (13)	3.366 (12)	160 (7)
N2—H2C⋯Br1^{iv}	0.80 (8)	2.80 (9)	3.439 (12)	138 (7)
N2—H2C⋯Br1^{i}	0.80 (8)	2.93 (8)	3.410 (6)	121 (7)

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

interactions (Köroglu *et al.*, 2005). The symmetry-unique species are related by a pseudo-inversion center and are joined by two sets of N—H⋯Cl⋯H—N hydrogen-bonding interactions (see Table 3) involving the protonated amine groups. As shown in Fig. 5, these result in joined $R_4^2(8)$ rings which form a laddered structure parallel to [001], similar to those observed in halo-substituted anilinium halides (López-Duplá *et al.*, 2003). A combination of N—H⋯O and N—H⋯Cl interactions between pairs of (II*a*) formula units and pairs of (II*b*) formula units related by translations along the *c* axis form rings of type $R_3^2(11)$. The ladders are joined along the *a* axis by an N1—H1*B*⋯O2^{i} hydrogen bond in (II*a*) and an N4—H4*B*⋯O3^{i} hydrogen bond in (II*b*) (see Table 3). As seen in Fig. 6, the result is sheets parallel to (010), with stacked aromatic rings. π–π interactions with a centroid-to-centroid

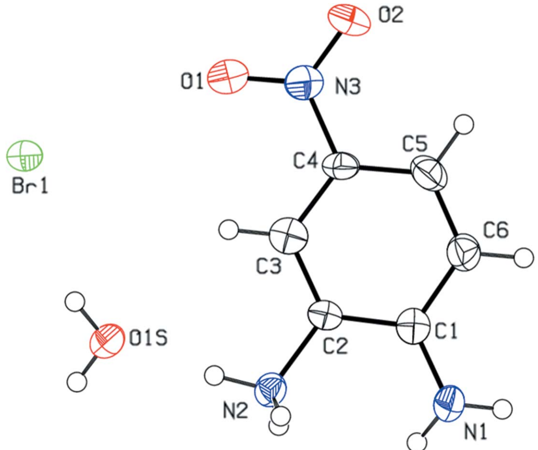
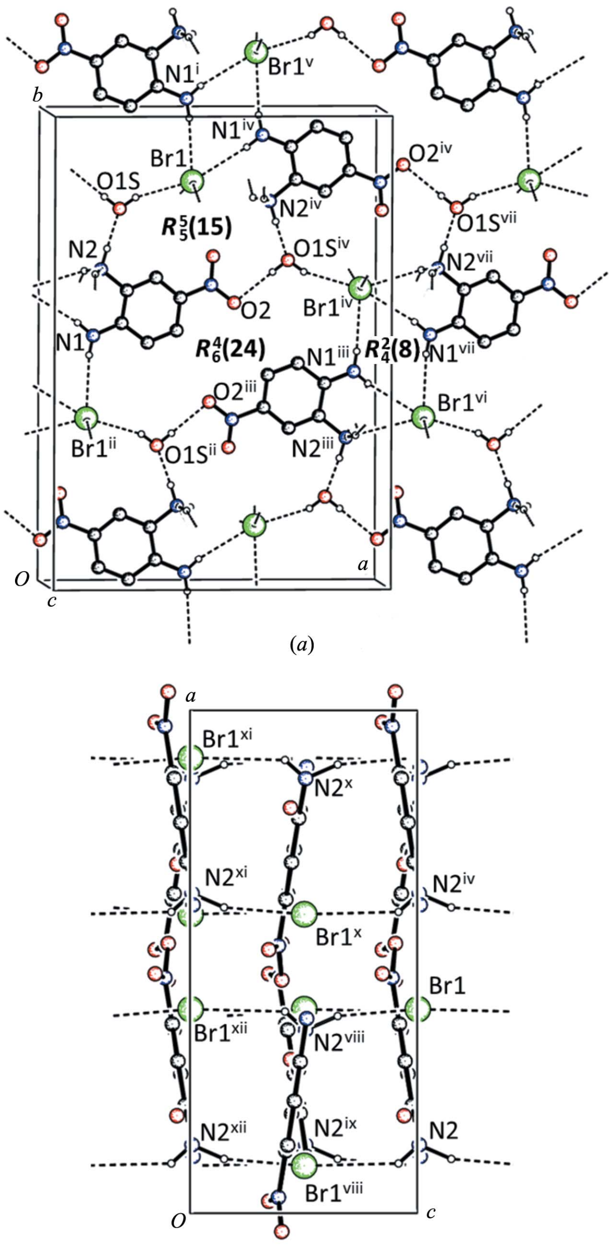


Figure 7
Perspective view of (III), showing the atom-labeling scheme. Displacement parameters for non-H atoms are displayed at the 50% probability level.



(*a*)

(*b*)

Figure 8
Two representations of the hydrogen-bonding network found in (III). Hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions have been omitted. (*a*) A view of the sheets formed parallel to the *ab* plane. (*b*) A view of the three-dimensional network resulting from N—H⋯Br interactions. [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $-x + 1, -y + 1, z$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z$; (v) $-x + 1, -y + 2, z$; (vi) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (vii) $x + 1, y, z$; (viii) $-x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ix) $x, -y + 1, z - \frac{1}{2}$; (x) $-x + 1, y, z - \frac{1}{2}$; (xi) $x + \frac{1}{2}, -y + \frac{3}{2}, z - 1$; (xii) $x, y, z - 1$.]

Table 5
Comparison of selected experimental and calculated parameters.

	C—NO$_2$ (Å)	C—N$_p$ (Å)	C—N$_o$ (Å)	C—N$_m$ (Å)	N—O (Å)	N···N (Å)	O—N—C—C (°)
(I)	1.433 (3)	1.356 (3)		1.415 (3)	1.241 (2), 1.243 (2)	2.813 (3)	−0.3 (3)
(I) DFT[*i*]	1.464	1.389		1.404	1.228, 1.229	2.739	1.6
(I) MP2[*ii*]	1.463	1.402		1.404	1.244, 1.244	2.700	1.6
(II*a*)	1.467 (9)	1.379 (9)		1.471 (9)	1.232 (8), 1.235 (8)	2.848 (10)	2.4 (10)
(II*b*)	1.460 (9)	1.366 (9)		1.473 (3)	1.210 (8), 1.240 (8)	2.843 (10)	−6.5 (10)
(II) DFT[*i*]	1.492	1.437		1.479	1.216, 1.221	2.643	0.2
(III)	1.439 (9)	1.347 (8)		1.462 (8)	1.229 (7), 1.239 (7)	2.824 (8)	−12.0 (10)
(IV)[*iii*]	1.4313 (15)		1.3642 (15)	1.4142 (16)	1.2420 (16), 1.2318 (15)	2.725	−3.8
(IV) DFT[*i*]	1.458		1.371	1.41	1.225, 1.240	2.696	3.3

Notes: (*i*) energy-minimized DFT-level calculations were performed with B3LYP/6–331++G**; (*ii*) energy-minimized Møller–Plesset level calculations were performed with MP2/6–31G**; (*iii*) structure reported previously (Betz & Gerber, 2011).

ring separation equal to the *a*-axis length [4.4743 (11) Å] are observed.

Fig. 7 shows the structure of (III). The aromatic ring is planar, with the greatest deviation being 0.009 (5) Å for atom C5. The plane of the nitro group is canted 12.8 (8)° from the plane of the benzene ring. As expected, the water of hydration has a dominant role in the hydrogen-bonding scheme. Each water molecule behaves in a two-donor/one-acceptor mode. The bromide ions act as sixfold acceptors (one water molecule, two amine groups and three protonated amine groups). Similar to (II), one of the N—H bonds associated with the protonated amine group is longer than the others as a result of a strong N—H···Br interaction (see Table 4). The strength of the N—H···Br interaction is evidenced by the short N···Br distance of 3.366 (12) Å. As seen in Fig. 8, all three structural components of (III) lie in planes parallel to (001). Two bromide anions and two amine groups compose $R^{2}_{4}(8)$ rings involving N1—H1*A*···Br1$^{\rm i}$ and N1—H1*B*···Br1$^{\rm ii}$ hydrogen bonds (see Table 4 for symmetry codes). Two additional rings are observed in the plane: an $R^{5}_{5}(15)$ ring formed by two water molecules (one donor and one acceptor linkage each), a bromide anion (double acceptor), an amine donor, two ammonium donors and a nitro acceptor, and an $R^{4}_{6}(24)$ ring composed of two bromide anions (double acceptor), two amine donors, two nitro acceptors and two water molecules (each a double donor). Fig. 8 also shows the N2—H2*B*···Br1$^{\rm iii}$ and N2—H2*C*···Br1$^{\rm iv}$ linkages (see Table 4) between planes to give the overall three-dimensional extended structure. The aromatic rings are farther separated in (III) than in (I) or (II). The closest ring centroid-to-centroid distance is 4.8566 (5) Å.

Table 5 shows a comparison of pertinent structural parameters of the DFT or MP2 energy-minimized structures with those obtained from the crystal structure. Also shown in Table 5 are metrics for 3-nitrobenzene-1,2-diamine, (IV) (Betz & Gerber, 2011), and energy-minimized parameters obtained for this compound. A comparison of the results obtained for DFT and MP2 calculations show they are internally consistent and each result compares favorably with the crystal structure of (I). In Table 5 and throughout the discussion, N$_o$, N$_m$, and N$_p$ refer to the amine N atoms that are *ortho*, *meta*, and *para*, respectively, to the nitro group. As has been noted previously, in hydrogen-bonded systems, geometry optimization often leads to structures that are substantially different from the crystallographic results because of the sometimes substantial intermolecular interactions in addition to hydrogen bonding that exist in the solid state (Hao, 2006), such as π–π stacking (Helttunen *et al.*, 2013). As Table 5 shows, the energy-minimized structures are consistant with the crystallographic results. A notable exception is the much shorter N1···N2 distance found in the energy-minimized structures of the protonated species, which may result from the over emphasis of the intramolecular N—H···N hydrogen-bonding interaction between the amine groups in the energy-minimized structures. As expected based on the adoption of a quinoidal structure, in both (I) and (IV), the C—N$_m$ bond distance is longer than the C—N$_p$ or C—N$_o$ distance.

As seen in Fig. 9, the calculated electrostatic charges in the energy-minimized structure for (I) and those obtained using the atomic coordinates from the crystallographic results are consistent with protonation of the N$_m$ atom, as observed for (II) and (III). The charges are also consistent with those reported for *p*-nitroaniline (Gross *et al.*, 2002). Based on DFT calculations (B3LYP method, 6-311++G** basis set), protonation of N$_m$ results in a structure that is about 1.5 kJ mol^{-1} lower in energy than that obained by protonating N$_p$. Crystallographic results for (I) show a decidedly planar *para*-amine group, whereas it is pyramidal in the energy-minimized structures. Although metrics involving H atoms in an X-ray

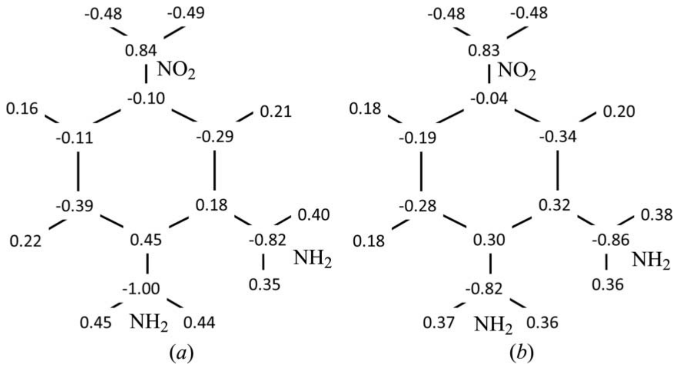


Figure 9
Electrostatic charges for (I) calculated using DFT. See *Experimental* (*Computations*; §2.3) for details. (*a*) Single-point results using the atomic coordinates from the crystal structure and (*b*) the energy-minimized structure.

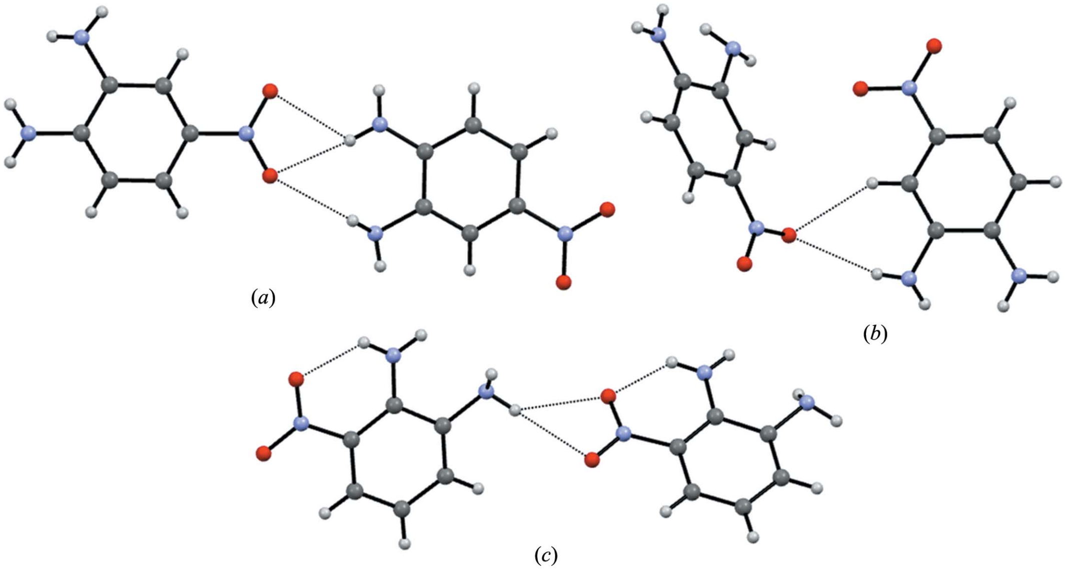


Figure 10
The amine–nitro group hydrogen-bonding motifs observed in (*a*)/(*b*) (I) and (*c*) (IV).

crystallographic result must be considered with caution, in the crystal structure, the C—N_p—H angles for (I) are 122.5 (18) and 120.8 (17)°, whereas the angles in the energy-minimized structure are 114.8 and 115.7° for (I). These results imply that the quinoidal structure observed in the solid state depends at least in part on intermolecular interactions. The differences between the charges obtained using the energy-minimized structure and the single-point calculation with the crystal coordinates may give insight into the hydrogen bonding observed in the crystal. The calculated atomic charges are less in the energy-minimized structure. The greater charge localization calculated for the molecules of the crystal is likely a result of the intermolecular hydrogen bonding, π–π stacking and other intermolecular interactions in the solid state. Regardless of the source, the result is that N_p is a poorer hydrogen-bond donor than N_m.

The strength of hydrogen bonding between the donor molecule (D) and the acceptor molecule (A) can be estimated as $\Delta E_{\rm HB} = E_{AD} - E_A - E_D$ (Helttunen *et al.*, 2013), where the various E terms correspond to the energies calculated for the adduct, acceptor and donor. Only the interactions observed for compounds (I) and (IV) are considered, as the presence of ionic and additional hydrogen-bonding interactions involving the halide counter-ions in (II) and (III) are much stronger than amine–nitro interactions. Fig. 10 shows two intermolecular amine–nitro interaction motifs observed in (I), labeled (*a*) and (*b*), and the hydrogen-bonding interaction found in (IV), labeled (*c*). Single-point, gas-phase DFT calculations at the B3LYP level using a 6-311++G** basis set for the monomer and adduct result in $\Delta E_{\rm HB} = -29.1$ kJ mol^{-1} for the structure labeled (*a*) and -20.3 kJ mol^{-1} for the structure labeled (*b*) in Fig. 10. A value of -19.7 kJ mol^{-1} was obtained for structure (*c*). These results agree well with the -16.4 to -35.8 kJ mol^{-1} range reported for intermolecular amine–nitro hydrogen-bond strengths (Johnstone *et al.*, 2010) and the -22.4 to -60.7 kJ mol^{-1} range determined for intramolecular interactions (Omelchenko *et al.*, 2012). As expected, when aqueous solvation effects are taken into account, the corresponding values are considerably less as a result of stabilization of the localized charges: for (*a*), (*b*), and (*c*), $\Delta E_{\rm HB} = -7.4$, -5.0 and -4.8 kJ mol^{-1}, respectively. Compound (IV) exhibits a short intramolecular hydrogen bond which is allowed by the proximity of the *ortho*-to-nitro amine group and driven by the formation of the resultant six-membered ring. No attempts were made to calculate the intramolecular hydrogen-bond energy.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SK3544).

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supporting information

Acta Cryst. (2014). C**70**, 681-688 [doi:10.1107/S2053229614013485]

Hydrogen bonding in 4-nitrobenzene-1,2-diamine and two hydrohalide salts

David K. Geiger and Dylan E. Parsons

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *APEX2* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) 4-Nitrobenzene-1,2-diamine

Crystal data

$C_6H_7N_3O_2$
$M_r = 153.15$
Orthorhombic, $P2_12_12_1$
$a = 3.7492$ (6) Å
$b = 10.2864$ (19) Å
$c = 17.238$ (3) Å
$V = 664.8$ (2) Å^3
$Z = 4$
$F(000) = 320$
$D_x = 1.530$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 99 reflections
$\theta = 4.6$–$21.5°$
$\mu = 0.12$ mm^{-1}
$T = 199$ K
Plate, clear orange
0.65 × 0.50 × 0.05 mm

Data collection

Bruker SMART X2S benchtop diffractometer
Radiation source: sealed microfocus tube
Doubly curved silicon crystal monochromator
Detector resolution: 8.3330 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
$T_{\min} = 0.46$, $T_{\max} = 0.99$
7773 measured reflections
1170 independent reflections
1010 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$
$\theta_{\max} = 25.0°$, $\theta_{\min} = 3.1°$
$h = -4 \rightarrow 4$
$k = -12 \rightarrow 12$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.072$
$S = 1.04$
1170 reflections
116 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.03917P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}
Absolute structure: Flack x determined using 354 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.8 (10)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.9592 (5)	1.03420 (17)	1.12307 (9)	0.0569 (6)
O2	0.7070 (5)	0.85290 (16)	1.08963 (9)	0.0520 (5)
N1	0.9475 (7)	1.1026 (2)	0.76269 (11)	0.0475 (6)
H1A	1.060 (7)	1.174 (3)	0.7478 (15)	0.067 (10)*
H1B	0.850 (7)	1.055 (3)	0.7259 (15)	0.055 (8)*
N2	0.6432 (6)	0.8605 (2)	0.79985 (12)	0.0391 (5)
H2A	0.543 (7)	0.902 (3)	0.7594 (17)	0.056 (8)*
H2B	0.525 (8)	0.804 (3)	0.8184 (17)	0.066 (10)*
N3	0.8486 (5)	0.95831 (19)	1.07251 (9)	0.0363 (5)
C1	0.9249 (6)	1.0660 (2)	0.83812 (11)	0.0300 (5)
C2	0.7666 (6)	0.9449 (2)	0.85884 (11)	0.0286 (5)
C3	0.7492 (5)	0.90992 (19)	0.93576 (11)	0.0294 (5)
H3	0.6461	0.8291	0.9502	0.035*
C4	0.8828 (5)	0.9931 (2)	0.99237 (11)	0.0289 (5)
C5	1.0380 (5)	1.11164 (19)	0.97364 (12)	0.0299 (5)
H5	1.1292	1.1671	1.013	0.036*
C6	1.0567 (6)	1.1467 (2)	0.89689 (12)	0.0323 (5)
H6	1.1615	1.2276	0.8833	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0906 (14)	0.0496 (11)	0.0305 (8)	−0.0074 (11)	−0.0053 (9)	−0.0078 (8)
O2	0.0811 (13)	0.0360 (9)	0.0389 (9)	−0.0070 (10)	0.0097 (9)	0.0071 (8)
N1	0.0657 (16)	0.0484 (13)	0.0282 (10)	−0.0118 (12)	−0.0008 (10)	0.0069 (10)
N2	0.0504 (13)	0.0339 (11)	0.0329 (10)	−0.0044 (11)	−0.0031 (10)	−0.0060 (9)
N3	0.0470 (12)	0.0314 (11)	0.0304 (9)	0.0057 (9)	0.0025 (8)	−0.0011 (9)
C1	0.0306 (11)	0.0293 (12)	0.0301 (10)	0.0047 (9)	0.0025 (9)	0.0018 (9)
C2	0.0298 (12)	0.0248 (10)	0.0312 (10)	0.0044 (10)	−0.0001 (9)	−0.0042 (9)
C3	0.0324 (11)	0.0212 (10)	0.0347 (10)	0.0026 (10)	0.0039 (11)	−0.0014 (9)
C4	0.0335 (12)	0.0249 (11)	0.0282 (10)	0.0058 (10)	0.0022 (8)	−0.0013 (8)
C5	0.0318 (12)	0.0264 (11)	0.0316 (10)	0.0009 (10)	0.0002 (10)	−0.0050 (9)
C6	0.0335 (11)	0.0253 (10)	0.0380 (11)	−0.0010 (10)	0.0023 (9)	0.0009 (9)

Geometric parameters (Å, º)

O1—N3	1.241 (2)	C1—C6	1.399 (3)
O2—N3	1.243 (2)	C1—C2	1.426 (3)

N1—C1	1.356 (3)	C2—C3	1.375 (3)
N1—H1A	0.88 (3)	C3—C4	1.391 (3)
N1—H1B	0.88 (3)	C3—H3	0.95
N2—C2	1.415 (3)	C4—C5	1.389 (3)
N2—H2A	0.90 (3)	C5—C6	1.373 (3)
N2—H2B	0.80 (3)	C5—H5	0.95
N3—C4	1.433 (3)	C6—H6	0.95

C1—N1—H1A	122.5 (18)	N2—C2—C1	119.50 (18)
C1—N1—H1B	120.8 (17)	C2—C3—C4	119.89 (19)
H1A—N1—H1B	117 (2)	C2—C3—H3	120.1
C2—N2—H2A	113.6 (18)	C4—C3—H3	120.1
C2—N2—H2B	110 (2)	C5—C4—C3	121.86 (18)
H2A—N2—H2B	115 (3)	C5—C4—N3	118.74 (18)
O1—N3—O2	121.65 (17)	C3—C4—N3	119.36 (18)
O1—N3—C4	119.33 (19)	C6—C5—C4	118.40 (19)
O2—N3—C4	119.02 (18)	C6—C5—H5	120.8
N1—C1—C6	120.5 (2)	C4—C5—H5	120.8
N1—C1—C2	120.6 (2)	C5—C6—C1	121.6 (2)
C6—C1—C2	118.94 (17)	C5—C6—H6	119.2
C3—C2—N2	121.1 (2)	C1—C6—H6	119.2
C3—C2—C1	119.32 (18)		

N1—C1—C2—C3	179.6 (2)	O2—N3—C4—C5	179.37 (18)
C6—C1—C2—C3	−0.4 (3)	O1—N3—C4—C3	−178.08 (19)
N1—C1—C2—N2	2.1 (3)	O2—N3—C4—C3	1.6 (3)
C6—C1—C2—N2	−177.9 (2)	C3—C4—C5—C6	0.3 (3)
N2—C2—C3—C4	177.97 (19)	N3—C4—C5—C6	−177.4 (2)
C1—C2—C3—C4	0.5 (3)	C4—C5—C6—C1	−0.2 (3)
C2—C3—C4—C5	−0.5 (3)	N1—C1—C6—C5	−179.8 (2)
C2—C3—C4—N3	177.19 (19)	C2—C1—C6—C5	0.2 (3)
O1—N3—C4—C5	−0.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N2^{i}	0.88 (3)	2.37 (3)	3.249 (3)	177 (2)
N1—H1*B*···O1^{ii}	0.88 (3)	2.31 (3)	3.178 (3)	169 (2)
N1—H1*B*···O2^{ii}	0.88 (3)	2.54 (3)	3.073 (3)	120 (2)
N2—H2*A*···O1^{ii}	0.90 (3)	2.44 (3)	3.257 (3)	151 (2)
N2—H2*B*···O2^{iii}	0.80 (3)	2.55 (3)	3.335 (3)	165 (3)
C3—H3···O2^{iii}	0.95	2.59	3.411 (3)	145

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

(II) 2-Amino-5-nitroanilinium chloride

Crystal data

$C_6H_8N_3O_2^+\cdot Cl^-$	$F(000) = 392$
$M_r = 189.60$	$D_x = 1.547$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.4743$ (11) Å	Cell parameters from 123 reflections
$b = 29.757$ (7) Å	$\theta = 0.2–20.7°$
$c = 6.1706$ (15) Å	$\mu = 0.43$ mm^{-1}
$\beta = 97.774$ (8)°	$T = 200$ K
$V = 814.0$ (3) Å^3	Plate, colourless
$Z = 4$	0.50 × 0.20 × 0.05 mm

Data collection

Bruker SMART X2S benchtop diffractometer	5088 measured reflections
Radiation source: sealed microfocus tube	2353 independent reflections
Doubly curved silicon crystal monochromator	1707 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3330 pixels mm^{-1}	$R_{int} = 0.073$
ω scans	$\theta_{max} = 25.1°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)	$h = -5 \rightarrow 4$
$T_{min} = 0.58$, $T_{max} = 0.98$	$k = -34 \rightarrow 35$
	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.94$	$\Delta\rho_{max} = 0.44$ e Å^{-3}
2353 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
251 parameters	Absolute structure: Flack *x* determined using 460 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
1 restraint	Absolute structure parameter: 0.50 (12)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.8425 (4)	0.50092 (5)	0.4491 (3)	0.0314 (5)
Cl2	0.4721 (4)	0.45202 (5)	0.9346 (3)	0.0304 (4)
N3	0.3963 (13)	0.2867 (2)	0.0126 (10)	0.0315 (15)

O1	0.3220 (15)	0.24711 (17)	−0.0179 (10)	0.0579 (18)
O2	0.5645 (12)	0.30679 (18)	−0.0977 (9)	0.0437 (15)
N6	1.0347 (14)	0.1643 (2)	0.6032 (11)	0.0345 (17)
O3	1.2238 (12)	0.14523 (19)	0.5058 (10)	0.0452 (15)
O4	0.9319 (14)	0.20114 (19)	0.5553 (10)	0.0528 (18)
N1	−0.0631 (16)	0.3809 (2)	0.6825 (11)	0.0326 (16)
H1A	0.021 (16)	0.405 (2)	0.725 (12)	0.04 (2)*
H1B	−0.182 (17)	0.363 (3)	0.748 (14)	0.05 (3)*
N2	0.3191 (14)	0.4262 (2)	0.4200 (12)	0.0296 (17)
H2A	0.428 (19)	0.428 (3)	0.508 (15)	0.044*
H2B	0.174 (14)	0.458 (2)	0.461 (12)	0.044*
H2C	0.435 (18)	0.436 (2)	0.336 (14)	0.044*
C1	0.0597 (15)	0.3576 (2)	0.5228 (13)	0.0244 (17)
C2	0.2439 (15)	0.3784 (2)	0.3848 (12)	0.0230 (16)
C3	0.3534 (14)	0.3556 (2)	0.2208 (12)	0.0235 (17)
H3	0.4796	0.3701	0.1303	0.028*
C4	0.2770 (14)	0.3110 (2)	0.1892 (12)	0.0251 (17)
C5	0.0995 (16)	0.2888 (2)	0.3176 (12)	0.0280 (17)
H5	0.0506	0.2581	0.291	0.034*
C6	−0.0098 (16)	0.3116 (2)	0.4882 (13)	0.0311 (19)
H6	−0.1301	0.2963	0.5804	0.037*
N4	0.6182 (17)	0.0721 (2)	1.2972 (12)	0.0339 (17)
H4A	0.728 (15)	0.049 (2)	1.367 (12)	0.04 (2)*
H4B	0.538 (19)	0.086 (3)	1.364 (14)	0.04 (3)*
N5	1.0075 (15)	0.0276 (2)	1.0387 (11)	0.0276 (16)
H5A	1.093 (18)	0.018 (2)	0.937 (13)	0.041*
H5B	0.796 (16)	0.007 (2)	1.028 (11)	0.041*
H5C	1.152 (16)	0.025 (2)	1.176 (14)	0.041*
C7	0.7333 (15)	0.0956 (2)	1.1374 (12)	0.0241 (17)
C8	0.9220 (15)	0.0750 (2)	1.0006 (12)	0.0245 (17)
C9	1.0259 (16)	0.0970 (2)	0.8319 (12)	0.0271 (17)
H9	1.1573	0.0825	0.7452	0.032*
C10	0.9352 (16)	0.1412 (2)	0.7896 (12)	0.0276 (16)
C11	0.7525 (15)	0.1635 (2)	0.9185 (13)	0.0300 (19)
H11	0.6961	0.194	0.89	0.036*
C12	0.6552 (15)	0.1405 (2)	1.0886 (12)	0.0253 (17)
H12	0.5294	0.1556	1.1772	0.03*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0422 (11)	0.0317 (10)	0.0222 (10)	−0.0059 (8)	0.0111 (8)	−0.0012 (8)
Cl2	0.0399 (11)	0.0302 (9)	0.0231 (10)	−0.0051 (8)	0.0111 (8)	−0.0013 (8)
N3	0.034 (4)	0.037 (4)	0.025 (4)	0.005 (3)	0.009 (3)	−0.002 (3)
O1	0.087 (5)	0.029 (3)	0.066 (5)	−0.002 (3)	0.041 (4)	−0.015 (3)
O2	0.054 (4)	0.050 (3)	0.034 (4)	−0.002 (3)	0.030 (3)	−0.002 (3)
N6	0.045 (4)	0.035 (4)	0.025 (4)	−0.009 (3)	0.011 (3)	0.000 (3)
O3	0.054 (4)	0.054 (4)	0.032 (3)	−0.001 (3)	0.022 (3)	0.005 (3)

O4	0.089 (5)	0.029 (3)	0.045 (5)	0.004 (3)	0.025 (4)	0.017 (3)
N1	0.044 (4)	0.032 (4)	0.025 (4)	−0.012 (3)	0.017 (3)	−0.005 (3)
N2	0.038 (4)	0.029 (4)	0.023 (4)	−0.006 (3)	0.008 (3)	0.001 (3)
C1	0.023 (4)	0.027 (4)	0.023 (5)	0.000 (3)	0.004 (3)	−0.003 (3)
C2	0.027 (4)	0.022 (4)	0.021 (4)	0.000 (3)	0.005 (3)	0.004 (3)
C3	0.021 (4)	0.029 (4)	0.022 (5)	0.000 (3)	0.009 (3)	0.001 (3)
C4	0.024 (4)	0.026 (4)	0.026 (5)	0.006 (3)	0.007 (3)	−0.003 (3)
C5	0.036 (4)	0.024 (3)	0.024 (5)	−0.005 (3)	0.005 (3)	0.000 (3)
C6	0.039 (5)	0.031 (4)	0.025 (5)	−0.004 (3)	0.010 (4)	0.003 (3)
N4	0.047 (5)	0.032 (4)	0.026 (4)	0.007 (4)	0.018 (4)	0.004 (3)
N5	0.035 (4)	0.027 (4)	0.022 (4)	0.011 (3)	0.011 (3)	0.000 (3)
C7	0.027 (4)	0.030 (4)	0.017 (4)	−0.006 (3)	0.008 (3)	−0.003 (3)
C8	0.028 (4)	0.026 (4)	0.019 (4)	0.004 (3)	0.001 (3)	0.003 (3)
C9	0.033 (4)	0.029 (4)	0.022 (5)	0.000 (3)	0.013 (4)	−0.006 (3)
C10	0.036 (4)	0.029 (4)	0.020 (4)	−0.004 (3)	0.011 (3)	0.002 (3)
C11	0.034 (4)	0.020 (3)	0.038 (5)	0.002 (3)	0.013 (4)	0.002 (3)
C12	0.025 (4)	0.029 (4)	0.024 (4)	0.007 (3)	0.009 (3)	−0.010 (3)

Geometric parameters (Å, º)

N3—O1	1.232 (8)	C5—C6	1.395 (10)
N3—O2	1.235 (8)	C5—H5	0.95
N3—C4	1.467 (9)	C6—H6	0.95
N6—O4	1.210 (8)	N4—C7	1.366 (9)
N6—O3	1.240 (8)	N4—H4A	0.91 (7)
N6—C10	1.460 (9)	N4—H4B	0.72 (8)
N1—C1	1.379 (9)	N5—C8	1.473 (9)
N1—H1A	0.84 (7)	N5—H5A	0.83 (8)
N1—H1B	0.89 (8)	N5—H5B	1.12 (7)
N2—C2	1.471 (9)	N5—H5C	1.00 (8)
N2—H2A	0.68 (8)	C7—C12	1.403 (9)
N2—H2B	1.19 (7)	C7—C8	1.412 (9)
N2—H2C	0.83 (9)	C8—C9	1.364 (10)
C1—C2	1.407 (9)	C9—C10	1.390 (9)
C1—C6	1.411 (9)	C9—H9	0.95
C2—C3	1.364 (9)	C10—C11	1.385 (10)
C3—C4	1.378 (8)	C11—C12	1.373 (10)
C3—H3	0.95	C11—H11	0.95
C4—C5	1.364 (10)	C12—H12	0.95

O1—N3—O2	123.4 (7)	C5—C6—C1	119.5 (7)
O1—N3—C4	117.8 (6)	C5—C6—H6	120.3
O2—N3—C4	118.8 (6)	C1—C6—H6	120.3
O4—N6—O3	123.9 (7)	C7—N4—H4A	119 (5)
O4—N6—C10	118.2 (7)	C7—N4—H4B	112 (7)
O3—N6—C10	117.9 (7)	H4A—N4—H4B	117 (9)
C1—N1—H1A	117 (5)	C8—N5—H5A	111 (5)
C1—N1—H1B	110 (5)	C8—N5—H5B	108 (3)

H1A—N1—H1B	130 (8)	H5A—N5—H5B	104 (6)
C2—N2—H2A	109 (8)	C8—N5—H5C	110 (4)
C2—N2—H2B	132 (3)	H5A—N5—H5C	107 (7)
H2A—N2—H2B	96 (8)	H5B—N5—H5C	117 (5)
C2—N2—H2C	113 (5)	N4—C7—C12	122.4 (7)
H2A—N2—H2C	92 (9)	N4—C7—C8	121.6 (7)
H2B—N2—H2C	106 (6)	C12—C7—C8	115.9 (6)
N1—C1—C2	122.2 (6)	C9—C8—C7	122.8 (6)
N1—C1—C6	119.7 (7)	C9—C8—N5	118.3 (6)
C2—C1—C6	118.0 (7)	C7—C8—N5	118.9 (6)
C3—C2—C1	121.9 (6)	C8—C9—C10	118.5 (7)
C3—C2—N2	119.6 (6)	C8—C9—H9	120.8
C1—C2—N2	118.5 (7)	C10—C9—H9	120.8
C2—C3—C4	118.5 (7)	C11—C10—C9	121.7 (7)
C2—C3—H3	120.7	C11—C10—N6	119.6 (6)
C4—C3—H3	120.7	C9—C10—N6	118.7 (7)
C5—C4—C3	122.4 (7)	C12—C11—C10	118.2 (6)
C5—C4—N3	119.6 (6)	C12—C11—H11	120.9
C3—C4—N3	118.1 (7)	C10—C11—H11	120.9
C4—C5—C6	119.7 (7)	C11—C12—C7	123.0 (7)
C4—C5—H5	120.2	C11—C12—H12	118.5
C6—C5—H5	120.2	C7—C12—H12	118.5

N1—C1—C2—C3	−177.0 (6)	N4—C7—C8—C9	176.2 (7)
C6—C1—C2—C3	0.3 (10)	C12—C7—C8—C9	0.5 (10)
N1—C1—C2—N2	3.0 (10)	N4—C7—C8—N5	−2.9 (10)
C6—C1—C2—N2	−179.7 (6)	C12—C7—C8—N5	−178.5 (6)
C1—C2—C3—C4	0.8 (10)	C7—C8—C9—C10	−1.8 (11)
N2—C2—C3—C4	−179.2 (6)	N5—C8—C9—C10	177.3 (6)
C2—C3—C4—C5	−0.8 (10)	C8—C9—C10—C11	2.3 (11)
C2—C3—C4—N3	−179.9 (6)	C8—C9—C10—N6	−177.3 (6)
O1—N3—C4—C5	2.4 (10)	O4—N6—C10—C11	−6.5 (10)
O2—N3—C4—C5	−177.7 (7)	O3—N6—C10—C11	172.3 (6)
O1—N3—C4—C3	−178.5 (6)	O4—N6—C10—C9	173.1 (7)
O2—N3—C4—C3	1.4 (9)	O3—N6—C10—C9	−8.1 (10)
C3—C4—C5—C6	−0.2 (11)	C9—C10—C11—C12	−1.5 (11)
N3—C4—C5—C6	178.9 (6)	N6—C10—C11—C12	178.1 (6)
C4—C5—C6—C1	1.3 (11)	C10—C11—C12—C7	0.2 (11)
N1—C1—C6—C5	176.0 (7)	N4—C7—C12—C11	−175.3 (7)
C2—C1—C6—C5	−1.3 (10)	C8—C7—C12—C11	0.3 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl2	0.84 (7)	2.64 (7)	3.410 (7)	152 (6)
N1—H1*B*···O2^{i}	0.89 (8)	2.30 (8)	3.176 (9)	170 (7)
N2—H2*A*···Cl2	0.68 (8)	2.70 (9)	3.249 (7)	139 (10)
N2—H2*B*···Cl1^{ii}	1.19 (7)	1.95 (7)	3.103 (7)	161 (5)

N2—H2*C*···Cl1	0.83 (9)	2.69 (7)	3.217 (6)	123 (7)
N2—H2*C*···Cl2^{iii}	0.83 (9)	2.55 (9)	3.254 (7)	143 (7)
C3—H3···Cl2^{iii}	0.95	2.72	3.449 (7)	134
C5—H5···O4^{ii}	0.95	2.46	3.134 (9)	128
C6—H6···O2^{i}	0.95	2.58	3.390 (10)	144
N4—H4*A*···Cl1^{iv}	0.91 (7)	2.54 (7)	3.426 (8)	164 (6)
N4—H4*B*···O3^{i}	0.72 (8)	2.48 (8)	3.182 (10)	166 (9)
N5—H5*A*···Cl1^{v}	0.83 (8)	2.49 (8)	3.269 (6)	157 (7)
N5—H5*A*···Cl2^{iv}	0.83 (8)	2.80 (7)	3.225 (6)	114 (6)
N5—H5*B*···Cl2^{vi}	1.12 (7)	2.06 (7)	3.128 (7)	157 (5)
N5—H5*C*···Cl1^{iv}	1.00 (8)	2.42 (8)	3.240 (7)	139 (6)
N5—H5*C*···N4^{vii}	1.00 (8)	2.54 (7)	3.253 (10)	128 (6)

Symmetry codes: (i) $x-1, y, z+1$; (ii) $x-1, y, z$; (iii) $x, y, z-1$; (iv) $-x+2, y-1/2, -z+2$; (v) $-x+2, y-1/2, -z+1$; (vi) $-x+1, y-1/2, -z+2$; (vii) $x+1, y, z$.

(III) 2-Amino-4-nitroanilinium bromide monohydrate

Crystal data

$C_6H_8N_3O_2^+\cdot Br^-\cdot H_2O$
$M_r = 252.08$
Orthorhombic, *Iba*2
$a = 14.352$ (2) Å
$b = 20.086$ (3) Å
$c = 6.4851$ (9) Å
$V = 1869.5$ (5) Å^3
$Z = 8$
$F(000) = 1008$

$D_x = 1.791$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 3357 reflections
$\theta = 2.8–24.6°$
$\mu = 4.38$ mm^{-1}
$T = 200$ K
Plate, clear yellow
0.40 × 0.40 × 0.05 mm

Data collection

Bruker SMART X2S benchtop diffractometer
Radiation source: sealed microfocus tube
Doubly curved silicon crystal monochromator
Detector resolution: 8.3330 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
$T_{min} = 0.48$, $T_{max} = 0.81$

8617 measured reflections
1695 independent reflections
1387 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$
$\theta_{max} = 25.3°$, $\theta_{min} = 2.8°$
$h = -17 \rightarrow 16$
$k = -24 \rightarrow 24$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.071$
$S = 0.96$
1695 reflections
146 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Absolute structure: Flack *x* determined using 554 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.006 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Br1	0.40567 (3)	0.86365 (3)	1.00289 (17)	0.0284 (2)
O1S	0.1940 (4)	0.8047 (3)	0.9423 (9)	0.0418 (16)
H1SA	0.240 (6)	0.830 (4)	0.969 (13)	0.07 (3)*
H1SB	0.153 (5)	0.827 (3)	0.933 (10)	0.02 (2)*
N1	0.1130 (4)	0.5386 (3)	1.0132 (19)	0.0363 (14)
H1A	0.069 (4)	0.567 (3)	0.973 (12)	0.030 (19)*
H1B	0.105 (4)	0.500 (4)	1.002 (19)	0.041 (19)*
N2	0.1359 (4)	0.6782 (3)	1.0088 (19)	0.0291 (12)
H2A	0.152 (4)	0.721 (4)	1.008 (19)	0.05 (2)*
H2B	0.108 (6)	0.671 (6)	1.15 (2)	0.09 (4)*
H2C	0.099 (5)	0.675 (5)	0.918 (14)	0.04 (3)*
N3	0.4682 (4)	0.6423 (3)	0.8891 (10)	0.0387 (15)
O1	0.4761 (3)	0.7017 (3)	0.8467 (10)	0.0555 (16)
O2	0.5364 (3)	0.6047 (3)	0.9039 (8)	0.0497 (15)
C1	0.1988 (4)	0.5642 (3)	0.9848 (15)	0.0283 (15)
C2	0.2146 (4)	0.6330 (3)	0.9782 (16)	0.0242 (16)
C3	0.3024 (5)	0.6591 (4)	0.9466 (9)	0.0316 (19)
H3	0.3118	0.7059	0.9422	0.038*
C4	0.3762 (4)	0.6159 (4)	0.9216 (11)	0.0293 (17)
C5	0.3645 (5)	0.5471 (4)	0.9300 (11)	0.038 (2)
H5	0.4164	0.5181	0.9156	0.046*
C6	0.2769 (4)	0.5222 (4)	0.9592 (10)	0.036 (2)
H6	0.2683	0.4753	0.9624	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0240 (3)	0.0334 (3)	0.0277 (3)	−0.0004 (3)	0.0005 (5)	−0.0017 (6)
O1S	0.028 (3)	0.032 (3)	0.065 (5)	−0.003 (3)	−0.002 (3)	0.007 (3)
N1	0.034 (3)	0.024 (3)	0.051 (4)	−0.003 (2)	−0.005 (5)	0.000 (6)
N2	0.029 (3)	0.026 (3)	0.033 (3)	−0.003 (2)	−0.008 (5)	−0.004 (5)
N3	0.030 (3)	0.039 (4)	0.047 (4)	−0.001 (3)	0.003 (3)	−0.003 (3)
O1	0.030 (3)	0.043 (4)	0.093 (5)	−0.002 (3)	0.003 (3)	−0.001 (3)
O2	0.026 (2)	0.046 (3)	0.078 (4)	0.010 (3)	0.003 (3)	−0.004 (3)
C1	0.032 (3)	0.030 (3)	0.022 (4)	0.000 (2)	−0.005 (4)	0.000 (4)
C2	0.023 (2)	0.031 (3)	0.019 (5)	0.003 (2)	−0.002 (4)	0.003 (3)

C3	0.034 (4)	0.039 (4)	0.022 (5)	0.000 (3)	−0.004 (3)	−0.002 (3)
C4	0.019 (3)	0.037 (4)	0.032 (4)	0.002 (3)	−0.001 (3)	−0.002 (3)
C5	0.031 (4)	0.034 (4)	0.049 (5)	0.009 (3)	−0.006 (3)	−0.004 (3)
C6	0.036 (3)	0.029 (4)	0.042 (6)	0.001 (3)	−0.007 (3)	0.002 (3)

Geometric parameters (Å, º)

O1S—H1SA	0.85 (8)	N3—C4	1.439 (9)
O1S—H1SB	0.74 (7)	C1—C2	1.401 (8)
N1—C1	1.347 (8)	C1—C6	1.413 (8)
N1—H1A	0.89 (6)	C2—C3	1.380 (9)
N1—H1B	0.79 (7)	C3—C4	1.379 (9)
N2—C2	1.462 (8)	C3—H3	0.95
N2—H2A	0.89 (7)	C4—C5	1.393 (10)
N2—H2B	1.03 (12)	C5—C6	1.366 (9)
N2—H2C	0.80 (8)	C5—H5	0.95
N3—O1	1.229 (7)	C6—H6	0.95
N3—O2	1.239 (7)		

H1SA—O1S—H1SB	106 (8)	C3—C2—C1	121.8 (6)
C1—N1—H1A	112 (4)	C3—C2—N2	119.3 (6)
C1—N1—H1B	120 (5)	C1—C2—N2	118.9 (5)
H1A—N1—H1B	120 (6)	C4—C3—C2	118.6 (7)
C2—N2—H2A	113 (4)	C4—C3—H3	120.7
C2—N2—H2B	110 (6)	C2—C3—H3	120.7
H2A—N2—H2B	104 (10)	C3—C4—C5	121.8 (6)
C2—N2—H2C	112 (7)	C3—C4—N3	119.4 (7)
H2A—N2—H2C	104 (10)	C5—C4—N3	118.8 (6)
H2B—N2—H2C	114 (7)	C6—C5—C4	118.6 (6)
O1—N3—O2	122.4 (6)	C6—C5—H5	120.7
O1—N3—C4	118.3 (6)	C4—C5—H5	120.7
O2—N3—C4	119.3 (6)	C5—C6—C1	121.9 (6)
N1—C1—C2	121.9 (6)	C5—C6—H6	119.1
N1—C1—C6	120.9 (6)	C1—C6—H6	119.1
C2—C1—C6	117.2 (6)		

N1—C1—C2—C3	−179.2 (9)	O2—N3—C4—C3	167.0 (7)
C6—C1—C2—C3	0.5 (15)	O1—N3—C4—C5	167.7 (7)
N1—C1—C2—N2	1.7 (17)	O2—N3—C4—C5	−12.0 (10)
C6—C1—C2—N2	−178.6 (9)	C3—C4—C5—C6	1.5 (11)
C1—C2—C3—C4	−0.2 (14)	N3—C4—C5—C6	−179.5 (6)
N2—C2—C3—C4	178.9 (9)	C4—C5—C6—C1	−1.2 (11)
C2—C3—C4—C5	−0.8 (11)	N1—C1—C6—C5	179.9 (8)
C2—C3—C4—N3	−179.8 (7)	C2—C1—C6—C5	0.2 (14)
O1—N3—C4—C3	−13.3 (10)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*S*—H1*SA*···Br1	0.85 (8)	2.48 (8)	3.284 (6)	158 (7)
O1*S*—H1*SB*···O2[i]	0.74 (7)	2.17 (7)	2.914 (8)	178 (7)
N1—H1*A*···Br1[i]	0.89 (6)	2.73 (6)	3.565 (6)	156 (6)
N1—H1*B*···Br1[ii]	0.79 (7)	2.74 (7)	3.524 (6)	173 (10)
N2—H2*A*···O1*S*	0.89 (7)	1.83 (8)	2.708 (7)	166 (12)
N2—H2*B*···Br1[iii]	1.03 (12)	2.38 (13)	3.366 (12)	160 (7)
N2—H2*C*···Br1[iv]	0.80 (8)	2.80 (9)	3.439 (12)	138 (7)
N2—H2*C*···Br1[i]	0.80 (8)	2.93 (8)	3.410 (6)	121 (7)

Symmetry codes: (i) *x*−1/2, −*y*+3/2, *z*; (ii) −*x*+1/2, *y*−1/2, *z*; (iii) −*x*+1/2, −*y*+3/2, *z*+1/2; (iv) −*x*+1/2, −*y*+3/2, *z*−1/2.

Comparison of selected experimental and calculated parameters.

	C—NO$_2$ (Å)	C—N$_p$ (Å)	C—N$_o$ (Å)	C—N$_m$ (Å)	N—O (Å)	N···N (Å)	O—N—C—C (°)
(I)	1.433 (3)	1.356 (3)		1.415 (3)	1.241 (2), 1.243 (2)	2.813 (3)	-0.3 (3)
(I) DFT[i]	1.464	1.389		1.404	1.228, 1.229	2.739	1.6
(I) MP2[ii]	1.463	1.402		1.404	1.244, 1.244	2.700	1.6
(II*a*)	1.467 (9)	1.378 (9)		1.471 (9)	1.232 (8), 1.235 (8)	2.848 (10)	2.4 (10)
(II*b*)	1.460 (9)	1.366 (9)		1.472 (9)	1.210 (8), 1.240 (8)	2.843 (10)	-6.5 (10)
(II) DFT[i]	1.492	1.437		1.479	1.216, 1.221	2.643	0.2
(III)	1.440 (9)	1.347 (8)		1.462 (8)	1.229 (7), 1.239 (7)	2.824 (8)	-12.0 (10)
(IV)[iii]	1.4313 (15)		1.3642 (15)	1.4142 (16)	1.2420 (16), 1.2318 (15)	2.725	-3.8
(IV) DFT[i]	1.458		1.371	1.41	1.225, 1.240	2.696	3.3

Notes: (i) energy-minimized DFT-level calculations were performed with B3LYP/6-331++G**; (ii) energy-minimized Møller-Plesset level calculations were performed with MP2/6-31G**; (iii) structure previously reported (Betz & Gerber, 2011).